Damage function for poly(vinyl chloride) in heritage collections

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A R T I C L E   I N F O

A B S T R A C T

Yellowing of plastic objects as a consequence of chemical degradation is a common heritage conservation challenge. In the case of poly(vinyl chloride) elimination of hydrogen chloride leads to the formation of polyene sequences that act as chromophores. The objective of this work was to quantitatively evaluate the rate of degradation observed as yellowing, as relevant to room conditions during long-term storage of heritage collections. Degradation was quantified as increase in the b* colour coordinate during accelerated degradation at 50 and 70 °C as a function of temperature, relative humidity, plasticizer content, and polymer molecular weight. The significance of each variable was investigated with multiple linear regression. Lower temperature, lower relative humidity, higher polymer molecular weight and higher plasticizer content were associated with lower degradation rates. The activation energy of 86 kJ/mol was calculated. The concept of '1- °C-equivalent' is introduced to enable variable prioritisation from a heritage management aspect. The resulting model can be used to shape environmental management guidelines and identify the most vulnerable objects in heritage collections.

1. Introduction

Poly(vinyl chloride) (PVC) is one of the less stable polymeric materials that is widely used in all aspects of our daily lives, from designer furniture, plastic sculptures, inflatable objects to toys and objects for daily use [1,2]. Although the polymer type of many objects in contemporary collections remains unknown, PVC can represent as much as 13% of these collections [2]. The degradation of PVC objects involves several damage processes – dehydrochlorination of the polymer leads to yellowing (Figs. 1 and Supplementary S1), the accumulation of plasticizer can cause surface stickiness, and the loss of plasticizers [3] leads to loss of mechanical properties and cracking, the degradation of pigments and dyes leads to discolouration [4,5]. In this paper, we focus on yellowing, as changes in the visual appearance of heritage objects are quickly noticed and recognised by conservators and the general public. It is generally perceived as negative and connected to the object being degraded. Therefore, preserving the original colour is closely related to preserving the value of the object and the collection.

Most research on stabilization of PVC has focused on preventing early-stage degradation and ensuring the service lifetime of industrial products. This period depends largely on the application and ranges from a few years (a plastic bag) to a few decades (window frames).

Despite that, late-stage degradation of PVC objects is not understood well. As cultural heritage, objects retain their value and become part of museum collections long after their intended lifetime has ended [6]. Addressing advanced stages of degradation is therefore important in the preservation of such objects.

The polymer is prone to degradation by elimination of hydrogen chloride, which initially starts at structural irregularities in the polymer chain, such as allylic and tertiary chlorine sites (labile chlorine) [7,8]. Thermal dehydrochlorination proceeds in a ionic or quasi-ionic manner, likely through an ion-pair intermediate, due to low polarity of the material [7]. The reaction is autocatalytic and leads to the formation of a new reactive site. Consequently, a polyene sequence is formed, making the object appear yellow. As the degradation progresses, the intensity of yellowing may increase or turn to orange, pink, reddish, brown and black [6,9,10]. Due to poor thermal stability, processing and moulding is difficult without the use of thermal stabilizers and lubricants. Other additives such as plasticizers, fillers, UV stabilizers, pigments, flame retardants and biocides are also commonly used [11]. Thermal stabilizers prevent thermal degradation by reacting with the labile chlorine in the polymer and acting as scavengers for the generated HCl [12–15]. Mixed metal salts of organic acids, organotin compounds and lead-based stabilizers have been commonly used for the production of PVC objects.

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Fig. 1. Inflatable chair, 1967, Cooper Hewitt, Smithsonian Design Museum. In the photograph from 2022, yellow discolouration is visible in the bottom segment of the chair. "Chair, Blow; Designed by Jonathan de Pas (Italian, 1932 - 1991); Manufactured by Zanotta S.p.A. (Italy); seam-welded sheet pvc (poly-vinyl chloride); H x W x D (inflated): 83.8 × 120 × 102.9 cm (33 in. × 47 1/4 in. × 40 1/2 in.); Gift from the George R. Kravis II Collection; 2019–29–20″ Photo: Matt Flynn © Cooper Hewitt, Smithsonian Design Museum.

Heavy metals, such as lead and cadmium, have been phased out of use in the EU [11].

Many studies have investigated the relationship between yellowing, dehydrochlorination and the length of polyene sequences in PVC. They have determined the wavelengths of absorption maxima corresponding to the number of conjugated unsaturated sites using UV/Vis [16] spectroscopy and Raman spectroscopy [17,18]. The latter was found to be highly sensitive, especially for the detection of sequences longer than 10 conjugated units [17,18]. In most cases, sequences from 7–20 units long were observed [17,19]. The method is limited by bleaching effects, which can decrease the concentration of polyenes. It was suggested that the distribution of polyene sequences largely depends on the tacticity of the polymer, with syndiotactic polymers being more prone to promoting the unzipping reaction [19,20]. These techniques are good at detecting polyenes and characterizing the current state of the material but cannot predict the effect of yellowing.

The study of PVC degradation at temperatures higher than 100 °C or under outdoor conditions (in the presence of UV radiation) is unsuitable for describing degradation processes at room temperature, as the mechanisms of chemical and physical degradation may differ significantly [21,22]; the issue has been reviewed recently [23]. The degradation of PVC is rarely studied at low temperatures relevant to long-term storage. So far, few studies have been carried out at temperatures lower than 80 °C [4,24–26]. These indicate that degradation by dehydrochlorination depends on a variety of variables apart from temperature, such as materials in contact and concentration of additives. The effects of other experimental variables, such as air velocity (accelerated degradation in ventilated ovens or in closed vessels) and humidity have not been clarified yet. Previous studies of colour change of PVC reported diverging results. Shashoua [27] reported on accelerated degradation at 70 °C of purpose-made samples with different plasticizer concentrations and noted that discoloration was more prominent at lower plasticizer concentrations. Additionally, no differences in the rate of yellowing during degradation in a closed compared to an open environment were observed, although plasticizer loss was significantly affected. Royaux et al. have focused on the effect of conditioning and cleaning of a 30-year-old naturally aged protective PVC cover, additionally exposed to accelerated degradation at 80 °C for 2 days and then 25 °C for 1 day at 65% relative humidity [4]. Yellowing proceeded slower in the closed environment compared to the open environment and naturally aged PVC turned more yellow than a model sample [28]. Materials in contact with PVC, such as low density polyethylene, polyester or silk can affect the rate of its degradation [26,29]. Royaux et al. have shown that mechanical cleaning does not significantly affect the yellowing of PVC.

