

REVIEW

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Plasticiser loss in heritage collections: its prevalence, cause, effect, and methods for analysis

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Abstract

Plasticiser loss is a topic frequently mentioned in discussions on the degradation of plastic artefacts in museum collections, particularly for plasticised poly (vinyl chloride) and cellulose acetate. Plasticisers may migrate to the plastic's surface and remain as a deposit, or volatilise into the surrounding environment, both presenting an aesthetic issue and impacting the future stability of the plastic. This paper draws on the work of conservation science, materials degradation, and indoor air quality/emissions studies, to review our current understanding of plasticiser loss. The influence of the material's intrinsic properties, and environmental factors on migration rates are discussed and related to preventive conservation practices. The methods by which plasticiser migration is studied, including characterisation, are also reviewed, with a particular focus on minimally invasive and non-destructive methods suitable for heritage science research.

Keywords: Plasticiser loss, Migration, Phthalates, Plastic degradation, Analytical methods

Introduction

Plastics' lack of durability compared to other artists materials presents a challenge for conservators seeking to slow degradation. Estimates suggest between 15–30% of plastic objects in institutions across Europe to be in poor or unacceptable condition for display [1]. Conservation strategies may be determined by the extent of degradation perceptibly occurring; at which point preventive conservation methods cannot reverse the damage and interventive methods are limited. Today heritage organisations and academic groups are making concerted efforts to conserve plastic objects, by studying a range of degradation mechanisms and their interplay.

Plastics comprise one or more polymers alongside additives such as colourants, inorganic fillers, flame retardants, heat stabilisers and plasticisers [2, 3]. While nature has evolved to produce polymers of relatively high

thermal and kinetic stability, e.g. cellulose and DNA, some synthetic plastics have proven less robust. Alongside chemical reactions that alter the polymer (e.g. oxidation, hydrolysis, photolysis), additive migration is a degradation pathway common to multiple plastic types, which can result in significant damage or vulnerabilities. Complex degradation behaviour can arise where reactions occur concurrently or synergistically; for example, both polymer and plasticiser hydrolysis is observed with Naum Gabo's *Construction in Space "Two Cones"* [4, 5].

Plasticisers are required to ease the processing of synthetic and semi-synthetic polymers, such as polyvinyl chloride (PVC) and cellulosic esters [6, 7]. Camphor was the first plasticiser widely used for cellulose nitrate (CN). In contrast, cellulose acetate (CA) formulations included dimethyl phthalate, diethyl phthalate (DEP), triphenyl phosphate (TPP), toluene sulphonamide, *N*-ethyl toluene sulphonamide, or mixtures of the same [8]. A variety of compounds have been used to plasticise PVC, including sebacates, adipates, and trimellitates, among many others [7]. From the 1930s onwards, patent literature records the evaluation of various plasticisers' compatibility

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with cellulosic and vinyl polymers [9]. Today, phthalates (esters of phthalic acid) account for the majority of the plasticiser market, as higher molecular weight and branched analogues are used to plasticise PVC (e.g. DINP) [10].

Phthalate migration is well documented in medical literature, ecological pollution, food packaging studies, and in studies of consumer products such as furniture, flooring, and toys [11, 12]. Research into the effect of some phthalate plasticisers on human and animal health means their use is now regulated, and the use of non-phthalate and bio-based plasticisers is increasing [13–15]. Some polymeric plasticisers are also marketed for applications requiring low migration rates. Unlike some additives, such as lubricants which help in the manufacturing process only, plasticisers are designed to remain in the plastic matrix and contribute to the plastic article's final properties. They can be present in high concentrations (up to 40%); therefore, migration of plasticisers can cause significant physical changes, such as embrittlement and dimensional changes. For this reason, plasticisers and particularly phthalates are the main target of this review.

Migration occurs when interactions between polymer chains and weakly bound low molecular weight additives are overcome, for example, on contact with a solvent, with the application of heat, or due to changes to the molecular structure of the polymer or additive which modifies the strength of interaction at ambient temperature. The loss of additives, which are typically volatile or semi-volatile organic compounds (VOC/SVOCs), can cause visible and physical changes to objects, including a loss of mass, distortion, and embrittlement. Such changes can make an object more fragile and vulnerable to damage from handling, exhibition, or when supporting its own weight [16, 17].

The appearance of surface deposits can also result from additive migration (Figs. 1 and 2). In traditional polymer science, the terms 'bloom' and 'bleeding' describe the appearance of additives such as stabilisers, lubricants, or

plasticisers on a plastic surface. IUPAC defines bloom as "the process in which one component of a polymer mixture...undergoes phase separation and migration to the external surface" [18]. In conservation literature, observational terms such as "[crystalline] deposits" or "tacky surface", are used to describe visible evidence of additive migration. References to sticky/tacky deposits, 'weeping' or 'sweating' are equivalent to 'bleeding' whereby a thin layer of oily film is formed from liquid plasticiser exuding onto the surface. Furthermore, residues can trap dust, adhere storage materials to the object, and transfer to adjacent materials. As Shashoua notes, this can "reduce their value both commercially and culturally" [19].

In this article, we aim to demonstrate how identifying plastic formulations can be informative for conservation planning and identify future research needs of the sector. For example, identifying additives which may migrate can help to avoid plasticisation of adjacent objects when mixed materials are stored together [20, 21]. Furthermore, for some formulations evaporative loss can dominate, and degradation may occur without visible evidence such as deposits forming. Therefore, we describe methods for additive identification and discuss the intrinsic material properties and environmental factors which influence migration behaviour.

We also aim to place recent research from other fields into the context of conservation; reviews of additive loss from plastics have addressed ways to determine the dominant loss mechanism, measure key mass transport parameters, and model changes to the plastic and surrounding environment as emission occurs [17–19]. Quantitative methods of analysis enable researchers to monitor the concentration, distribution, and loss of additives over time, and ultimately contribute to our understanding of aging behaviour.

Conservation strategies to date

Surveys have frequently found plasticised objects to be some of the most vulnerable in collections. Keneghan's

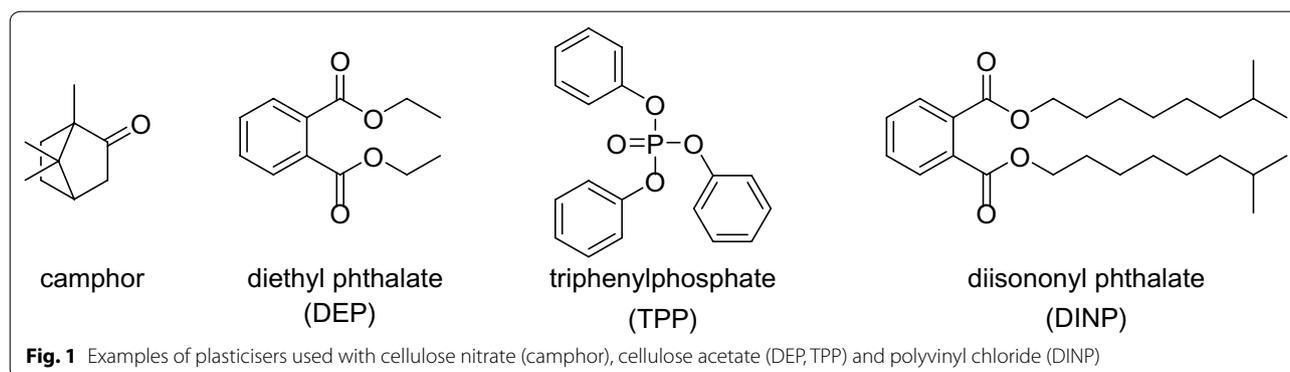




Fig. 2 (Left) Bloom of triphenyl phosphate plasticiser and (right) phthalate plasticiser exudation from dolls made of cellulose acetate. Images reproduced with permission of Tate, London. Both dolls form a part of 'Mouth Open, Teeth Showing (I)'; 2000, Zoe Leonard, Tate X717743 L04293

