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Effect of indoor climate on the rate and degradation mechanism of plasticized poly (vinyl chloride)

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Received 13 December 2002; accepted 21 January 2003

Abstract

Many PVC materials deteriorate only 5 years after manufacture. The extent, rate and mechanisms of deterioration of model and naturally aged PVC containing di (2-ethylhexyl) phthalate (DEHP), have been examined during thermal ageing in various environments. Weight loss was used to quantify loss of DEHP, attenuated total reflection fourier transform infrared spectroscopy to quantify concentration of DEHP at surfaces and optical densitometry to examine darkening of samples. The rate and extent of deterioration of plasticized PVC and the migration and loss of DEHP plasticizer were related. DEHP inhibited degradation of the PVC polymer, therefore when it was lost, discolouration, tackiness and embrittlement resulted. Less plasticized materials degraded more rapidly than those more highly plasticized. Degradation was inhibited in both model sheets and naturally aged materials by enclosing them in a non-adsorbent material such as glass, containing non-agitated air or storing them in a freezer.

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Keywords: PVC; Plasticizer; Phthalate; ATR-FTIR; DEHP; Museum; Indoor climate

1. Introduction

Plasticized poly (vinyl chloride) (PVC) has been one of the most economically and technically important plastics materials since the 1950s. Of the one million tonnes of plasticizers used annually in Europe, approximately 90% comprise phthalate esters, the most frequently used for general purposes being di (2-ethylhexyl) phthalate (DEHP). As a result, the investigation described here focussed on PVC plasticized with DEHP.

In real time, thermal degradation of PVC materials plasticized with DEHP is frequently observed as migration of the plasticizer from the bulk phase to surfaces [1]. From there, the plasticizer evaporates at a rate dependant on its vapour pressure. This process may be detected as a tacky feel to the plastic, increasing embrittlement and subsequent discolouration of the bulk plastic, due to progressive 'unzipping' of neighbouring chlorine and hydrogen atoms to form a conjugated polyene system. As the conjugated polyene system develops, the polymer begins to absorb radiation at longer wavelengths.

In many international museum collections, degradation of plasticized PVC materials, in the form of clothing and footwear, furniture, electrical insulation, medical equipment, housewares, vinyl records and cassette tapes, toys and packaging materials used to store objects, has been detected as early as 5 years after acquisition [2].

After acquisition by museums, PVC materials are usually stored in a reasonably stable indoor climate, with low exposure to light. Although there has been much research into the influence of outdoor exposure or weathering on the degradation of plasticized PVC [3,4], less attention has been paid to the effect of indoor climate. The purpose of the research described here was to examine the influence of various environments on the thermal degradation mechanism of plasticized PVC and to apply the findings to prolong the longevity of such materials in museum collections.

2. Experimental

Model PVC sheets and naturally aged material, plasticized with DEHP, were exposed to various environments

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1 Table 1
2 Examination techniques applied to model sheets and deteriorated PVC materials during thermal ageing

3 Technique	4 Frequency of measurement	5 Depth of analysis	6 Information
7 Visual examination/photography	8 7 days	9 Whole sample	10 Change in colour, surface appearance and tackiness
11 Weight loss	12 7 days	13 Whole sample	14 Quantitative loss of volatiles e.g. plasticizer
15 Attenuated total reflection-fourier transform infrared (ATR-FTIR) spectroscopy	16 7 days	17 Approximately 2 μm , depending on wavelength	18 Functional groups and quantitative measurement of plasticizer at surface
19 Optical densitometry	20 Before and after ageing period	21 Whole sample (approximately 0.5 mm)	22 Optical density and extent of darkening

23 under accelerated thermal ageing. Non-destructive examination techniques were used to identify and quantify changes in visual, chemical and structural properties of samples during thermal ageing (Table 1).

24 Weight loss was used to quantify loss of plasticizer. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was used to quantify concentration of DEHP at surfaces. Optical densitometry was used to quantify darkening of samples.