The aim of this work was to describe the degradation of PVC observed as yellowing in the form of a damage function. Damage functions relevant in the context of heritage science have already been successfully developed for a few materials in heritage context, e.g., historical paper, photographs and iron gall ink documents [30]. The first objective of our research was to quantify the role of temperature and humidity in the PVC degradation process. However, objects made of PVC are characterized by a number of intrinsic properties, such as molecular weight, plasticizer identity and content, and stabilizers. These could have a significant effect on the degradation, so their influence on yellowing was investigated by creating a damage function. Our second objective was to prioritise the variables that contribute most to degradation. Since the experiments were conducted at moderate temperatures and realistic humidity levels, the results are expected to be useful for predicting degradation at room temperatures. Thus, the model could be used for practical collection management.

2. Materials and methods

2.1. Sample description

Thirty-nine transparent and colourless PVC objects were included in this study to create the damage function. Twenty of these were exposed to accelerated degradation experiments at 50 and 70 °C and 30% and 80% relative humidity (80 accelerated degradation experiments). Nineteen objects were evaluated for their natural yellowing at room temperature and included in the damage function. Most of the samples are transparent document folders or pouches. They have been characterized according to plasticizer identity and content, molecular weight of the polymer, metal content and thickness. The samples were 0.1 mm – 0.25 mm thick with no to low surface roughness. The samples are part of our reference collection and are available for further research studies.

2.2. Qualitative and quantitative determination of plasticisers

Commercial diisononyl phthalate (DINP), di(2-propylheptyl) phthalate (DPHP), and diisononyl cyclohexane-1,2-dicarboxylate (DINCH) by BASF were supplied by OQEMA. Dibutyl phthalate (DBP, 99.5%), di(2-ethylhexyl) phthalate (DEHP, ≥99.5) and dioctyl terephthalate (DOTP, ≥96%) were purchased from Sigma-Aldrich (Germany). Diisodecyl phthalate (DIDP) was purchased from TCI (Japan). Inhibitor-free tetrahydrofuran (THF, Sigma-Aldrich, >99.9%), hexane (Honeywell, >95%) and acetone (Honeywell, ≥99.8%) were used. 1 mg/mL stock solutions of DBP, DEHP, DOTP, DPHP, DINP, DIDP, and DINCH were prepared in acetone. Working solution for calibration in the range 5–50 mg/L were prepared daily by dilution in hexane for GC-FID and GC–MS analysis. 22-mm 0.45-µm nylon filters and 2 mL DEHP-free and PVC-free syringes (Chirana T. Injecta) were used for filtration.

The identity and content of plasticisers were determined using gas chromatography with a flame-ionization detector (FID) and/or with a mass spectrometric detector (MS) as published in our previous investigation [31]. Briefly, 10 mg of the sample was accurately weighed and dissolved in 1 mL of THF. The polymer was then precipitated with 2 mL of hexane and filtered. The filtrate was then diluted with hexane before analysis using Thermo GC Trace 1300 with an FID detector. The average coefficient of variation of the method is 5%.

2.3. Size-exclusion chromatographic analysis for determination of polymer molecular weight

The sample solutions were prepared by accurately weighing 1.500 mg of sample, dissolving it in 1.5 mL THF and filtering through a 0.45-µm nylon filter. The analyses were performed using Dionex UltiMate 3000 HPLC equipped with an isocratic pump and Refractive Index detector RefractoMax520. Two Agilent PLgel 5 µm MIXED-D columns

(300 x 7.5 mm) were used at 30 °C. Inhibitor-free THF was used as a mobile phase with a flow rate of 1 mL/min. The system was calibrated with 6 narrow polystyrene standards in the range of 8.210–246.000 g/mol. 50 μL of the solution was injected. The coefficient of variation of the method is 2%.

2.4. Fourier-transform infrared spectroscopy (FTIR)

Infrared spectroscopy was used to identify the objects made of PVC. FTIR spectra of samples with no plasticizers were recorded using a Perkin Elmer Spectrum Two FT-IR Spectrometer with an attenuated total reflectance accessory (ATR). The spectra were recorded between 4000 and 450 cm^{-1} with a 4 cm^{-1} spectral resolution. For each spectrum, 10 scans were co-added. As a background spectrum, air was used.

2.5. Accelerated degradation

Climate chambers Vötsch VC 0020 and Vötsch VC 0018 were used at 50 and 70 °C, and 30% and 80% relative humidity, for 1–4 months. In order to prevent possible accumulation of emissions in the sample headspace, we exposed the samples to accelerated degradation by hanging the samples freely in the ventilated chamber. The 20 selected samples were held in place by a white cotton thread. The environmental conditions were monitored using HOBO T/RH data loggers.

2.6. Colorimetry

The measurements were carried out with a handheld portable spectrophotometer Spectrolino by GretagMacbeth in reflectance mode with D50 illumination source at 2° observer angle with no filter. The white colour patch (0.05) on x-rite's ColorChecker Classic was used as the background. Measurements were carried out on areas not in contact with the cotton thread. Spectrophotometric measurements were carried out in suitable intervals ranging from every second day (70 °C) to weekly (50 °C) in at least four points of the sample. The measurement uncertainty was 0.15 Δb*.