survey of 7900 plastic objects within the Victoria and Albert Museum's collection showed evidence of chemical damage (classified as bloom, brittleness, discolouration, or sweating) in ~10% of surveyed objects [22]. A more detailed output arose from the use of a condition form including terms specific to additive migration in the pan-European 'POPART' survey [1]. Evidence of additive migration was classified by plastic type; bloom, bleeding, and 'solid exudates' were each observed in 30% of the CA and CN objects surveyed, and "sweating" or a "sticky surface" was observed in 23% of PVC objects.

Strategies proposed for the conservation of vulnerable plastics are primarily environmental control, including cold storage to reduce degradation rates following the assumption that the kinetic parameters follow an Arrhenius relationship. However, the storage space required along with refrigeration infrastructure costs are typically prohibitive for a whole collection. Refrigeration also impedes access to the object and typically is not used during exhibition. Therefore, non-refrigerated storage with macroenvironment climate control may be more achievable.

For cellulose acetate (CA), early research found that cold storage reduces the auto-catalytic reaction rate of polymer hydrolysis or 'vinegar syndrome' [23, 24]. Others recommend ventilated storage or scavengers to minimise a build-up of acidic species arising from hydrolysis of CA and CN [25, 26]. However, a recent study suggests replication as the only viable long-term preservation method for triacetate film [27]. Plasticiser migration occurs

alongside the deacetylation of CA; although, its relative rate, importance, and impact is understudied.

For PVC, evidence of both dehydrochlorination and plasticiser migration have been observed in collections. Thermal and/or photo-oxidative degradation mechanisms have been extensively studied [28–30]. A comprehensive review by Wypch highlights varied aging behaviour between formulations, that plasticiser loss generally occurs before dehydrochlorination during thermal aging experiments, but also that plasticiser evaporation, plasticiser hydrolysis and polymer degradation can be interlinked [31]. Yellowing provides visible evidence of dehydrochlorination, and the appearance of surface exudates and hardening generally results from additive migration.

Thermal aging experiments have shown that enclosure reduces the migration rate of plasticisers from PVC samples relative to non-enclosed samples [32, 33]. Royaux et al. have used similar experiments to investigate the effect of wrapping materials for new and historic PVC samples. Colour changes were particularly evident for samples wrapped in LDPE and PET during thermal aging, and phthalate hydrolysis was also induced on contact with PET. Conversely, rates of yellowing and phthalate migration did not increase for samples wrapped in silk paper versus non-wrapped. However, migration of an oil-based co-plasticiser and proteinaceous component were slowed, which suggests wrapping in suitable materials could be used to slow dirtying and protect the visible appearance of the surface [34, 35].

Plasticiser loss mechanism and rate

Briefly, the migration process is governed by two mass transfer steps (Fig. 3);

- Internal diffusion of additive molecules through the material bulk to the surface
- External mass transfer of additive molecules from the surface to the surroundings (sometimes generalised as evaporation)

The slowest step or ‘rate-limiting step’ controls the overall loss rate from the object. Therefore, the loss may be either “diffusion-controlled” or “evaporation-controlled”. In some cases, a change in the dominant transport step can occur during the ageing period.

The term ‘evaporation-control’ describes the case where the convective mass transfer of molecules between the material surface and adjacent air controls the loss rate. When this process is slower than the internal diffusion rate, thin films of additives can build up on surfaces as seen in conservation studies [16]. However, any accumulation is not necessarily macroscopically visible.

Diffusion-controlled loss occurs when the rate of plasticiser emission from the surface is faster than the rate at which additive molecules are replenished by diffusion from the bulk. Without surface accumulation, no direct observation of the process occurs, but a concentration gradient along a cross-section may be measured [36].

Inhomogeneous concentrations may be hypothesised to result in internal stresses or risk moisture gradients developing, for example, if plasticisers lend hydrophobic properties to the plastic.

The shapes of concentration distance-profiles for both diffusion and evaporation-controlled loss are shown in Fig. 4. Evaporation-controlled systems show a relatively flat concentration profile throughout the sample thickness, while a clear gradient develops under diffusion-controlled conditions. Due to the low volatility of some additives at room temperature, thermal ageing may be used to accelerate the loss rate and ensure measurable changes in additive concentration over shorter experimental time frames.

Aside from concentration-distance profiles, the change in additive concentration as a function of time, or the square root of time can be plotted from analysis of the sample or environment. For example, evaporation-controlled loss results in a sigmoidal-shaped profile of mass loss as a function of the square root of time [37]. While beyond the scope of this review, the concentration–time profile shapes derive from ratios between key evaporation and diffusion parameters [38–40].

The key parameters shown in Fig. 5 are used to model either VOC or SVOC emission rates from solid materials. The World Health Organisation classifies VOCs as having a boiling point range between 50/100 °C and 240/260 °C and SVOCs between 240/260 °C and

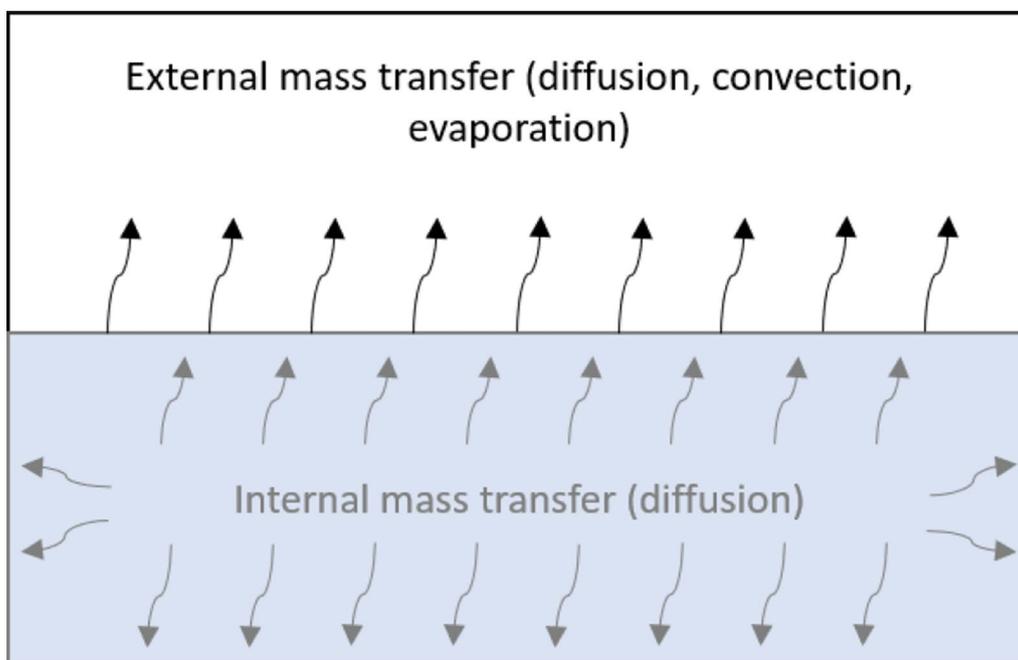


Fig. 3 Schematic showing the two mass transfer steps of plasticiser migration and loss