25 2.1. Materials

26 Sheets were prepared from a PVC plastisol, prepared by Hydro Polymers in Norway, comprising a liquid dispersion of medium molecular weight PVC polymer, DEHP plasticizer and barium/zinc laurate as thermal inhibitor. Chemical composition of the plastisol was characterized by thin-layer chromatography of an ethereal extract. To produce model sheets representing the range of plasticizer concentrations found in museum collections, the plastisol was diluted using DEHP, resulting in plasticizer concentrations of 33.3, 37.5, 44.4 and 50.0% by weight. Pigments were omitted since they were likely to confuse perception of discolouration by the PVC component.

27 Plastisols were heat pressed at 180 °C for 90 s, achieving complete fusion between PVC and DEHP with minimal yellowing and without solvent residues. Sheets 0.5 mm thick were produced and conditioned for 14 days under ambient condition (ASTM D 2115-67 1980). Rectangular-shaped samples weighing 1 g (approximately 50×30 mm) were cut from the sheets for exposure to various environments.

28 Two naturally aged PVC materials, were included in the experimental work to evaluate the effect of various environments on deteriorated PVC. A microscope cover in use for 15 years had developed slight opacity and a tacky outer surface. Dust particles and fibres adhered to the outer surface. Samples (1 g) were cut from a side panel.

29 A transparent, flexible PVC tube (1 cm outside diameter, wall thickness 0.2 cm) had been used to transport

30 water for 5 years. Since its 'retirement', 10 years ago, it had been suspended vertically and was open to air at the lower end. The tube appeared yellow, and was tacky to touch.

31 2.2. Preparation of indoor climates

32 Model sheets were exposed to various environments (Table 2). Adsorbent materials were used either to modify the properties of the environment prior to ageing or to remove degradation products formed during the ageing process. The major degradation product from the PVC polymer is hydrogen chloride which, if not removed from the reaction site, is thought to lead to rapid, autocatalytic degradation.

33 Environments were created within wide-neck Pyrex glass flasks (100 mL) fitted with heavy-duty melamine resin screw caps lined with Teflon[®] (polytetrafluoroethylene); materials were selected for their very low absorption of phthalates and high chemical stability. Samples were suspended in the centres of flasks in order to provide equal opportunity for movement of gaseous materials around all surfaces of the sample.

34 Since volatile loss of plasticizers from PVC compounds is evaluated commercially at 70 °C (DIN53-405-1981, ASTM D1203-94), this temperature was used to accelerate the thermal ageing process in this study. It was also higher than the glass transition temperature of all model formulations used. Thermal ageing was conducted using a convection oven, with the exception of samples exposed to a low temperature, which was achieved using a domestic freezer (-20 ± 1 °C) for a period of 65 days. An initial trial suggested that this period was sufficient to initiate visible deterioration in all model sheets.

35 2.3. Examination of samples

36 2.3.1. Weight loss

37 Weight loss was one of the earliest techniques used to evaluate the performance of plasticized PVC [5]. Model sheets were weighed to four decimal place accuracy

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1 Table 2

2 Environments used to thermally age model sheets and deteriorated PVC materials

3 Environment ^a	4 Function	5 How achieved
6 Closed	7 Exclude dust, minimise climate variations	8 Samples suspended in closed flask
9 Open	10 Ventilate materials to avoid build-up of pollutants	11 Samples suspended in convection oven
12 Glass plate	13 Physical support	14 Samples placed on Pyrex glass plate in convection oven
15 Activated carbon (AC)	16 Filter air of volatiles	17 AC placed in base of closed flask
18 Ageless [®] oxygen absorber	19 Inhibit oxidation/pest control	20 Ageless [®] Z sachets, used in food industry, placed in base of flasks, before flushing with N ₂
21 Silica gel	22 Dry air	23 Silica gel placed in base of flasks
24 High relative humidity	25 Humidify air	26 Water (20 ml) in base of flasks
27 Low density polyethylene (LDPE) bag	28 Exclude dust and facilitate handling	29 Samples placed in LDPE bags before sealing
30 Freezer	31 Inhibit chemical deterioration	32 Samples suspended in flasks in domestic chest freezer

^a All environments were maintained at 70 ± 1 °C with the exception of the freezer (−20 °C).

before and during ageing. Samples were removed from their ageing environment and conditioned for 5 h at ambient temperature (20–23 °C) prior to weighing.