2.7. Data modelling

Determination of degradation rates was carried out in Python 3.8 within PyCharm 2020.1.2 (Community Edition) with numpy 1.19.0, pandas 1.0.5 and scikit-learn 0.24.1. Modelling was carried out using 101 points with R (version 4.1.3) in RStudio with dplyr, mosaic, Metrics, and ggplot2 packages.

3. Results and discussion

The objective of this study was to model the degradation of PVC observed as progressive yellowing. Twenty samples, varying in age, storage history, molecular weight and composition were exposed to four experiments of accelerated degradation at 50 and 70 °C, at 30% and 80% relative humidity. These temperatures were considered suitable low to enable the extrapolation of degradation rates to room temperature. Transparent objects were selected to represent a population of suitable size without fillers and pigments, so that the mechanism of degradation wasn't masked or influenced by the possible degradation of colourants. To account for the natural progression of degradation, 19 samples with visible yellowing were included in the model. These naturally aged samples were 25–35 years old at the time of the study. Their exact storage history is unknown: some were stored at room temperature, while others were kept in an attic, with significant temperature fluctuations ranging from 45 °C in the summer to 0 °C in the winter. Some PVC sleeves were stored empty and stacked, while others contained paper. All of these variables could affect the rate of degradation, however by including a wide range of representative samples with different degradation histories, the model is expected to be reflect the diversity of

objects in heritage collections better. All results of the determined degradation rates and information on sample characterisation are gathered as a dataset in the supplementary materials.

3.1. Evaluation of colour change

During the degradation of poly(vinyl chloride), elimination of HCl leads to the formation of polyene sequences [32]. These sequences make the objects appear increasingly yellow. However, translucent objects absorb, transmit, reflect, and scatter light to different degrees [33]. The perceived colour of such materials can be affected by their thickness and shape, so accurate description of their optical and visual properties remains a challenge [34]. Scattering depends largely on surface roughness [35] and it is also wavelength-dependant [34]. A solution has been proposed by using an integrating sphere spectrophotometer in specular included and excluded modes [33], while others have investigated the effect of illumination source [36] and surface roughness [36,37]. The 20 samples this research is based on are all transparent document folders of similar thickness, without dyes, fillers and pigments, and surface structure. Therefore, the measurements are comparable, even if we have not quantified all the variables explicitly.

In this work, colour change (and thus damage) was expressed as a change in the b* coordinate in the CIEL*a*b* colour space. The b* axis ranges from negative (blue colour) to positive values (yellow colour). The change in b* was considered to be more relevant than ΔE_{00}, as b* directly reflects the formation of yellow chromophores, as a result of the accumulation of polyene sequences and thus closely reflects the actual chemical degradation of the polymer. In our observations, the Δb* had a predominant effect on ΔE_{00}, while ΔL* and Δa* had a smaller contribution. Measurements of the b* coordinate are also more accurate for transparent objects, where the surface of the samples ranged from glossy to slightly rough. Namely, Cuppo et al. investigated the effect of roughness of translucent paint films on colour measurements [37] and found that the L* coordinate was very sensitive to surface roughness, while a* and b* were insensitive.

3.2. Determination of degradation rates

For all the 20 samples the increase in b* at accelerated degradation at 50 and 70 °C proceeded linearly, indicating a zero-order process, an example is shown in Fig. 2. Since continuous elimination of HCl proceeds autocatalytically at allylic sites, the number of active sites remains
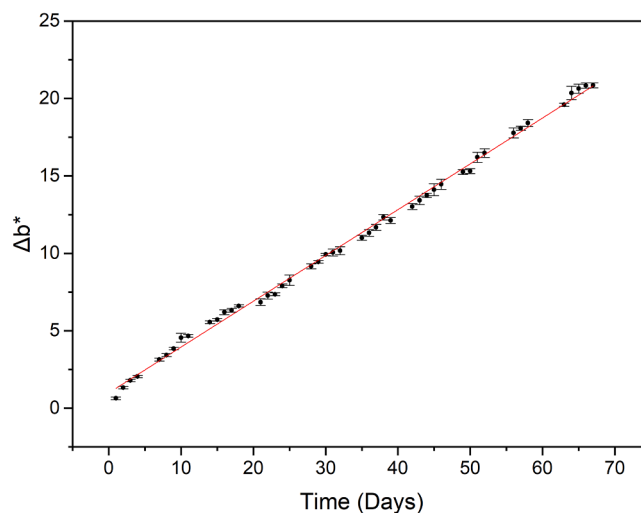

Fig. 2. Sample P4A degraded at 70 °C and 30% RH. Δb* was calculated as the difference between b* at time *t* and b* before degradation. The rate of yellowing was calculated as the slope of a linear fit of the data. The error bars are a standard deviation of four measurements.

constant. The degradation curves expressed as Δb* vs. *t* appeared to have plateaued for some historical samples at prolonged exposure times, indicating the onset of a different degradation mechanism. In such case, the rate was calculated based on the initial linear slope. In a significant minority (3/80 experiments) a rapid initial stage of degradation was observed (lasting a week at 70 °C and 3 weeks at 50 °C), that could be ascribed to residual manufacturing compounds in the virgin material.

While the exact storage histories of the investigated historical samples are unknown, we approximate that they were kept at an average of 18 °C and 50% RH, a typical domestic indoor environment. The yellowing rates of 19 objects at 18 °C were estimated by measuring their current b* value and subtracting the average b* value for new transparent objects. The determined rates range from 0.0002 to 0.002 Δb*/day with an average of 0.0007 Δb*/day.