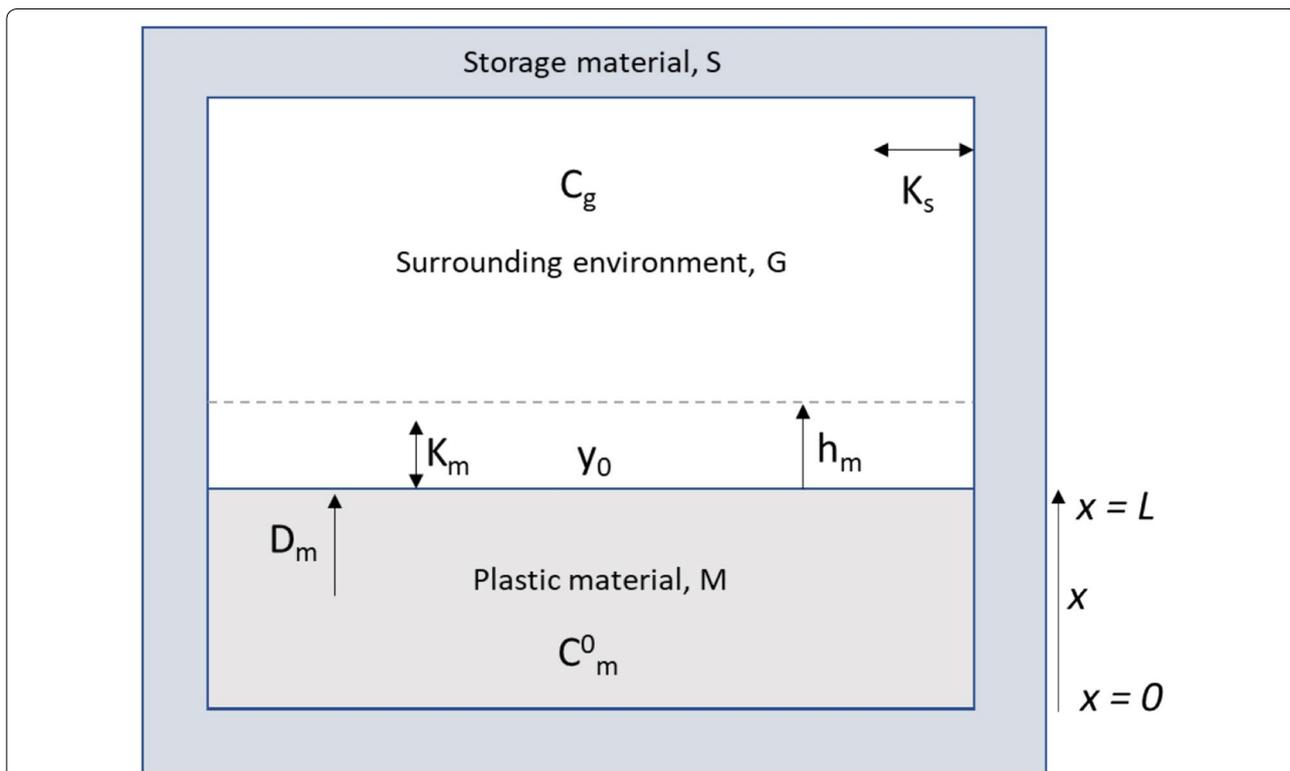
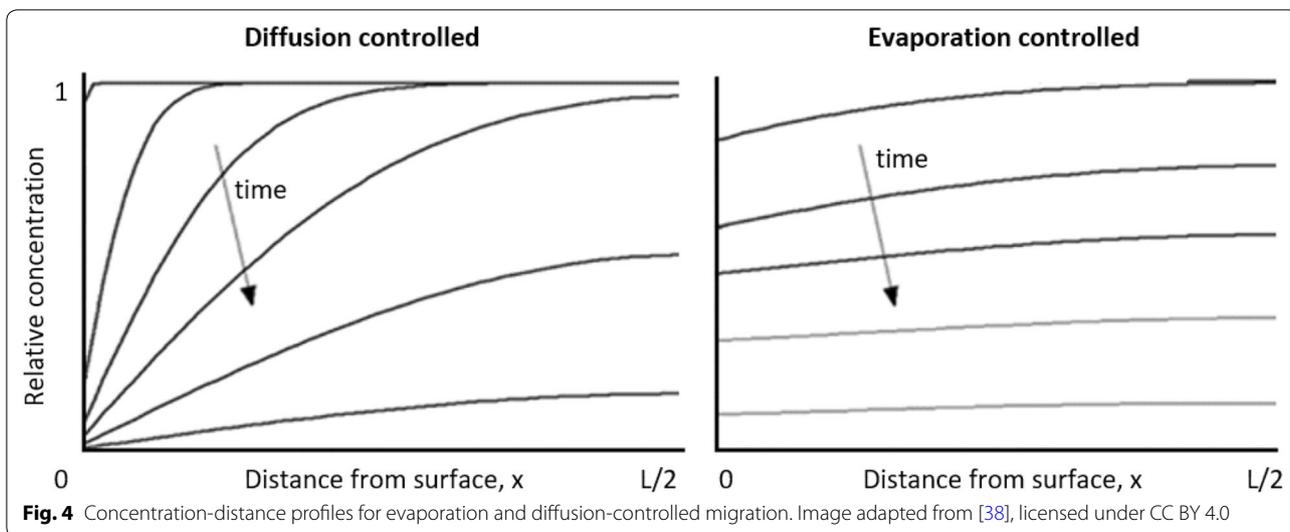


Fig. 5 Schematic showing key mass transport parameters used to describe the emission of additives into the surrounding environment. The dashed line illustrates the conceptual air-boundary layer used in many emissions models. Parameters used in emissions models include the diffusion coefficient through the material, D_m , the material/air partition coefficient K_m , the convective mass transfer coefficient, h_m , and the concentration in the air boundary layer at the surface, y_0

380/400 °C; others classify SVOCs by vapour pressures of 10^{-9} to 10 Pa at room temperature [41].

VOC emission is typically diffusion-controlled and can be modelled if specific parameters are known:

- The material phase diffusion coefficient of the additive, D_m
- A material/air partition coefficient to describe the equilibrium between material surface and adjacent air, K_m
- The additive's initial material phase concentration, C_m^0 (generally assumed constant within the material) [40, 42].

Later VOC models have incorporated the external mass transfer parameter (h_m) to describe the initial loss from the surface into adjacent air which occurs early in the emission period, and others have sought to incorporate sink effects.