2.3.2. FTIR spectroscopy

ATR-FTIR spectroscopy was used to quantify levels of DEHP present at surfaces of all samples [6]. Spectra were collected over 30 scans at a resolution of 4 cm^{−1} between 4000 and 600 cm^{−1}, using ASI DurasamplIR single reflection accessory in a Perkin-Elmer Spectrum 1000 FTIR spectrometer. Differences in the refractive index of the diamond internal reflection element compared with that of plasticized PVC (2.4 and 1.5 respectively) allowed absorbance data to be collected from a depth approximately 2 μm [7]. Intimate contact between the diamond internal reflection element and the samples was achieved using a pre-set pressure device.

Beer's Law was applied to the spectra. Concentrations of DEHP at surfaces of model sheets, microscope cover and tube were calculated by ratioing the absorbance intensities of bands at 2860 cm^{−1} (C–H stretch, due only to DEHP) against those at 1426 cm^{−1} (C–H stretch, due only to PVC) on raw absorbance spectra [8]. It is more usual to use the band at 1724 cm^{−1}, assigned to the carbonyl stretch in DEHP but, since it partly overlapped with a co-plasticizer, Eastmans TXIB, under investigation in a parallel experiment, an alternative band was selected (see Fig. 1) [9].

The level of significance of ten measurements at random locations at surfaces of each sample, was determined using a t-distribution statistical test [10]. Mean concentrations of DEHP after ageing were compared with those measured for unaged materials to establish whether a minimum 95% confidence interval (considered to be a significant difference) existed between the mean values.

2.3.3. Darkening

An electronic densitometer model Densy 301 from Barbieri was used in transmission mode to measure the optical density of model films and degraded PVC before and after ageing [11]. Since all colour changes were due to yellowing, a blue density filter was applied. The mean reading at three positions at surfaces of each sample was calculated.

3. Results

3.1. Weight loss

The environment in which model sheets were aged, clearly influenced the extent and rate of loss of plasticizer during ageing. Table 3 shows the ageing environments rated in increasing order of plasticizer loss. Although the results presented are those for model sheets containing 33.3% DEHP, the same rating applied to all concentrations. After 65 days, samples aged with silica gel, in open conditions, on a glass plate or enclosed in a LDPE bag continued to lose weight while, in other ageing environments, weight loss had ceased.

Model sheets aged in high relative humidity (RH) and freezer environments lost less than 1% of the original plasticizer content, while those aged in open conditions, on glass plate and in LDPE bags lost more than 5%, resulting in increased stiffness. There was very little difference between weight lost during ageing in a freezer and that lost in a closed microclimate at 70 °C for the same period of time, indicating that the storage temperature was a less important factor than the opportunity for plasticizer to evaporate.