The distribution of the rates of yellowing, expressed as Δb*/day, are presented in Fig. 3. The highest rates, ranging from 0.03 to 0.54 Δb*/day, with an average of 0.13 were observed at 70 °C. At 50 °C the rates ranged from 0.01 to 0.06 Δb*/day, with an average of 0.03. The determined rates of yellowing show no deviation from normality considering residuals plots (Supplementary Figs. S2–S4). After 12 weeks of accelerated degradation, the samples from the study of Royaux et al. showed Δb* = 10 ± 1 and 14 ± 1 in a closed and an open environment, respectively, exposed to degradation at 80 °C for 2 days and 25 °C for 1 day [4]. The calculated rates are 0.12 Δb*/day and 0.17 Δb*/day. These are comparable to the rates observed in this study at 70 °C.

3.3. Molecular weight of the polymer

The results showed that all samples are made of PVC with a broad distribution of molecular weight. Sample molecular weights (MW) were in the range of 95,000–165,000 g/mol, which is typical for PVC [38]. The molecular weights for the samples were determined before and after accelerated degradation by calibration with narrow polystyrene

standards. The results showed no detectable changes to molecular weight, so the initial MW was included as a damage function variable. This also confirms that no chain scission or crosslinking occurs during thermal degradation.

3.4. Fourier-transform infrared spectroscopy (FTIR)

FTIR spectroscopy was used to investigate the structural changes during thermal degradation. Oxidation of the polymer can occur in the presence of oxygen, especially during photodegradation [39–41]. FTIR spectra of samples that contained no plasticizers were obtained before and after thermal degradation. The carbonyl absorption band (1730 cm^{-1}) is present in the samples already before the start of accelerated degradation and does not change in intensity (Supplementary Figs. S5 and S6, Supplementary Table S1), indicating that no oxidation can be detected. The carbonyl group observed in non-degraded samples can be introduced to the polymer by oxidation during polymerization or during processing [40]. An absorption band at 1637 cm^{-1}, characteristic for C=C stretching, is observed to slightly increase in intensity for sample P4A. The experiments of accelerated degradation were conducted as thermal degradation, so photodegradation was not expected to occur.

3.5. Metal content

Metal salts and organotin compounds are used as heat stabilizers to prevent dehydrochlorination by acting as stabilizers and acid scavengers. Metal ions of Ba, Zn, Mg, Ca, Cd, Pb, Ni, K, Al and Sn were found in different combinations with single concentrations ranging from 0 to 32 μmol/g (described in the supplementary materials). All the results are presented in Supplementary Fig. S7 and gathered in the supplementary dataset.
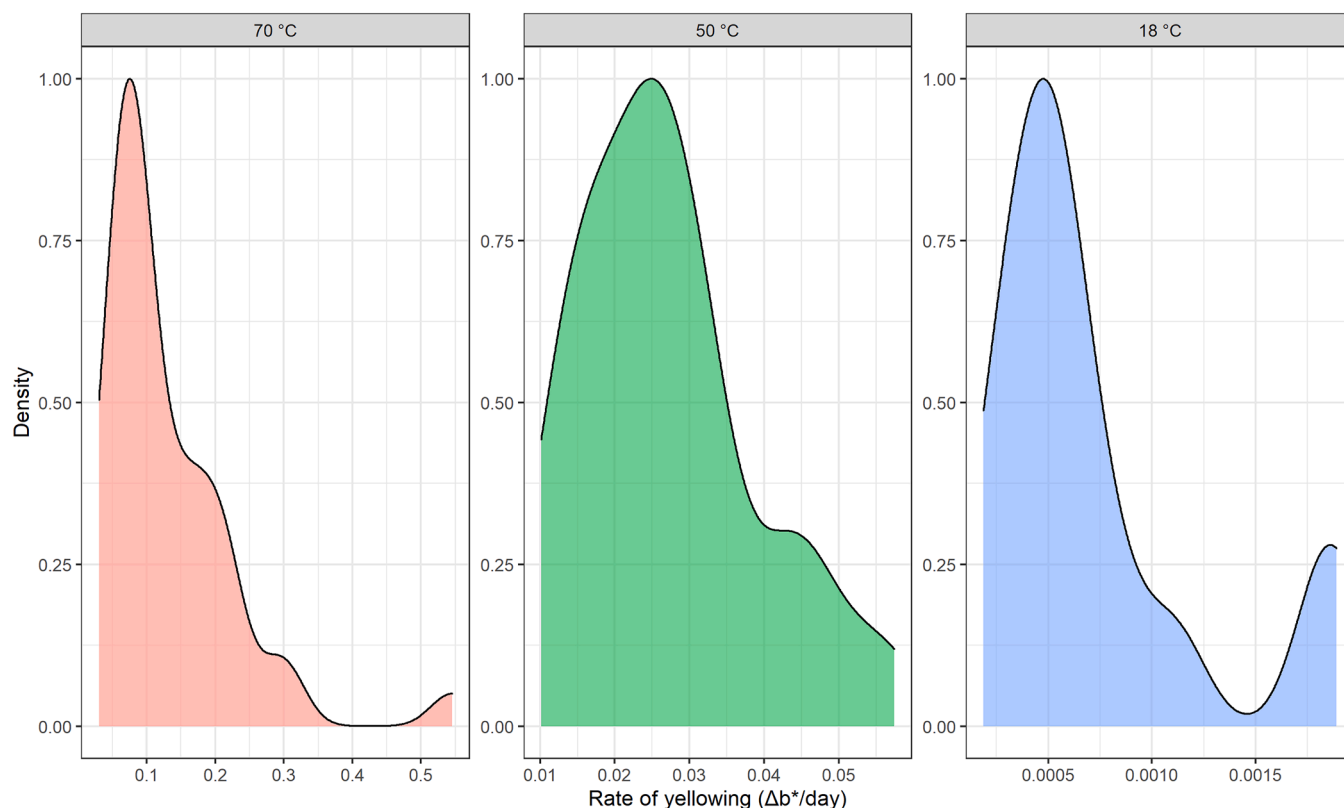

Fig. 3. Distributions of the rates of yellowing. The rates were either measured at 70 °C (and 30% or 70% RH) and 50 °C (and 30% or 70% RH) or approximated at 18 °C (and 50% RH).