Conversely, for SVOCs, evaporation-controlled emission modelling requires knowledge of:

- The gas-phase concentration of the SVOC in equilibrium with the material phase, y_0
- The convective mass transfer coefficient from the material surface to air, h_m [43].

In non-ideal environments (e.g. indoors) the partitioning of SVOCs from the gas-phase to surfaces, airborne particles, and settled dust is significant; therefore, models also require:

- The concentration of dust/particles
- The mass transfer coefficient from air to the surrounding surfaces, h_s
- Partition coefficients describing transfer to condensed phases, such as airborne particles (K_p) and settled dust (K_d) or onto indoor surfaces (K_s) [42].

These parameters are challenging to measure, and research is ongoing to improve the accuracy of the measurement methodology [44–46]. System parameters include the emitting surface area, room volume, ventilation rate, and room surface area are also required.

It should be noted that the validity of ignoring the diffusion process for other SVOCs has been evaluated with limited formulations. To date, the evaporation-controlled SVOC emission models best describe low volatility phthalates (e.g. DEHP, DINP, BBzP) in solid materials with a high initial concentration. Furthermore, diffusion and partitioning coefficients may become influential as additive concentration decreases over time.

Other examples highlight the variation in behaviour which may be observed in plastic collections where many additive/polymer combinations will be present. Benzenesulfonamide plasticisers have been found in plastics dating from the 1950s, and are classified as VOCs with a boiling point at the higher end of the range [16]. A recent study reported the diffusion-controlled migration of n-butyl benzenesulfonamide from a polyamide pipe [37]. Organophosphate flame retardants were also found to migrate under diffusion-controlled rates from rigid foam materials, despite their classification as SVOCs [39].

Factors affecting migration

Parameter values will vary with environmental factors (Table 1), affecting both the loss rate and, potentially, switching the dominant step. A range of environmental and intrinsic factors have been extensively researched and reviewed for indoor air quality audiences [47, 48]. The relevance of their findings to conservation research is outlined below.

The cornerstones of environmental control in preventive conservation, temperature, relative humidity, and ventilation or enclosure, provide accessible means for conservators to exert influence on the rate and extent of degradation. There is also evidence that storage type and material can influence the emission rate. Intrinsic factors of the plastic formulation also play a significant role, including the concentration, chemical, and physical properties of the plasticiser. For example, short-chain phthalates (e.g. dimethyl phthalate and diethyl phthalate) have vapour pressures four orders of magnitude greater than longer chain analogues such as di(2-ethylhexyl) phthalate (DEHP) [41].

Temperature Evaporation-controlled rates and gas-phase concentrations increase with temperature, a trend observed in multiple studies of phthalate emissions [49–

Table 1 Factors affecting migration rate

Extrinsic factors (environmental)	Intrinsic factors (material dependent)
Temperature	Plasticiser concentration
Relative humidity	Plasticiser properties (e.g. volatility)
Volume of surrounding air and airflow rate	Sample thickness and surface area
Storage material and air quality	

52]. Increasing the temperature also leads to a larger solid diffusion coefficient and thus a faster diffusion rate, as described by an exponential Arrhenius type relationship; $D = D_0 \exp\left(-\frac{E_a}{RT}\right)$. Deng has proposed a modified equation to account for the temperature dependence of the diffusion coefficient for VOCs in porous materials; $D = B_1 \exp\left(\frac{B_2}{T}\right)$ where B1 and B2 are constants for a specific VOC/material pair [53].

Storage at a low temperature is regarded as a constructive action for plastics conservation, as it reduces the rate of both mass transfer processes. However, lowering the temperature has induced additive bloom in at least one conservation treatment; lubricant bloom appeared on PVC dolls stored at a yearly average temperature of 11–12 °C over 10 years [54]. Phthalate and citrate plasticisers were identified in a cohort of the dolls by ATR-FTIR spectroscopy; although, GC-MS analysis of the bloom showed stearyl alcohol as the dominant component. Bloom reappeared within 6 months of cleaning and a return to the same cool conditions. Despite the reappearance, objects were returned to cool storage in order to retain high plasticiser levels, as plasticiser loss could cause long term stability issues compared to the migration of the lower concentration moulding lubricant.

Relevance for ageing studies The Arrhenius relationship relating temperature and the diffusion rate constant is the basis of accelerated ageing studies. Thermal ageing accelerates the rate of the degradation processes which occur at lower use temperatures (e.g. room/storage temperature in heritage contexts), to ensure the chemical and physical changes are measurable over a shorter timeframe than the years/decades-long natural ageing process. Accelerated ageing is used in the conservation community to understand long term ageing behaviour under controlled environmental conditions (typically temperature, and relative humidity) [55–57]. However, some caveats apply; the polymer, degradation mechanism and rate-limiting step should remain unchanged at both temperatures; a change in the slope of an Arrhenius plot (log(measured variable) vs 1/T), occurs when the rate-limiting step changes [37, 58, 59]. If so, diffusion-controlled migration behaviour initiated by a high ageing temperature will not be representative of an evaporation-controlled system at room temperature. Wei et al. collated examples of plasticiser loss studied by thermal ageing and found that most evaporation-controlled regimes generally become diffusion-controlled around 100 °C [38].

While Wei's critical temperature range is useful to consider when conducting ageing experiments on specific formulations, it cannot be considered alone. The importance of other environmental parameters is demonstrated

by Shashoua's accelerated ageing of 30 year-old DEHP-plasticised PVC at 70 °C [60]. Ageing in a sealed container led to evaporation-controlled migration, but the removal of the enclosure enhanced the evaporation rate so that diffusion became rate-limiting. Indeed, ageing environments are not always able to replicate real conditions; therefore, the potential for influence by other environmental factors is discussed below.

Relative Humidity The effect of humidity is highly dependent on the formulation. For evaporation-controlled regimes, two studies of 20 wt.% DEHP/PVC samples at 100 °C have suggested that the emission rate was not affected by humidity changes [12, 13]. An accelerated ageing study for CA thin films also suggested that plasticiser loss is independent of relative humidity between 30–70% [61]. However, the opposite was recently reported for thicker phthalate plasticised CA samples by Kemper et al. [62].

To date, no study has conclusively reported if relative humidity, deacetylation and plasticiser migration are related in CA degradation. Hydrolysis of phthalate esters is also known in humid conditions on surfaces and, under non-neutral pHs, has been postulated to cause the formation of phthalic acid crystals. However, no case studies are available [20, 63]. The water contents within the object and the air may also have different effects which makes a full assessment challenging; for example surface sorption of SVOCs is known to be affected by relative humidity changes in some cases [47].

Ventilation In chamber studies approximating a sealed enclosure, SVOC emission from the material phase reaches a steady-state equilibrium over time. In chamber studies more closely representing indoor environments, the impact of the air exchange rate (AER) or ventilation rate is more challenging to study. As noted by Rackes et al. 'mass transfer from a material surface-air interface to the bulk room air depends on the air concentration, which in turn depends on the AER' [64].

