Investigating the efficacy of interleaving materials in the preservation of plasticised PVC slip-cover notebooks in Yang Zhichao's artwork *Chinese Bible*

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Plasticised poly(vinyl chloride) (PVC-P) is known to degrade rapidly and emit acidic gases and, as such, it is ideally stored separately from other materials. However, due to historic or aesthetic value, PVC-P book covers in paper-based collections cannot always be removed or replaced. There is currently a gap in the literature addressing strategies for storing PVC-P associated with paper materials. Prompted by a case study of the Chinese artist Yang Zhichao's *Chinese Bible* (2009)—a performance installation artwork of 3000 notebooks including approximately 1000 notebooks with PVC-P covers—three potential interleaving materials (Mylar®, Hollytex®, and buffered tissue) were tested to simulate use during long-term storage. Notebooks and PVC-P book covers were purchased and assembled to model stacked storage conditions, and thermally aged at 70ºC and 50% relative humidity for 130 days. Before and after ageing, samples were analysed using visual examination techniques, ATR-FTIR spectroscopy, colourimetry, and weighing. It was found that all three interleaving materials lowered the probability of ink offsetting. However, cover deformation and a blotchy surface haze were more commonly observed in interleaved samples compared to non-interleaved samples. More research is necessary to identify a suitable strategy to manage PVC-P degradation in close contact storage with paper materials. This study contributes to a better understanding of the storage of plastic-covered books that may be found in libraries and archives, highlighting the complexity of conserving plastic and paper composite materials.

Keywords**:** books; plastics; accelerated ageing; interleaving; contemporary art; archives

Introduction

Poly(vinyl chloride) (PVC) plastic, also known as vinyl, is an affordable, strong, lightweight and versatile material. These properties make it desirable for use in many applications. In its plasticised non-rigid form, PVC plastic can be found in paper-based collections as imitation leather book cloths, early lamination films,[1] and pocketed sleeves in photographic albums.[2] Although its use as a storage

[1] See Yash Pal Kathpalia, *Conservation and Restoration of Archive Materials* (Paris: UNESCO, 1973), 47.

material has been cautioned against since the early 1990s—due its tendency to emit acidic gases and exude plasticisers[3]—plasticised PVC (PVC-P) still remains in paper-based collections in components that cannot be removed due to historic or aesthetic value.

While it has been found that sealed environments and wrapping techniques can extend the lifespan of PVC-P objects,[4] there is a gap in the literature regarding strategies for storing these objects in close contact with paper-based materials. Paper is often acid-sensitive and absorbent, so it appears incompatible with PVC-P. An example of this combination of materials is found in books with PVC-P covers.

The research presented here aimed to identify suitable interleaving materials that could preserve the physical integrity of the contemporary Chinese artist Yang Zhichao's *Chinese Bible*

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[2] See, for example, Jennifer Hain Teper, 'An Introduction to Preservation Challenges and Potential Solutions for Scrapbooks in Archival Collections', *Journal of Archival Organization* 5, no. 3 (2008): 51, https://doi.org/10.1080/15332740802174183 (accessed 21 April 2021).

[3] See, for example, John Morgan, *Conservation of Plastics: An Introduction to Their History, Manufacture, Deterioration, Identification and Care* (London: Plastics Historical Society: Conservation Unit, Museums & Galleries Commission, 1991), 10; Alan Calmes, 'Plastics Found in Archives', in *Saving the Twentieth Century: The Conservation of Modern Materials*, ed. David W. Grattan (Ottawa, Canada: Canadian Conservation Institute, 1993), 97; Edward P. Adcock, Marie-Thérèse Varlamoff, and Virginie Kremp, *IFLA Principles for the Care and Handling of Library Material*, International Preservation Issues 1 (Washington, DC: International Federation of Library Associations and Institutions, Core Programme on Preservation and Conservation, 1998), 49.

[4] See, for example, Yvonne R. Shashoua, 'Inhibiting the Deterioration of Plasticized Poly (Vinyl Chloride): A Museum Perspective' (PhD thesis, National Museum of Denmark, 2001); Adeline Royaux et al., 'Long-Term Effect of Silk Paper Used for Wrapping of Plasticized PVC Objects: Comparison between Ancient and Model PVC', *Polymer Degradation and Stability* 155 (2018): 183–93, https://doi.org/10.1016/j.polymdegradstab.2018.07.016 (accessed 20 July 2021).

(2009), a performance installation artwork of 3000 notebooks including approximately 1000 PVC-P book covers.[5] Results are applicable to collections containing PVC-P covered books, such as libraries and archives.