3.6. Plasticizer and polymer content

The samples included unplasticized as well as plasticized PVC, in the range of 7–30% plasticizer content. Di (2-ethylhexyl) phthalate (DEHP), dioctyl terephthalate (DOTP) or diisodecyl phthalate (DIDP) were identified, as described previously [31]. The polymer content was calculated as per Eq. (1):

$$w_{PVC} = 100\% - w_{plast}, \tag{1}$$

assuming that the composition involved predominantly the PVC polymer and plasticizers. The material may also contain thermal stabilizers and antioxidants; however, these are contained in only trace amounts (<1%). Since the study investigated only transparent objects, fillers and pigments were not present.

3.7. Modelling the rate of degradation

The accelerated degradation experiments with 20 samples at 4 different environmental conditions led to 80 rate constants. In addition, rate constants for one sample at 60 °C and 55% RH, at 80 °C and 55% RH and for 19 samples that were 20–30 years old and aged under natural conditions, were also used to build a multiple linear regression (MLR) model describing the rate of yellowing (Eq. (2)):

$$k = \Delta b^* / t \tag{2}$$

where Δb^* denotes the change in b^*, t represents time in days, as a function of predictor variables, denoted by x in Eq. (3):

$$\ln k = C_0 + C_1 x_1 + C_2 x_2 \ldots \tag{3}$$

In Eq. (3) the rate of degradation ($\ln k$) is predicted from variables (x_i), that can be directly measured, mathematically transformed or represent combinations of the individual variables, temperature (T), relative humidity (RH) and plasticizer content (w_{plast}). C_0, C_1, C_2 etc. are the modelled regression coefficients. MLR estimates the regression coefficients by minimizing the sum of squared residuals. The following variables, representing the environmental conditions as well as material properties, were measured:

- temperature, T (K),
- relative humidity, RH (%),
- plasticizer content, w_{plas} (%),
- molecular weight, MW (g/mol),
- metal content (μmol/g).

Different models were built using different combinations of the measured variables and their mathematical transformations and combinations. The adjusted coefficient of determination (Adj. R^2), value of the root mean square error (RMSE) and a decrease in residual sum of squares (RSS) were used to select the optimal model (Table 1). Variables with p-values > 0.05 were excluded from the damage function.

The temperature term is present as the inverse value of temperature [K], following the Arrhenius equation. The second term is a logarithm of the quotient of the polymer content of the object [%] and molecular weight of the polymer [g/mol]. This expresses the concentration of PVC

per gram of object material. The third term is relative humidity, expressed in [%]. The model with all the collected data had an adjusted R^2 of 0.891 and a 0.6618 RMSE.

Metal ions are commonly added to the material in the form of metal carboxylates as thermal stabilizers during the production process [42]. They usually act as acid scavengers by reacting with HCl to prevent further discolouration [43]. The inclusion of all individual metal contents, the sum of their contents or a selection of metal contents did not lead to an improvement of the damage function (Supplementary Table S2). Since p-values were >0.05, their inclusion would not be statistically significant. Materials in contact with the object, such as LDPE, silk or paper, may also affect the degradation rate [29].

The optimal damage function is the following:

$$\ln k = C_0 + C_1 \frac{1}{T} + C_2 \ln\left(\frac{w_{PVC}}{MW}\right) + C_3 RH. \tag{4}$$

Cook's distance was calculated and the triple mean distance was selected as outlier threshold. Seven data points were excluded from the model. The values and statistical results of the optimal damage function are given in Table 2. The relative standard errors of the estimated coefficients show that the temperature term has the smallest uncertainty, which increases considerably for the terms with polymer content, molecular weight and relative humidity. The uncertainty in making predictions from experiments of accelerated degradation can originate from measurement errors, structural uncertainty of the model and interpolation/extrapolation uncertainties [44].

For the purpose of modelling and statistical interpretation, the dependant variables were standardized (Supplementary Table S3). The values of coefficients indicate that temperature has the biggest effect on the rate constant. Relative humidity and logarithm of coefficient of plasticizer content and molecular weight are comparable in their influence, but roughly an order of magnitude smaller than the temperature term.

3.7.1. Evaluation of the model

Fig. 4 presents the model fit by plotting predicted vs. observed rates of degradation. The R^2 value of 0.9126 and the RMSE of 0.533 indicate that some variance remains unexplained. The range of yellow colouration as measured for naturally degraded samples of the same age, e.g., 27 years old, is from 2 to 30 b* units, i.e., well beyond the visually perceptible threshold [45]. However, the data scatter for naturally aged samples is high also because their exact environmental histories are unknown. The model fit is further imperfect due to possible differences between natural and accelerated degradation (e.g., presence of atmospheric pollutants, exposure to light), which are not explicitly included in the model but contribute to realistic object variability in collections.

Pure plasticizers (DEHP, DOTP, DIDP) were found to remain colourless during accelerated degradation experiments, so only the plasticizer content and not the plasticizer type was included in the model. The model confirms that yellowing of PVC is indifferent to the plasticizer type, as evident from the random scatter in Fig. 4. To test this assumption, an additional model for samples with DEHP plasticizers was constructed and the comparison with the comprehensive model is shown in Table 3. F-test showed that variances of the models are comparable.

Table 1
Increasing the complexity of the damage function by addition of new variables.