For evaporation-controlled systems the emission rate from a material is governed by the mass transfer coefficient, surface area, and the difference in concentration between the surrounding air (C_g) and the air adjacent to the material's surface (y_0) or $ER = h_m A (y_0 - C_g)$. Theoretically, increasing the air flow rate will reduce the gas-phase concentration (C_g) by dilution. Little has noted that AER has only a small impact on the air speed over a surface, suggesting y_0 is not significantly affected by ventilation rate [65]. This combination creates a greater concentration gradient between the source and surrounding air which increases the driving force for emission as ventilation/ACH increases.

Additionally, Liang et al. suggested the convective mass transfer coefficient, h_m , was increased by a higher air velocity above an emission source [66]. These findings support the experimental work of Shashoua and others; where greater loss was measured over the same time frame when ventilation was enhanced [33, 60, 67]. Ekelund et al. also observed that the loss rate of DEHP increases linearly with gas flow rate, before reaching a limiting flow rate (75 ml min^{-1}) beyond which no effect was observed [68].

In non-steady state environments (e.g. real environments such as open shelf storage), the precise effects of ventilation are challenging to quantify. However, higher emission rates would be expected versus stagnant environments. For CA, the relative rates of polymer deacetylation and plasticiser loss are unknown; therefore, the effectiveness of ventilated containers has been questioned [27].

As enclosure is not theorised to have any adverse effect on polymer degradation for PVC, Royaux has proposed wrapping PVC objects [34]. Furthermore, an enclosure can minimise the amount of airborne particles and dust in contact with an object [69]. Some gas-phase SVOCs can sorb to (and desorb from) airborne particulate matter and settled dust present in the surrounding environment; a process called 'dynamic partitioning' [70–72]. A study of DEHP emission from vinyl flooring found that the emission rate was enhanced when airborne particles were introduced [73]. One hypothesis is that the emission rate is driven by a greater concentration difference ($y_0 C_g$), owing to a reduced gas-phase SVOC concentration when partitioning occurs.

Storage material Both VOCs and SVOCs will also rapidly partition from the gas phase onto surfaces at room temperature in indoor environments [74]. Indoor surfaces such as glass, painted surfaces, plaster, wood and plastics can host reservoirs of SVOCs; by adsorption onto the surface, or absorption into the material [51, 66, 75]. A study by Wu et al. measured similar phthalate partition coefficients across non-absorbing materials (glass, stainless steel and acrylic), which suggests partitioning can also occur into thin films of organic grime on a surface, independent of the surface's chemical or physical properties [76]. Once again, partitioning to adjacent surfaces can enhance emission rates from the source.

In the context of heritage conservation, potential sink materials include adsorbents, packing materials, and even different materials found in composite objects. For example, Shashoua's artificial ageing of PVC in a sealed glass vessel showed a greater DEHP migration rate from PVC due to the inclusion of silica, Ageless® oxygen absorber, and activated charcoal absorbents. The same

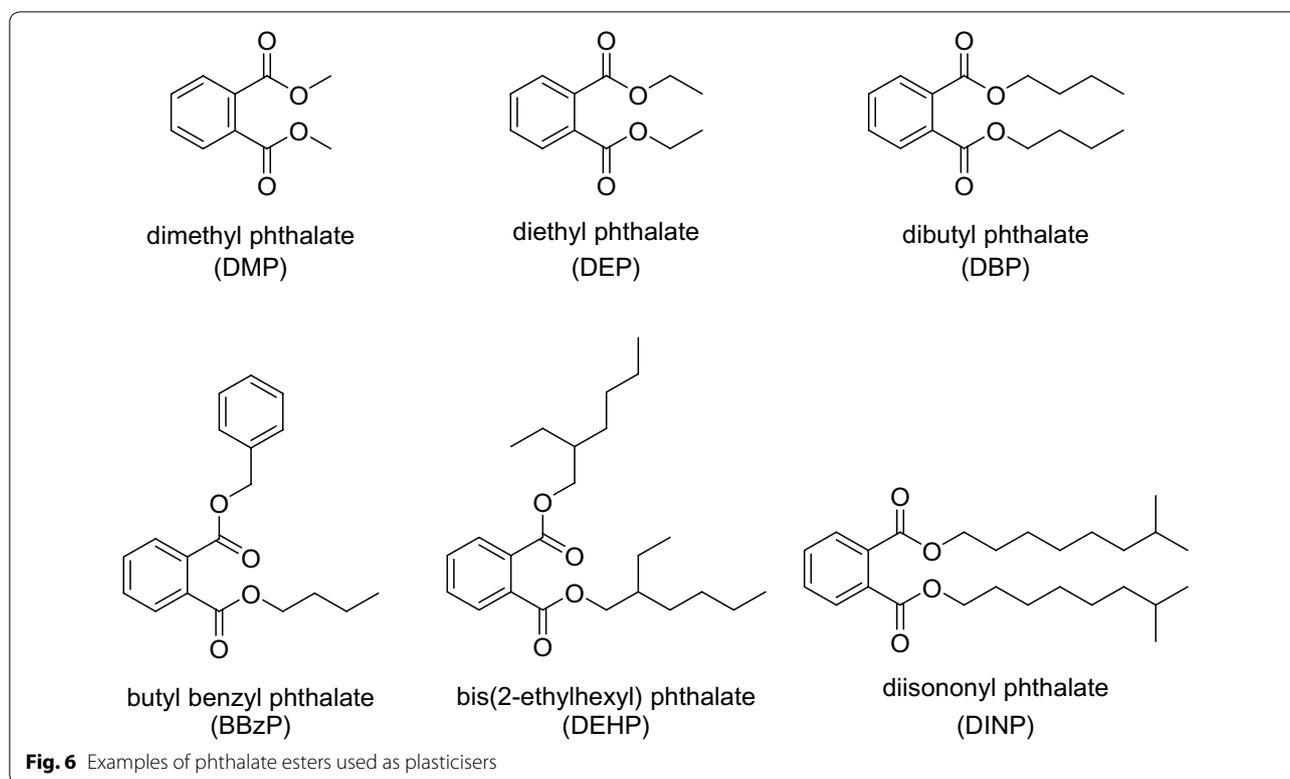
trend was observed for samples aged in an LDPE bag versus the sealed glass container [60].

For mixed material objects, partitioning to adjacent components could occur, but the effect of additive sorption onto other materials, including other plastic formulations, have yet to be studied. There may also be broader implications in terms of storing multiple objects together; Curran et al. have begun this work by demonstrating the effect of VOCs emitted from plastics on paper [21]. Other examples highlight the potential for cross migration between different plastics; DEHP migrated from a PVC object and plasticised the LDPE tray it was stored in, causing irreversible damage [20]. Royaux et al. recently observed phthalate and azelate plasticiser migration from a PVC object through an LDPE wrap during artificial ageing in a closed container but found no significant difference in migration rate versus the unwrapped reference material. Ageing in contact with a PET product (Melinex®) appeared to induce the hydrolysis of dioctyl phthalate to phthalic acid. However, it is unknown if similar behaviour would be replicated under less extreme environmental conditions [35].

Material surface area & thickness Material thickness and surface area are important parameters for SVOC emission models. For surface area; the larger exposed area of an object, the greater the emission rate [43]. As the diffusion rate is dependent on diffusion distance, the material thickness will have a significant role in the loss rate in diffusion-controlled emissions. It follows that loss from thin samples is more likely to be evaporation controlled. Uniformity cannot be assumed in a plastic object as thickness variations are possible from manufacture; for example, variable shrinkage is common in amorphous and semi-crystalline polymers used in injection moulding. The longer-term creep behaviour of plastics under load can also cause significant non-uniform deformation [77].