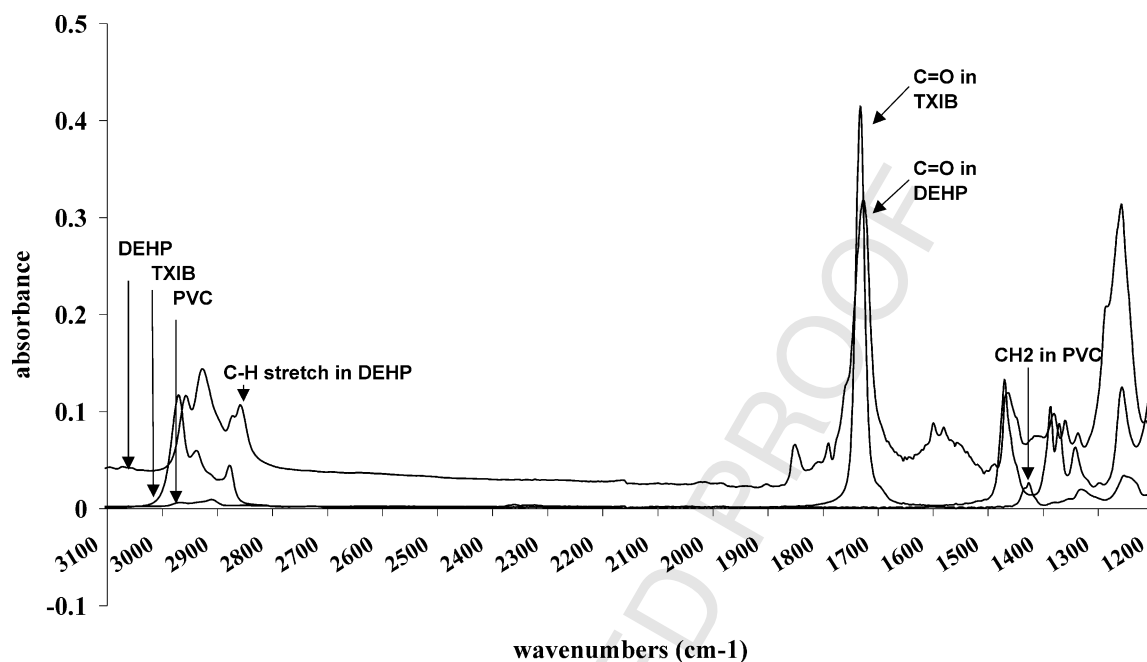


Fig. 1. ATR-FTIR absorbance spectra of PVC, DEHP and Eastman TXIB, a co-plasticizer under investigation in a parallel investigation. C–H stretch band present only in DEHP and CH₂ band present only in PVC, both used to quantify concentration of plasticizer at surfaces are marked.

Loss from sheets hanging in an oven, with all surfaces available for evaporation was almost the same as that from sheets aged on open glass plates, despite the fact that the surface in contact with glass was not readily accessible by moving air to promote evaporation. In fact, DEHP was lost from the surface in contact with glass, observed by the presence of droplets between the underside of sheets and the glass. These droplets remained on the glass when sheets were removed for weighing.

In all environments, DEHP was lost rapidly within the first 7–10 days of the ageing period, after which it was lost more gradually at a rate proportional to time. Other researchers have observed a similar change in rate of weight loss [5]. In closed environments and those containing activated carbon, loss of DEHP ceased after 14 days, suggesting that the concentration of plasticizer vapour in the air surrounding the model sheets and the

concentration at their surfaces, had equilibrated. This was a good indication that the rate of loss was evaporation-controlled.

Model sheets in high RH did not lose weight, but, in some cases, gained it, probably by adsorbing water vapour or liquid water from condensed vapour. This was explained by the fact that water vapour is an efficient plasticizer for the PVC polymer [12]. After 65 days, model sheets containing 33.3% DEHP had gained more weight (0.005 g) than those containing 50.0% plasticizer (0.0025 g).

Percentage weight losses from degraded materials were lower than those from model sheets (between 0.0 and 2.8%) during the experimental period. This was attributed to the fact that during their 15–20 year period of natural ageing, some plasticizer and other volatile materials had already been lost. As for model sheets, the environment in which degraded PVC materials were

Table 3

DEHP lost by model sheets containing 33.3% plasticizer after thermal ageing for 65 days in various environments

Thermal ageing environment ^a	DEHP lost after 65 days (%)	Mass DEHP lost after 65 days (g)
High relative humidity (lowest DEHP loss)	0.0	0.000
Freezer	0.4	0.002
Closed	0.7	0.004
Ageless [®] oxygen absorber	3.0	0.015
Silica gel	3.6	0.019
Activated carbon	3.7	0.021
Open	5.7	0.031
Glass plate	5.9	0.032
LDPE bags (highest DEHP loss)	10.1	0.044

^a All environments were maintained at 70±1 °C with the exception of freezer (–20 °C).

aged, influenced the extent and rate of loss of volatiles. Loss was greatest when materials were stored in LDPE bags and lowest when aged in high RH environments.