Original dataset	Adj. R^2	RMSE	RSS
T	0.8616	0.7535	57.3
T + RH	0.8656	0.7390	55.2
1/T	0.8734	0.7209	52.5
$1/T$ + w_{PVC}	0.8787	0.7018	49.7
$1/T + \ln\left(\frac{w_{PVC}}{MW}\right)$	0.8871	0.6773	46.3
$1/T + \ln\left(\frac{w_{PVC}}{MW}\right)$ + RH	0.8910	0.6618	44.2

Table 2
Coefficients of the final model for the damage function.

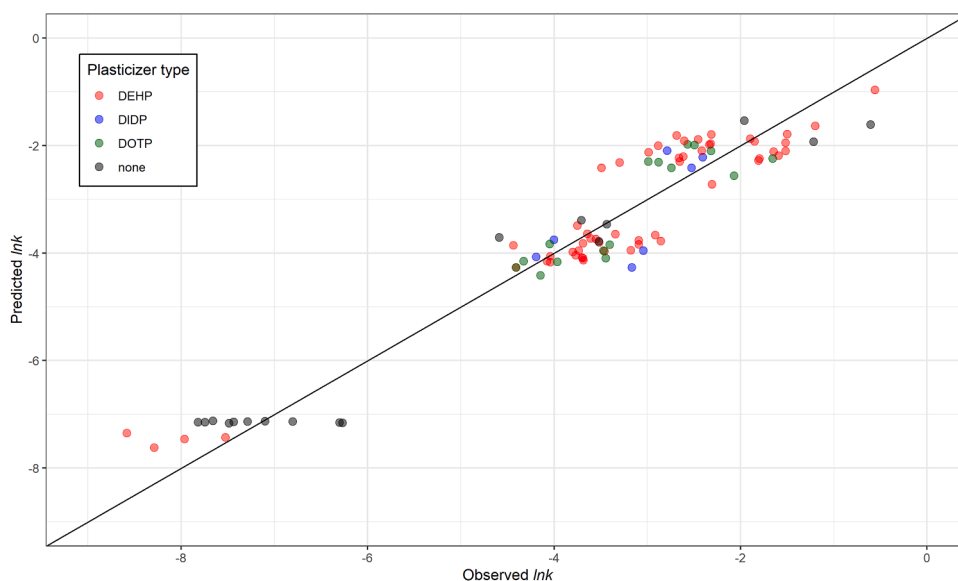| Coefficients	Value	Std. Error	Relative Std. Error	p-Value
C_0	34.2	2.7	8%	< 0.0001
C_1	−10,300	350	3%	< 0.0001
C_2	0.9	0.3	33%	0.0026
C_3	0.0063	0.0025	40%	0.0120

Adjusted R^2 = 0.9126, RMSE = 0.5334, RSS = 26.74.

Fig. 4. Plot of predicted vs. observed ln*k* values. Three distinct groups correspond to three experimental temperatures. The leftmost set represents the values observed at 18 °C, the middle set at 50 °C and the rightmost at 70 °C.

Table 3
Comparisons of damage functions created by including data for all samples or only those with DEHP as plasticizer.

	All data included	DEHP data only
C_0	34.2	41.4
SE (standard error)	2.7	4.0
C_1	−10,300	−10,300
SE	350	510
C_2	0.9	1.9
SE	0.3	0.5
C_3	0.0063	0.0053
SE	0.002	0.003
Adj. R^2	0.9126	0.8935
RMSE	0.5334	0.5147

3.7.2. Sensitivity analysis

Sensitivity analysis was carried out two different ways (Fig. 5) – (a) using the one-factor-at-a-time method on each of the variables used for regression, with the step size being quarter of a standard deviation from the mean value of the standardized dataset. This demonstrates the model's sensitivity to change in a singular variable. The individual impact of each variable on the yellowing rate was also examined (b) in value intervals realistically expected in museum environments - these are (16 ± 2) °C and (50 ± 20)% RH as typical storage conditions. A wide range of samples were included within the intervals of (120,000 ± 25,000) g/mol and (85 ± 15)% polymer content. Fig. 5a demonstrates that the effect of a 0.25 step in T (∼ 5 °C) results in a 36–57% change in the predicted rate of yellowing (k), while a 0.25 step in RH (∼ 6%) results in a 4% change. The results indicate that amongst the investigated parameters, temperature (in the interval of experimental temperatures) has the biggest effect on degradation of PVC, while the other two variables have a considerably smaller, almost negligible effect. However, Fig. 5b shows that within realistic intervals all variables have a comparable effect on the yellowing rate.

Temperature has an important contribution to degradation, as is in accordance with the Arrhenius principle. Polymers with a high MW are more stable than short chain polymers. This could indicate that either (i) shorter polymers have more degrees of freedom leading to higher
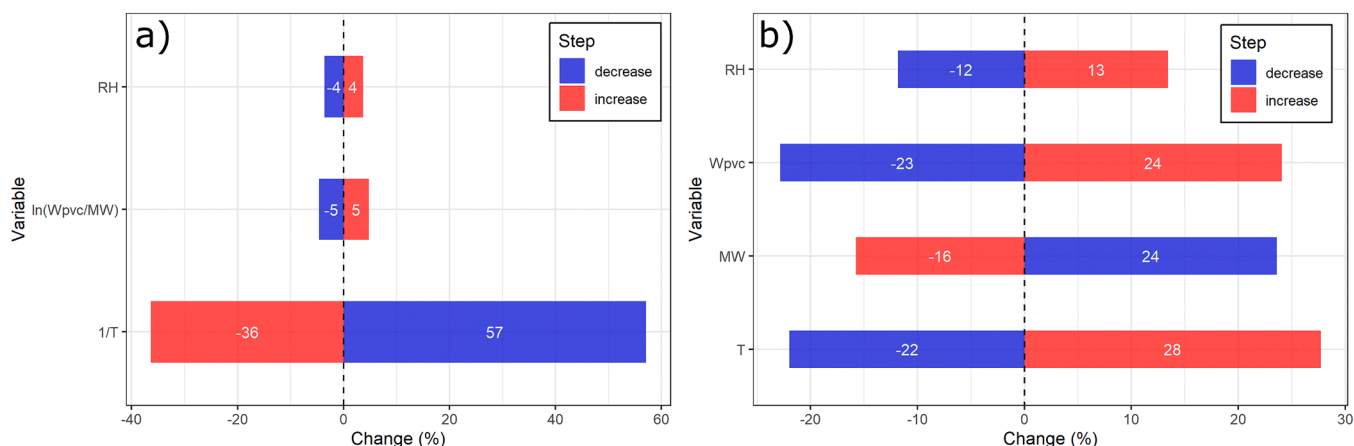