Plasticiser characteristics No covalent bond exists between polymers and external plasticisers; their retention within the matrix relies on intermolecular interactions (dipole–dipole in one study of a phthalate-CA system [78]) determined by the chemical structure of the plasticisers and polymers. This interaction disrupts the network of polymer chains, allowing increased polymer chain mobility which is evident by a decrease in the polymer's glass transition temperature.

Over decades of use and development, the general trend has been to reduce phthalates' migration tendency by increasing the length or branching of the alcohol constituent (Fig. 6). Dimethyl and diethyl phthalates were used in the early to mid-twentieth century to plasticise



cellulosic polymers [55, 79]. More recently higher molecular weight phthalates, including the branched DEHP, have been observed frequently in studies of the indoor environments owing to their efficient plasticisation of PVC and widespread use [80–82]. Owing to their enhanced volatility, the migration rate of low molecular weight phthalate plasticisers can be orders of magnitude higher than the larger additives [83].

Phosphate esters are another class of plasticiser, and can also be used as flame retardants in PVC, PU and, historically, in CA. In particular, the presence of triphenyl phosphate (TPP) appears to induce significant degradation and damage in some CA objects [16]. As previously discussed, temperature changes can affect solubility and induce bloom, but TPP appears to offer a slightly different case study; two studies have proposed that recrystallisation occurs within historic CA objects. TPP was historically used as a phthalate co-plasticiser, and was solubilised by DEP. Therefore, McGath et al. suggested that the crystallisation of TPP occurs as phthalate plasticisers migrate away over time [84]. It is unclear if migration occurs for TPP, but mapping of phosphorous signals suggested aggregation of phosphorous-rich species. More recently, a study of twentieth century Chinese CA microfilm linked deacetylation of the film substrate to the migration of TPP and the

formation of microbubbles. The study also found increased hydrophilicity in areas of the film affected by microbubble formation [85]. In other studies, TPP's hydrolysis products of phenol and diphenyl phosphate have been detected, suggesting plasticiser and migration of by-products can also occur [4, 86].

An object's plasticiser concentration will also influence the rate of loss; the diffusion rate is more correctly described by a concentration-dependent diffusion coefficient and is explained more thoroughly elsewhere [87–89].

Qualitative and quantitative methods for the analysis of plasticised objects

Many examples of both qualitative and quantitative analysis are available; including spectroscopic and chromatographic techniques for regulatory testing of consumer products [90, 91]. Ageing studies use similar methods often in combination with mechanical tests [92]. Emission studies are also of interest and have led to the development of sensitive environmental sampling methods [44].

Analytical techniques suitable for use in heritage applications are typically assessed in terms of their destructive and invasive sampling requirements. Identification of additives is often simplified by their removal from the

host polymer matrix before analysis; therefore, published protocols are generally destructive and rely on separation by solvent extraction before identification by spectroscopy, chromatography or spectrometry. Increasingly non-destructive surface analysis and minimally invasive passive sampling methods have been employed. Examples from all research sectors and evaluation of their suitability for heritage objects are given below.

Non-invasive environment sampling Environmental sampling can be particularly useful when no visible signs of additive migration are present, e.g. under diffusion-controlled loss regimes. Due to the volatile nature of some species emitted from degrading plastics, passive sampling of the environment has previously been used to monitor historic plastics by SPME-GC/MS, as demonstrated by Curran et al. [93], and thermal desorption, as demonstrated by Mitchell et al. [94]. Similar techniques have been used on whole museum objects. For example, active sampling in a stainless steel chamber using pumped air and TENAX sorbent tubes followed by ATD-GC/MS has been successfully used to detect and measure the concentration of volatile naphthalene pesticide residues [95]. Recently, Kearney et al. showed the utility of SPME fibres for sorption of phthalates emitted from a visibly degraded object where it was not possible to sample via contact [4]. However, the variability of measurements in non-controlled museum environments discounts their use in quantitative studies [96].

GC/MS analysis of analytes captured in passive samplers (sorbent tubes, activated charcoal disks, SPME fibres) from sealed chamber emission studies have also been used for measurement of key parameters (γ_0 and K_m) to model semi-volatile phthalate migration from vinyl flooring at 25 °C [97]. The models focus on emissions from flat materials rather than the complex geometries found in heritage objects. However, a similar approach could be used to research emissions rates for samples of relevance to conservation.

Sampling and analysis of objects Sampling of surface deposits or exudates can be achieved by scalpel or swabbing with minimal effect on the object's surface. However, the use of solvent-wetted swabs is unsuitable for some plastics. Deposits formed under evaporation-controlled conditions are ideal candidates because there can be sufficient amounts of the deposit to measure [98]. Collected surface samples may be characterised by a range of spectroscopic techniques, including $^1\text{H}/^{13}\text{C}/^{31}\text{P}$ Nuclear Magnetic Resonance (NMR), Infrared, and Raman, or chromatography-mass spectrometry techniques [16, 79, 99–101].

Where destructive sampling is possible, small cut samples can also be analysed [98, 102]. For both CA and PVC samples, solvent extraction of additives simplifies the sample matrix prior to analysis [79, 103–105]. Where quantitative analysis is desired, care should be taken to ensure complete extraction of additives into the solvent, as demonstrated by Kemper et al. [79]. Thermal methods, such as Py-GC/MS or thermogravimetry techniques (e.g. TGA, TG-FTIR or TG-GC/MS) are also used for separation, including for determining a sample's plasticiser concentration by weight [5, 8, 58, 61, 98].

If a non-instrumental and less costly method is desirable, thin layer chromatography (TLC) allows separation of different plasticiser classes, e.g. adipates versus phthalates. Resolution by retention factors (R_f) of some homologous phthalates is also possible. However, known references should be run at the same time as unknown samples to improve the reliability of the interpretation. Sensitivity to sample amount and type (limit of detection) can also be limiting versus liquid or gas chromatography [106, 107].

In-situ analysis of objects Dependent on the sample's formulation, infrared spectroscopy (IR) may be suitable for additive identification when sampling is not possible.

Attenuated total reflectance sampling accessories (ATR-IR) can be used if the object's geometry is suitable (i.e. flat) and good contact between the object and spectrometer can be achieved. ATR-IR is also a good method for strongly absorbing plastics not suited to analysis in transmission mode. Pressurised contact with the ATR crystal is required to maximise the quality of a spectrum, but this can be impossible with fragile or vulnerable heritage objects. Reflectance modules can reduce the need for pressurised contact and allow polymer identification; however, low concentration additives can be challenging to distinguish from distorted spectra with low signal-to-noise ratios [108].

Ultimately, the utility of mid-IR methods is dependent on plastic type; overlap with polymer vibrational bands and relatively low additive concentrations (<30%) can make additive identification challenging from low-intensity peaks. For example, major peaks from phthalates and CA are indistinguishable due to overlapping carbonyl resonances [109]. ATR-IR spectroscopy has been used to detect the presence of phthalates in plasticised PVC samples, but the similarity of di-alkyl phthalate spectra complicates characterisation [110].