3.2. FTIR spectroscopy

Ageing in closed environments, freezer and with adsorbents, allowed plasticizer at the surfaces of model sheets to be replaced at the same rate as it was lost, by diffusion from the bulk of the sheet. As a result, no overall change in surface concentration was detected; evaporation was the rate-determining step by which DEHP was lost (see Fig. 2).

Ageing in open conditions, on glass plate and in LDPE bags significantly reduced the surface concentration of all model sheets. This suggested that loss of DEHP from surfaces occurred too rapidly for it to be replaced immediately by diffusion in such environments;

diffusion had become the rate-determining step of the loss process.

Samples of microscope cover had a mean DEHP concentration of 1.1 concentration units at its surfaces prior to ageing. Fitting this value to a calibration curve obtained for unaged model PVC sheets, using the quantitative technique described in Section 2.3.2, suggested that the surface concentration of DEHP was 46.5% (see Fig. 3).

Ageing in open conditions, on glass plate and in LDPE bags significantly reduced the concentration of DEHP at the surfaces of the microscope cover. All other environments enabled the microscope cover to retain its original surface concentration, indicating the presence of two mechanisms by which DEHP was lost. The rate-determining step by which DEHP was lost during ageing in a freezer and with adsorbents was evaporation. However, loss of DEHP from the surface of