Fig. 5. Sensitivity analysis of the damage function in heritage collections. The change in the predicted yellowing rate (k) as a result of a) a quarter of a standard deviation change from the mean standardized value of each variable included in the damage function (5 °C change in temperature and 6% change in RH) or b) variables changing within an interval of values realistically found in museum storage: (16 ± 2) °C and (50 ± 20)% RH, while the ranges of material properties were (120,000 ± 25,000) g/mol and (85 ± 15)% polymer content, as determined experimentally. The changes (%) are asymmetrical due to the transformation from a logarithmic scale to a nonlogarithmic.

reactivity, or that (ii) more recently produced PVC (and thus less yellow) is of better quality, i.e. higher MW and less structural irregularities and reactive impurities such as residual vinyl chloride monomer or polymerization initiator. In the population as a whole, objects with low MW are more likely to turn yellow faster than high-MW objects. The concentration of plasticizers is also included in the model to account for the dilution of yellowing, as plasticizers remained colourless during the accelerated degradation experiments. Relative humidity exhibits a smaller effect, although still statistically significant ($p = 0.012$). Higher humidity increases the rate of degradation; however, the reason for this is unclear. Supplementary Fig. S8 present a moisture sorption isotherm for a sample from this study, which confirms that some samples absorb water from the surrounding environment. The dehydrochlorination reaction proceeds through an ionic or quasi-ionic mechanism [7], so the increased polarity of the medium due to the water uptake could increase the rate of dehydrochlorination. The results of this study quantitatively confirm Shashoua's [27] and Royaux et al's [4,29] observations on the temperature dependence and the effect of lower concentration of plasticizers being associated with higher yellowing rates, while the effect of humidity on yellowing has not been reported yet.

For a more practical comparison of the influence of each variable, we here define the '1- °C-equivalent effect' as the change in the value of a variable that leads to the change in the yellowing rate that is equivalent to a 1 °C change in temperature (Table 4). The argument is that the typical temperature sensors as used in museums have an uncertainty of ±0.5 °C, which means that an uncertainty interval of 1 °C is what can typically be guaranteed during storage. If so, there is no point to prioritise control of other variables within equivalent intervals. It should be noted that while these predictions are accompanied by some uncertainty (Table 2), the intention here is to extract the underlying trends of practical value to preventive conservation, where temperature and often RH are seen as fundamental variables that require control, while the variability of material composition is often less well studied.

3.7.3. Calculation of the activation energy

The activation energy of degradation was determined to be 86 ± 3 kJ/mol. It was calculated from the C_1 temperature term in the MLR model. Kim et al. report values of 89.1–166.8 kJ/mol and 94.2–118.6 kJ/mol depending on the selected model of calculation for the decomposition up to 350 °C [46], while Bockhorn and Knumann [47] report it as 143 kJ/mol. Talamini and Pezzin [48] report activation energies 100–138 kJ/mol for degradation of PVC studied at 180 °C – 250 °C. The activation energy calculated in this study is lower, but in the same order of magnitude as those previously reported. Most of the reported constants were determined thermogravimetrically by degradation at significantly higher temperatures, which makes a direct comparison difficult.

3.8. Prediction of yellowing in heritage collections

The colour of an artwork is a property, immediately noticeable to museum visitors, curators, and conservators. Discolouration is innately associated with damage, and its prevention requires suitable conservation measures. In 2001, a study using the CIEDE2000 standard evaluated the definition of 'just perceptible change'. The colour difference of $\Delta E_{00} = 1.5$ units was suggested as one perceptible colour change (PCC) and 10 PCCs have been defined as the lifetime of an object [45].

The damage function in this study is based on two extrinsic and two intrinsic variables. As temperature has the most significant effect determined with the smallest uncertainty, its regulation can represent a

feasible practical measure. As indoor temperature is intrinsically related to RH, the effect of these two variables is normally jointly considered. More accurate predictions can be based on measurements of molecular weight and plasticizer content, e.g. using non-destructive methods for determination of plasticizer content in PVC by NIR and mid-IR spectroscopy [31].

The rate constant is defined as the change of yellowing in time. Based on the definition of PCC, a difference of $\Delta b^* = 1.5$ can be used to define the perceptible change in the yellowness of PVC, and $\Delta b^* = 15$ as the lifetime of a PVC object. Fig. 6 demonstrates how the storage conditions affect the lifetime of PVC in heritage collections. An increase in the temperature from 20 °C to 25 °C at 55% RH decreases the predicted lifetime of an object with a PVC content of 86% and a MW of 120,000 g/mol (average values in the investigated dataset) from 79 years to 30 years. From a collection management point of view, identification of objects that are most susceptible to damage (Supplementary Fig. S9) would thus be helpful. An increase in the storage RH from 20% to 70% at 25 °C for the same sample decreases the predicted lifetime from 36 years to 27 years. On average, the predicted lifetime of an object with a MW of 80,000 g/mol and 14% plasticizer content stored at 25 °C and 55% RH is 20 years, while the lifetime of an object with a MW of 140,000 is 34 years.