1 Overview of PVC-P composition

PVC polymers were first synthesised in 1872 by Eugen Baumann, a German chemist, with production following in the 1930s.[6] PVC is manufactured from vinyl chloride monomers, which before the 1960s were derived from reacting chlorine with acetylene. PVC polymers are now more commonly produced from reacting chlorine with ethylene, a petroleum industry by-product.[7]

PVC-P is composed of a PVC polymer base combined with tailored additives to achieve desired properties. Notably, plasticisers impart flexibility by lowering the glass transition temperature and can compose up to 50% by weight of PVC-P. The most common PVC plasticiser to date is a synthetic colourless liquid called di(2-ethylhexyl) phthalate (DEHP), also known as dioctyl phthalate (DOP) and a variety of other names.[8] Since the 2000s, DEHP production and use has been

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[5] The work is made from notebooks collected by the artist from Panjiayuan Market in Beijing and contain the personal writings of Chinese people from 1949 to 1999. Yang has said he used the books to represent the personal experiences of people during a century of political upheaval.

[6] Friederike Waentig, Plastics in Art: A Study from the Conservation Point of View, trans. Michael Scuffil (Petersberg: Michael Imhof Verlag, 2008), 241–4; Karel Mulder and Marjolijn Knot, 'PVC Plastic: A History of Systems Development and Entrenchment', *Technology in Society* 23, no. 2 (2001): 267–71, https://doi.org/10.1016/S0160-791X(01)00013-6 (accessed 17 October 2019).

[7] Y. Saeki and T. Emura, 'Technical Progresses for PVC Production', *Progress in Polymer Science* 27, no. 10 (2002): 2055–131, https://doi.org/10.1016/S0079-6700(02)00039-4 (accessed 22 July 2022).

[8] Tjaša Rijavec, Matija Strlič, and Irena Kralj Cigić, 'Plastics in Heritage Collections: Poly(Vinyl Chloride) Degradation and Characterization', *Acta Chimica Slovenica* 67, no. 4 (2020): 995, https://doi.org/10.17344/acsi.2020.6479 (accessed 22 December 2020); Joanna Czogała, Ewa Pankalla,

subject to legal regulations in many regions in the world due to its properties as an endocrine disruptor. Although DEHP has been partially replaced by alternatives such as higher weight phthalates, it continues to be the most common PVC plasticiser worldwide. Other common additives include stabilisers to improve tolerance to heat and ultraviolet (UV) radiation, fillers such as calcium carbonate ($CaCO_3$) to give opacity and rigidity, and colourants.

2 Degradation of PVC-P

PVC-P is inherently unstable. Even in controlled museum settings, degradation has been observed in as little time as five years.[9] Due to the potential for PVC-P to deteriorate rapidly and to accelerate the degradation of neighbouring materials, it is considered one of the five known malignant plastics.[10]

Processes involved in PVC-P degradation are well-described in existing literature.[11] Two principal mechanisms, dehydrochlorination and plasticiser migration, are briefly described here:

1 *Dehydrochlorination*: Thermal degradation of the PVC polymer chain leads to the formation of polyene chains of alternating single and double-bonded carbons, and the production of

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and Roman Turczyn, ‘Recent Attempts in the Design of Efficient PVC Plasticizers with Reduced Migration’, *Materials* (Basel) 14, no. 4 (2021): 844, https://doi.org/10.3390/ma14040844 (accessed 27 April 2022); Mengyan Bi et al., ‘Production, Use, and Fate of Phthalic Acid Esters for Polyvinyl Chloride Products in China’, *Environmental Science & Technology* 55, no. 20 (2021): 13980–9, https://doi.org/10.1021/acs.est.1c02374 (accessed 27 April 2022).

[9] Cf. Yvonne Shashoua, *Conservation of Plastics: Materials Science, Degradation and Preservation* (Oxford: Butterworth-Heinemann, 2008), 184.

[10] R. Scott Williams, ‘Care of Plastics: Malignant Plastics’, *WAAC Newsletter* 24, no. 1 (2002), https://cool.conservation-us.org/waac/wn/wn24/wn24-1/wn24-102.html (accessed 27 July 2022).

[11] See, for example, Shashoua, *Conservation of Plastics*, 184–7; Waentig, *Plastics in Art*, 246–50; Rijavec, Strlič, and Kralj Cigić, ‘Plastics in Heritage Collections’; George Wypych, *PVC Degradation & Stabilization*, 4th edn (Toronto: ChemTec Publishing, 2020).

acidic hydrogen chloride (HCl) gas (see **Fig. 1a**).[12] This reaction is autocatalytic, meaning that the rate of the chemical reaction increases if the degradation product HCl remains in the environment. Dehydrochlorination leads to discolouration progressing through the colours white, yellow, orange, red, brown, and black,[13] occurring in a pattern that is often spotted or appearing as a blackened surface.[14] Discolouration is accompanied by embrittlement due to cross-linking of the polymer chains. Dehydrochlorination occurs more rapidly in poor quality PVC polymers that have a greater number of imperfections in the polymer chain that act as initiation sites. The process is initiated and accelerated by exposure to UV and elevated temperatures.