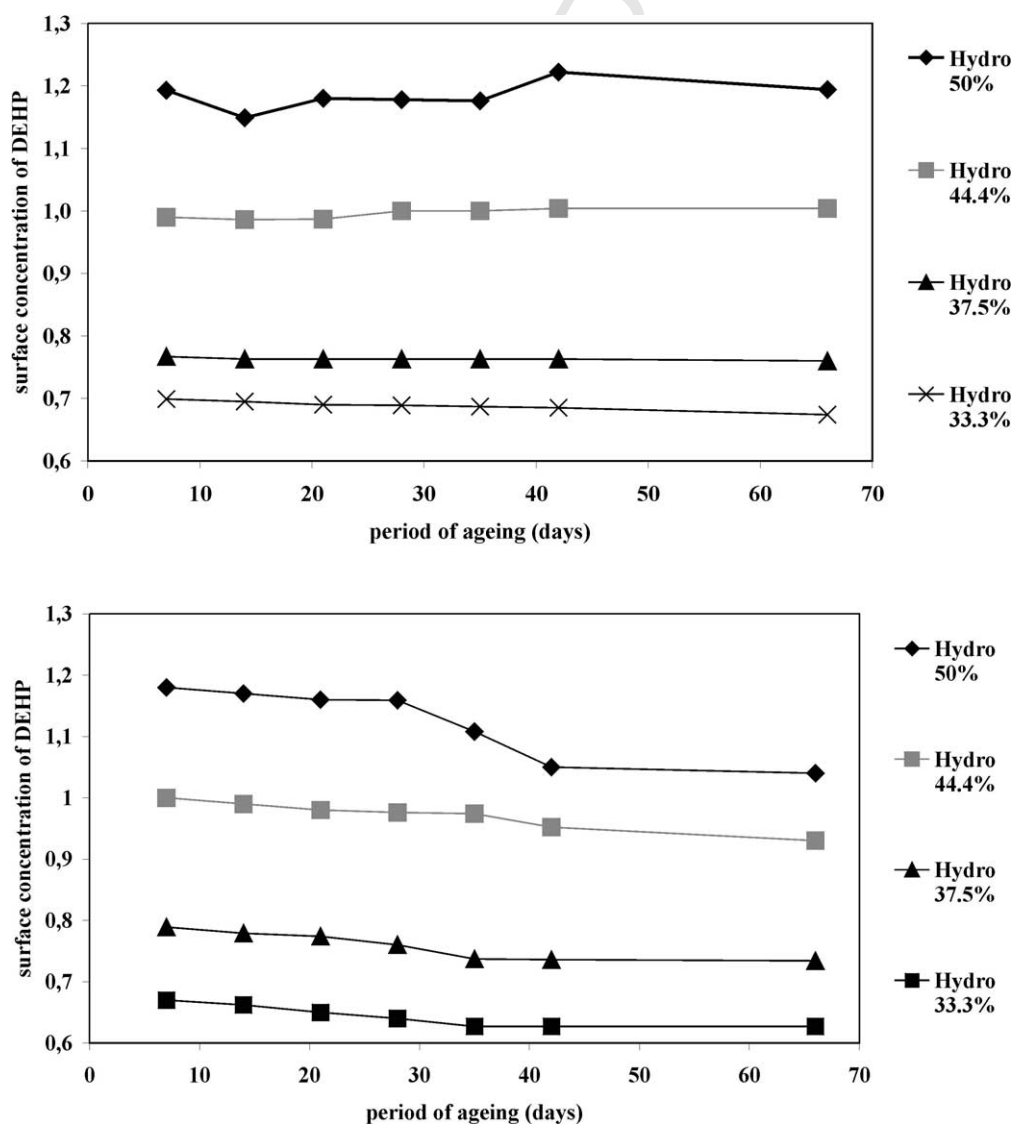


Fig. 2. Comparison of concentration of DEHP at surfaces of model sheets containing various concentrations of plasticizer during thermal ageing in a closed environment (upper) and LDPE bag (lower).

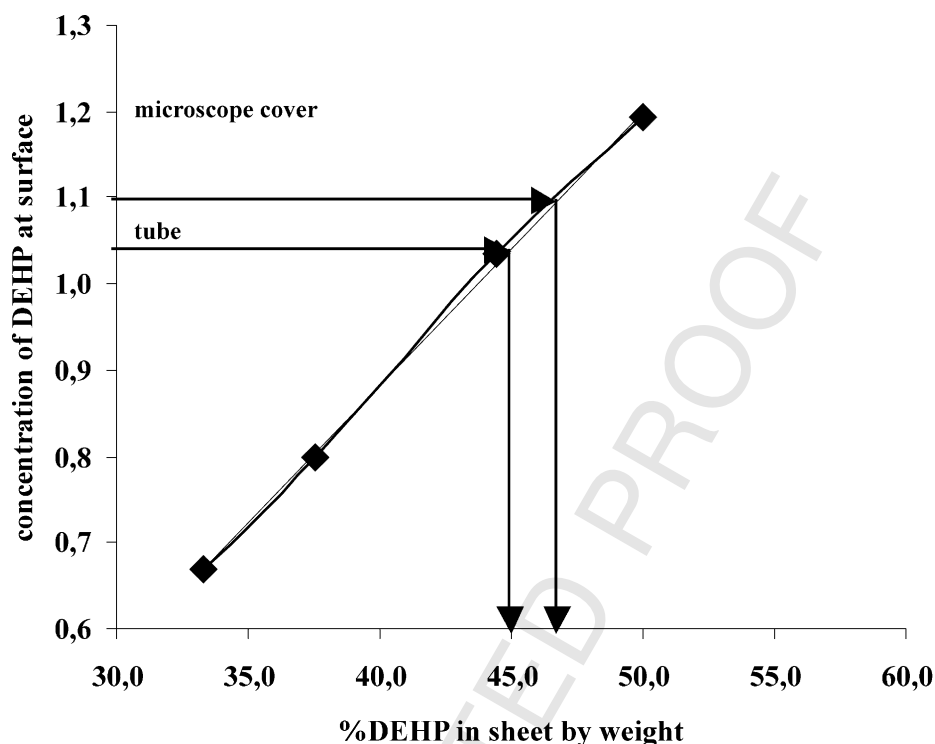


Fig. 3. Fitting concentration of DEHP at surfaces of deteriorated PVC materials to the best straight line for concentrations at surfaces of model sheets, determined using ATR-FTIR spectroscopy, suggested that the microscope cover contained 46.5% DEHP while the tube contained 44.8%.

the microscope cover during ageing in open conditions, glass plate and in LDPE bags occurred too rapidly for it to be replaced immediately by diffusion.