3.9. Model limitations

In creating the damage function, we have focused on the main environmental variables (T, RH) and material properties (MW, type and content of plasticizers, metal content) that could affect the yellowing of PVC objects. Further possible contributions could include polymer tacticity [19,20] or other additives (e.g., carboxylates and antioxidants) that could reduce the data scatter in the damage function. However, we hypothesize that this is unlikely as the dehydrochlorination reaction is an autocatalytic elimination reaction. As the model was built on the basis of naturally degraded real samples, additionally exposed to accelerated degradation, the differences in the prior exposure to environmental conditions, including light, pollutants and airflow, could have affected their condition. E.g. it is known that pollutants, such as NO_2, may contribute to the yellowing rate of PVC [49]. However, the same differences are typical for other historical collections so the observed data scatter may be indicative for real collections.

As the model was developed for thin and transparent samples, its application to coloured samples and materials with fillers needs to be tested. Pigments can prevent or exacerbate the degradation of PVC [50,
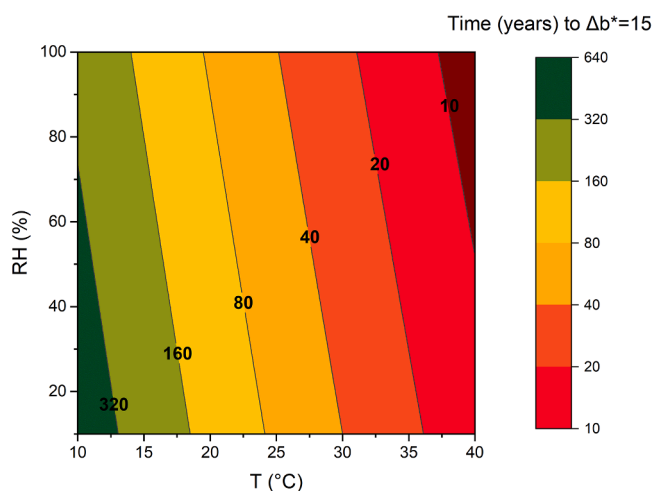

Fig. 6. Isochrone plot of lines connecting points of equal expected lifetimes demonstrating the effect of temperature and relative humidity. The isochrone plot was created for an object with an average plasticizer content (14%) and average molecular weight (120,000 g/mol).

Table 4
A '1 °C-equivalent effect' of the variables included in the damage function.

Temperature	RH	Plasticizer content	MW of PVC
+ 1 °C	+ 13%	- 20%	- 15 000 g/mol

51] and given their diversity their potential effect on discolouration cannot be easily generalised [36]. Furthermore, PVC can exhibit colour changes other than yellowing, e.g. darkening or brightening [52]. Titanium dioxide, a common pigment and filler in PVC objects, can act as a stabilizer or catalyse photodegradation, depending largely on the size of the particles [53,54]. Calcium carbonate has been found to improve the thermal stabilities of PVC [55]. However, despite the variability of PVC in heritage collections, the here developed damage function is currently the most comprehensive model. As it was built on the basis of a great diversity of material properties using naturally degraded objects, it is potentially useful for decision making in preventive conservation.

4. Conclusions

The purpose of this work was to create a damage function for PVC, to be used for predictions of degradation in heritage collections. Data on yellowing rates of twenty samples, exposed to accelerated degradation at four different conditions, and 19 naturally aged samples, was collected. The samples were characterized for plasticizer type and content, metal content and polymer molecular weight. This allowed us to successfully generalise some of the findings previously reported for single case studies and develop a general damage function.

The function accounts for degradation in the absence of light, i.e. during dark storage, taking into account intrinsic, sample-specific properties. In accordance with the principles of elimination reactions, temperature has an important effect on degradation. The activation energy was calculated to be 86 ± 3 kJ/mol. Higher humidity was shown to increase the yellowing rate of PVC objects and although water absorption isotherms have been measured, the effect of water on dehydrochlorination reactions needs further research. Molecular weight of the polymer and plasticizer content are specific to each individual object and significantly influence the rate of degradation. Objects with a higher molecular weight are more stable and while the type of plasticizer does not have a significant effect, their overall concentration does. A '1- °C-equivalent effect' was defined to clarify the implications of the model for collection management.

It is hypothesized that the observed data scatter originates from differences in the natural degradation prior to our experiments. It is also possible that other material properties such as presence of antioxidants and other additives affect the scatter. Tacticity was described to affect the dehydrochlorination and may further improve the damage function to be more sample-specific.

The model successfully describes the progression of yellowing, and the developed isochrone plot can help in the preventive conservation decision-making process in heritage collection management. The function can also be used to identify particularly vulnerable collection objects.

Future research based on structural studies of the degraded and non-degraded samples with NMR spectroscopy and Raman spectroscopy could contribute to a better understanding of the late-stage thermal dehydrochlorination of PVC and the resulting yellowing. It should be noted that yellowing is not the only damage process observed in PVC. Other processes include plasticizer loss leading to brittleness, or plasticizer migration leading to surface accumulation (pooling). However, for these processes, other damage functions need to be developed.

CRediT authorship contribution statement

Tjaša Rijavec: Conceptualization, Investigation, Methodology, Formal analysis, Visualization, Writing – original draft, Writing – review & editing. **Matija Strlič:** Conceptualization, Funding acquisition, Resources, Writing – review & editing. **Irena Kralj Cigić:** Conceptualization, Supervision, Resources, Writing – review & editing.

Declaration of Competing Interest

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

Data availability

The data used for this research is available in the supplementary files.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymdegradstab.2023.110329.

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