In situ identification of additives within historic polymeric objects has been most successfully demonstrated using Raman spectroscopy; including the use of a portable dispersive instrument (excitation at 785 nm) and laboratory-based FT-Raman instruments (excitation at

1064 nm) [111–113]. Using a portable spectrometer to survey historic aviation glasses, Madden et al. identified camphor in CN, alongside dimethyl phthalate, diethyl phthalate and TPP in CA. Similarly, Neves et al. used Raman microscopy to analyse CN film [114]. Madden et al. also reported the presence of a longer chain phthalate dioctyl phthalate in PVC; however, as with IR spectroscopy, the similarity of di-alkyl phthalate generally complicates the distinction of homologues [115]. Recently, destructive sampling and analysis by GC/MS were needed to distinguish dimethyl phthalate, dibutyl phthalate and DEHP in conserved PVC sculptures after analysis by a portable Raman instrument [116]. Fluorescent interference has been found to impede peak detection, and skilled control over the incident laser energy is also required to minimise the invasiveness of the technique for heritage objects. The advantages offered by Raman spectroscopy over infrared spectroscopy are especially apparent for CA objects, where detection of phthalates is unaffected by overlapping peaks derived from the polymer.

Spatially resolved techniques

While the techniques above record an averaged measurement from a single point, “chemical mapping” or imaging techniques can be used to detect the spatial distribution and concentrations of components over a given area. Imaging and mapping techniques record multiple individual spectra and their location, making these techniques suitable for microscopic surface and depth profiling. In general, mapping refers to the successive point-by-point collection of spectra across a defined area, while imaging collects multiple spectra concurrently over larger areas. Typically, a relative scale of a component’s concentration is obtained by mathematically correlating sample spectra with each other or the spectra of a pure component, to identify ‘component-rich’ and ‘component-poor’ phases [117]. Absolute concentrations may be obtained by the application of Beer’s law for spectroscopic analysis where distinct, well-resolved peaks are identified, and by comparison to calibration samples.

An example highlights the potential of spatially resolved composition analysis for plastics conservation. McGath et al. used SEM–EDX to detect the presence of phosphorous-containing additives (triphenyl phosphate confirmed by extractive sampling) in degraded CA objects [84]. Elemental mapping revealed phosphorous-rich areas concentrated around microscopic cracks, prompting the author to suggest that crystallisation of TPP was the cause of crack formation. Migration concentrated at the site of a pre-existing crack is another hypothesis. This example highlights the insights gained by seeking to map additive concentrations and relate

them to physical and macroscopic manifestations of damage.

Surface analysis Imaging versions of mid-infrared spectroscopy can be used for surface analysis of organic and inorganic components. For example, macro-ATR imaging was recently used to analyse the surface of historic leather book cover fragments in 0.6 mm² sections, where the spatial resolution of 15 µm showed the presence and location of degradation phenomena, including gelatinised collagen and metal soaps [118].

At larger scales, hyperspectral scanners are available that cover the short-wave infrared region. They can be used for non-destructive surface analysis of 2D or 3D objects; although, lower resolution images result from a larger field of view [119]. In some cases, plastics with low melting or glass transition temperatures may be affected by the heat from the high-intensity light sources used in some imaging techniques. Ultraviolet and near-infrared (NIR) scanners are commercially available, and NIR imaging is used to identify plastic type in the recycling industry; however, few studies demonstrate the distinction of specific formulations [61, 120, 121]. A hyperspectral NIR approach has been used to distinguish plastics by the polymer and the flame retardant used [122]. In terms of spatial distribution, Csefalyova demonstrated the use of NIR imaging and principal component analysis to map the spatial distribution of phthalate plasticiser across a planar historic PVC sample [119].

Aside from imaging techniques, point-based surface sampling and analysis can also be performed in a spatially resolved manner. In forensic science, manual swabbing protocols and robotic methods for precise sampling and location recording have been demonstrated for non-heritage 3D objects [58, 59].

Depth profiling Migration is unlikely to be uniform across an object owing to the non-uniform ageing behaviour of plastics, but whether this will impact the location of damage and have relevance to conservation measures remains unknown. Profiling the chemical characteristics throughout an object’s thickness can be important in heritage; for example, paintings conservators take cross-sections and make use of imaging spectroscopies for high-resolution analysis [123, 124].

Analysing the composition of a sample as a function of thickness/depth from the surface can be used to determine the loss mode for additives in plastics. Spatial resolution at the micrometre scale by coupling point-based vibrational spectroscopy to optical microscopes is useful for cut cross-section samples; infrared or Raman microspectroscopy offer spatial resolutions of between ~10–50 µm [125, 126]. Nano-scale resolution

(~100 nm) has also been achieved using AFM probes coupled with infrared absorption spectroscopy to map chemical components in plastic samples [127]. Therefore, aggregates of molecules are generally resolvable, but individual molecules (~1 nm) are not [128]. IR microscopy has been used to determine additive concentrations along cut cross-sections in diffusion and ageing studies of plastics [126, 129]. Focal plane array detectors for microscopic infrared imaging significantly enhance the speed of data collection, although at a higher cost and with a narrower spectral range (typically >900 cm⁻¹) than point-to-point mapping systems [130].

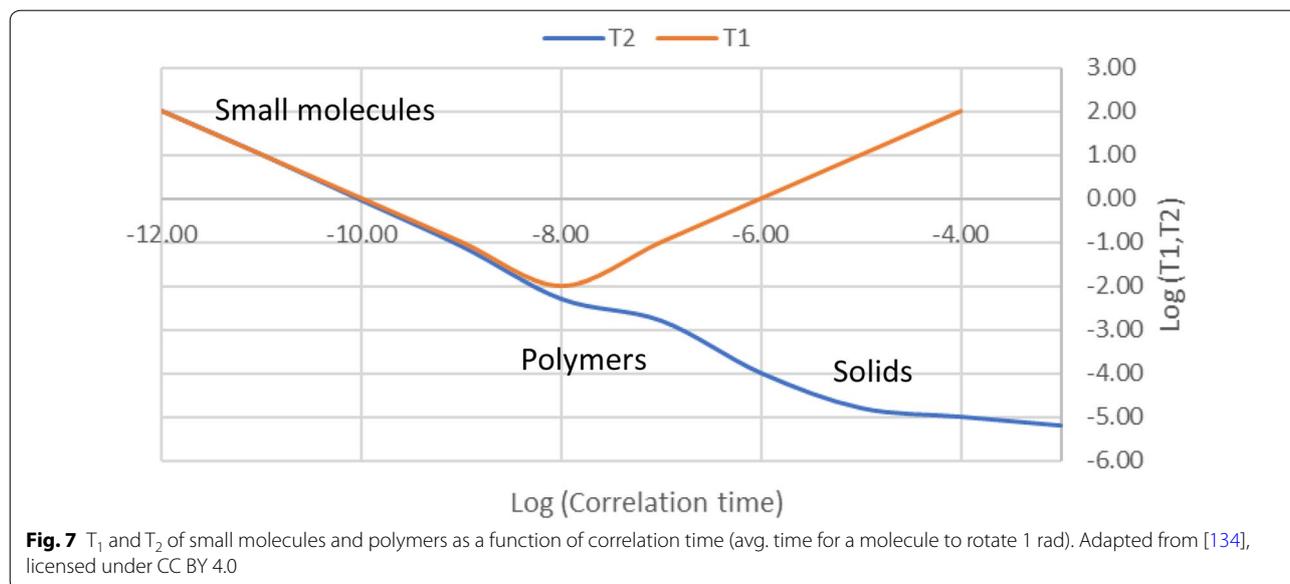
Currently, limited options exist for non-destructive depth profiling; vibrational spectroscopy is generally unsuitable due to the low penetration depths of the incident light. However, confocal Raman spectroscopy can achieve greater penetration depth [131, 132]. Adams et al. successfully used terahertz time-domain spectroscopy (THz-TDS) for concentration-depth profiling of known samples. However, the complexity of spectra means that it is only suited to samples of known history and formulation [133].