Loss of DEHP from surfaces of the microscope cover was compared with that lost by model sheets containing 44.4 and 50.0% DEHP by weight, since all three materials contained similar levels of plasticizer. After ageing, the extent and rate of loss of DEHP from the surface of the microscope cover were similar to that of the equivalent model sheets.

Unaged tube had a mean concentration of 1.04 concentration units at its surfaces. This value was fitted to the calibration curve obtained for unaged model sheets and found to be 44.8% DEHP (see Fig. 3). Loss of DEHP from the tube was compared with that lost by model sheet containing 44.4% plasticizer by weight after ageing. In the same period, the extent and rate of loss of plasticizer from the surface of the tube was similar to that of the equivalent model sheet. For example, ageing in a LDPE bag for 65 days resulted in a reduction of 0.1 concentration units for model sheet with 44.4% DEHP by weight; the same conditions produced a reduction of 0.3 units for the degraded tube.

3.3. Darkening and appearance

In general, where discolouration occurred, model sheets containing lower concentrations of DEHP exhibited

greater darkening than more highly plasticized formulations. Ageing in a closed environment produced no change in optical density, while ageing with activated carbon and silica gel produced pronounced. Discolouration was always first visible at the edges of samples. For both model sheets and degraded PVC, sides which had been closest to the adsorbents, became darker than those furthest from them. This suggested that adsorbents did not distinguish between pollutants and plasticizer vapour, and removed both from the enclosed air.

Ageing on a glass plate produced a pattern of brown patches on model sheets (see Fig. 4). Unchanged areas corresponded to the presence of droplets of plasticizer trapped between the surfaces of the PVC sheet and glass plate after ageing. The patches corresponded to dry, droplet-free areas. This suggested that the liquid plasticizer may have inhibited the discolouration which was due to dehydrochlorination of the PVC polymer.

Ageing model sheets in LDPE bags, caused the bags to soften and deform and samples to yellow (see Fig. 5). Droplets of DEHP were identified on an area corresponding to that of model sheet on inner surfaces of bags. Polyethylene is known to be an effective absorbent for phthalate plasticizers [13].

Exposure to high RH caused model sheets and degraded materials to become opaque (see Fig. 6). However, after returning to ambient conditions, little change in the original optical density was visible.

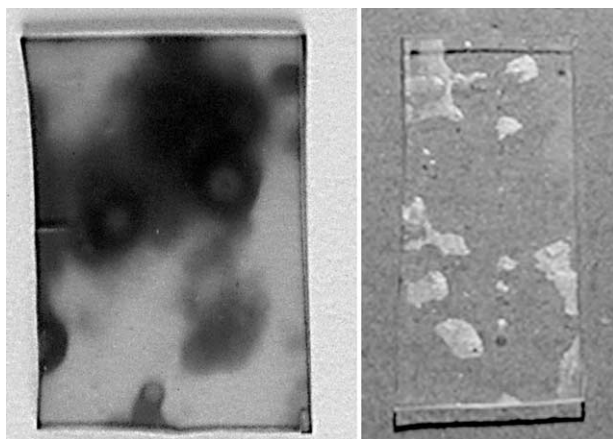


Fig. 4. Ageing on glass plates produced a pattern of brown patches on model sheets (left). Areas with no discolouration corresponded well with plasticizer droplets trapped between the glass plate and underside of the sheet (right).



Fig. 5. LDPE bags softened and crinkled after absorbing plasticizer during accelerated thermal ageing of PVC sheets.



Fig. 6. Thermal ageing of degraded PVC tube at high relative humidity caused them to become opaque. Opacity reversed on return to ambient conditions. Dimensions: 1.5 mm diameter \times 30 mm length.

4. Discussion

Findings from all analytical techniques indicated that the environment in which model sheets and PVC materials were aged, influenced the extent of plasticizer loss, the rate and mechanism by which it was lost. New model sheets and degraded materials containing similar levels of DEHP behaved in a similar way in the same environment, irrespective of their different histories. Despite the advanced state of degradation exhibited by the microscope cover and tube, the rate of further degradation could be slowed or accelerated by storage environment.

Enclosing samples of PVC with unstirred air was most effective at inhibiting loss of DEHP. Storage of samples in lightly stirred air further increased the extent and rate of loss of plasticizer. However, placing samples in contact with a highly adsorbent material caused the greatest plasticizer loss. Weight loss and ATR-FTIR spectroscopy results indicated that plasticizer was lost at a rate controlled by diffusion from the bulk to surfaces when stored in lightly stirred air or in contact with a highly adsorbent material. In all other environments, rate of loss was evaporation-controlled.

ATR-FTIR spectroscopy confirmed that ageing in closed environments and in the presence of adsorbents enabled samples to retain their original surface concentration of DEHP. Ageing in lightly stirred air (open conditions and glass plate) and in contact with highly adsorbent material (LDPE bag) significantly reduced the surface concentration of DEHP. Loss of plasticizer caused by storing in these environments was likely to have followed a diffusion-controlled mechanism since DEHP was lost too rapidly from the surfaces for it to be replaced immediately by diffusion.

Discolouration was influenced by environment for all model sheets and objects, but its magnitude was not solely related to plasticizer loss. The presence of droplets or a layer of plasticizer at surfaces seemed to act as a protective coating to inhibit dehydrochlorination, the cause of discolouration. This possibility was clearly illustrated by model sheets aged on open glass plates. The unchanged areas between the dark brown spots displayed good correlation with the location of DEHP droplets. Addition of phthalate plasticizers to PVC has been shown to reduce the rate of dehydrochlorination by the polymer, by inhibiting the growth of polyene sequences. Ester groups in DEHP are thought to solvate the labile groups of the polymer chain which are responsible for the instability, thus avoiding double bond formation [14]. The inhibitive properties of DEHP are usually considered in terms of compounded PVC. However, since plasticizers are only physically bonded to the polymer during compounding, it could be argued that they still function as inhibitors if simply placed in close contact with degrading PVC.

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It seemed that the inhibitive properties of DEHP were less effective for PVC at an advanced state of deterioration, as illustrated by the microscope cover and tube. It is also known that compatibility between DEHP and PVC changes with deterioration of one or both of the components [11].

5. Conclusions

The rate and extent of deterioration of plasticized PVC and the migration and loss of DEHP plasticizer were related. DEHP inhibited the degradation of the PVC polymer, therefore when it either migrated to surfaces or was absorbed by contact with polyethylene, PVC materials discoloured, became tacky to the touch and embrittled. Materials with lower levels of plasticizer degraded more rapidly than those more highly plasticized. Degradation was inhibited in both model sheets and naturally aged materials by enclosing them in a non-adsorbent material such as glass, containing non-agitated air.

Results clearly indicated that the useful lifetime of plasticized PVC materials may be greatly prolonged, by changing the storage environment from a polyethylene bag or open shelf to a closed glass container or freezer. Enclosing plasticized PVC materials, whatever their level of deterioration, is inexpensive to implement and of low practical complexity.

6. Standard test procedures

ASTM D2115-67 (1980), Recommended practice for oven heat stability of poly (vinyl chloride) compositions.

ASTM D1203-94, Standard test methods for volatile loss from plastics using activated carbon methods.

DIN 53-405-1981, Testing plasticisers; determination of migration of plasticisers.

Acknowledgements

The author would like to thank Mads Christian Christensen, Head of the Conservation Laboratory of the National Museum of Denmark for his advice concerning the development and results of this project.

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