Single-sided NMR, a low-field technique, also enables non-destructive concentration-depth profiling of a plastic sample. Scans performed at various distances from the sample using an adjustable height stage allow profiling through a material in ~100 μm slices [120]. Adams et al. demonstrated the first use of proton relaxometry to measure the concentration profile through a plasticised PVC sample of known formulation. A decrease in the concentration of plasticiser leads to a reduction in relaxation times related to both the additive (long T₂) and

polymer components (short T₂) and also the proton fraction; therefore, signals from low concentration (<13%) samples could not be discriminated. However, they also observed different relaxation behaviour with different additives, and suggest that the creation of a database recording two characteristic relaxation parameters and proton fractions from characterised samples could allow identification of additives without need for spectroscopic analysis.

Analysis of 3D objects Techniques such as terahertz pulsed imaging (THz) and magnetic resonance imaging (MRI) methods have been used to analyse 3D objects non-destructively. They are useful for non-planar samples, but they require expertise in operation and data analysis. For example, both THz-TDS and 3D THz pulsed imaging were used by Strlič et al. to distinguish plastic type in historic samples, as well as image features such as internal cracks and delamination. However, no spectral features differed between plasticised and non-plasticised PVC samples. The effects of plasticisation on other polymers' THz spectra has not been explored [135].

Finally, mid to high-field magnetic resonance systems are routinely used to image the distribution of mobile species within complex three-dimensional matrices; e.g. imaging water in human tissue in clinical research. The distinction of small molecules from larger polymeric components is reliant on differences in molecular mobility, and the associated differences in longitudinal (T₁) and transversal (T₂) magnetisation decay rates (Fig. 7). Proton signals from bound protons such as those in polymers will decay more quickly (short T₂) than those



from more mobile species, such as additives or free water (long T₂) [136]. Experimental parameters such as pulse echo (TE) and repetition times (TR), may be adjusted so that full recovery of the signal derived only from polymeric protons is achieved, and therefore does not contribute to the image unlike that from the additives. For example, O'Donnell et al. imaged the distribution of an organic lubricant within a solid polyethylene pipe; blisters with a high concentration of lubricant were observed [137], and Wiesenberger et al. monitored the absorption of an organic solvent into PMMA rods [138]. It should be noted that the additive concentration required to achieve a sufficient signal-to-noise ratio will be system dependent [139, 140]. Furthermore, analysis is also expensive, and spectral interpretation is non-trivial, so the practicality of such methods is significantly limited for heritage applications currently.

Conclusions

Plasticiser loss is a well-observed degradation mechanism for PVC and CA objects found in heritage collections, which has driven preventive conservation research. For plasticised objects, a principal conservation aim is to prevent plasticiser migration and loss over time, to limit the impact that its loss can have on the objects' physical appearance and stability. Both the display and storage environment will influence all mass transfer processes and the loss rate; therefore, conservation professionals are generally encouraged to use environmentally controlled storage. The impact of SVOCs partitioning to airborne particles, dust, and adjacent surfaces on the emission behaviour of plastic additives is increasingly clear from indoor air quality studies. There is scope for further research into the beneficial and adverse effects of adsorbents, object enclosure, and conservation storage materials.

As long-term preservation of cultural heritage is cost and resource-intensive, knowledge of intrinsic properties (formulations, additive concentration, and sample thickness) may help practitioners prioritise vulnerable objects. For example, when recommended storage environments are not achievable for a whole collection.

A range of qualitative and quantitative analytical methods for environmental and object sampling are discussed. Minimally invasive sampling of deposits can be followed by chromatographic or spectroscopic analysis. For objects without removable deposits, suitable techniques vary due to the material characteristics, but in situ characterisation of CA and CN has been most successfully demonstrated with Raman spectroscopy. However, destructive sampling and chromatographic separation is required where peak overlap or spectral similarity occurs with Infrared and Raman spectroscopy, e.g. PVC. Routine formulation

analysis of collection objects, for example, during collection surveys, would also help to assess if patterns exist between specific formulations, e.g. plasticiser type, and the risk of specific damage types occurring. Relatively low-tech methods, such as TLC, for additive identification, are discussed but require further development.

For scientific researchers, recent developments in spatially resolved analysis and non-destructive methods offer the chance to understand an additive's migration behaviour and impact, including within real objects as they age. Priorities for heritage scientists remain to develop minimally invasive methods for additive analysis, to determine if specific formulations are more vulnerable to degradation than others, to understand how migration correlates to physical damage on an object or adjacent objects, and to further study how migration behaviour can be minimised through preventive conservation measures.

Abbreviations

ATR: Attenuated total reflectance; AER: Air Exchange Rate; AFM: Atomic Force Microscopy; ATD: Attenuated Thermal Desorption; BBzP: Benzyl butyl phthalate; CA: Cellulose Acetate; CN: Cellulose Nitrate; DBP: Dibutyl phthalate; DEP: Diethyl phthalate; DEHP: Bis(2-ethylhexyl) phthalate; DINP: Diisononyl phthalate; DMP: Dimethyl phthalate; GC/MS: Gas Chromatography – Mass Spectrometry; IR: Infrared Spectroscopy; LDPE: Low Density Polyethylene; MRI: Magnetic Resonance Imaging; NIR: Near Infrared Spectroscopy; NMR: Nuclear Magnetic Resonance; PMMA: Poly(methylmethacrylate); PU: Polyurethane; PVC: Poly(vinylchloride); Py-GC/MS: Pyrolysis Gas Chromatography – Mass Spectrometry; SEM-EDX: Scanning Electron Microscopy—Energy-dispersive X-ray spectroscopy; SPME: Solid Phase Microextraction; SVOC: Semi-volatile organic compound; TGA: Thermogravimetric Analysis; THz: Terahertz Spectroscopy; THz-TDS: Terahertz – Time Domain Spectroscopy; TLC: Thin Layer Chromatography; TPP: Triphenyl phosphite; VOC: Volatile organic compound.

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Authors' contributions

RK critically analysed the literature and drafted the manuscript, KC and JGB helped to review and edit the manuscript. All authors participated in its design. All authors read and approved the final manuscript.

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Availability of data and materials

Data sharing is not applicable to this article as no datasets were generated or analysed during the current study.

Competing interests

The authors declare that they have no competing interests in this section.

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