2 *Plasticiser migration*: There are two distinct steps in plasticiser migration–internal diffusion and external evaporation (see **Fig. 1b**).[15] Plasticiser migration is influenced by surface area, temperature, and the difference in plasticiser concentration between the air and plastic.

2.a Firstly, due to the weak bond between the polymer and the plasticiser, the liquid plasticiser diffuses to the plastic surface, leading to increased gloss, tackiness, and adhesion of dirt and dust to the surface. If there is physical contact with soluble media, colour can transfer to the plastic in a process called vinyl offset or offsetting.[16]

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[12] Shashoua, *Conservation of Plastics*, 186; Rose King, Josep Grau-Bové, and Katherine Curran, 'Plasticiser Loss in Heritage Collections: Its Prevalence, Cause, Effect, and Methods for Analysis', *Heritage Science* 8, no. 1 (2020): 4, https://doi.org/10.1186/s40494-020- 00466-0 (accessed 7 December 2020).

[13] Shashoua, *Conservation of Plastics*, 186.

[14] Waentig, *Plastics in Art*, 249.

[15] King, Grau-Bové, and Curran, 'Plasticiser Loss'.

[16] Calmes, 'Plastics Found in Archives', 97; Image Permanence Institute, 'Vinyl Offset', *DP3 Digital Print Preservation Portal*, http://www.dp3project.org/ deterioration/vinyl-offset (accessed 27 July 2022).

2.b Secondly, the plasticiser evaporates, leading to deformation such as shrinking and warping, and loss of flexibility leading to cracking.[17]

Plasticisers act as a barrier between the polymer and the environment, so plasticiser loss can accelerate dehydrochlorination of the polymer. Simultaneously, dehydrochlorination creates an acidic environment that can catalyse plasticiser degradation. Therefore, the degradation processes of the polymer and plasticiser are interrelated.[18]

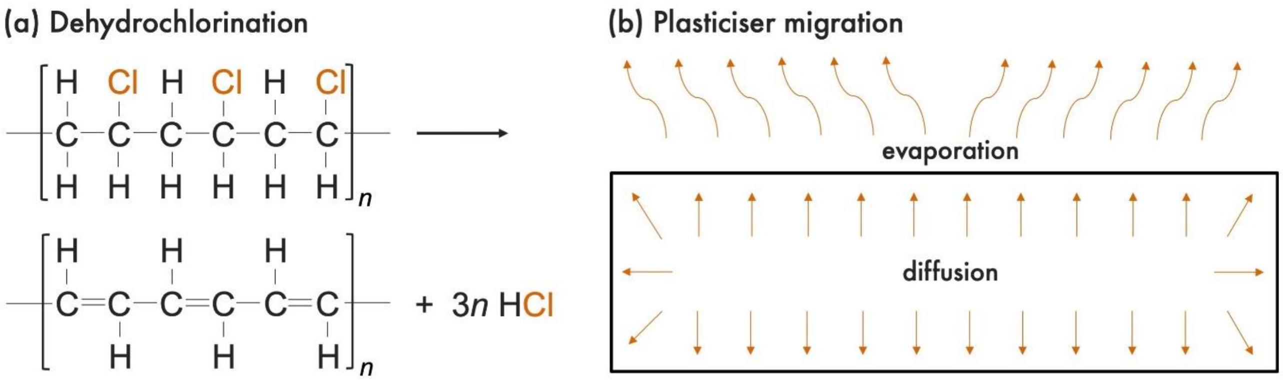


Fig. 1. Degradation processes of PVC-P: (a) dehydrochlorination of polymer; and (b) plasticiser migration. Adapted from Shashoua and King et al.

3 Storage of PVC-P

In the earlier stages of plastics conservation in the 1990s, preventive conservation techniques focussed on controlling environmental fluctuations and physical protection from soiling. Storage recommendations for PVC-based objects included storage in cool temperatures (10–20ºC), 50% relative humidity, minimising UV exposure, and providing protection from dirt and dust with acid-

[17] Cf. Rijavec, Strlič, and Kralj Cigić, ‘Plastics in Heritage Collections’, 997.

[18] Cf. Shashoua, *Conservation of Plastics*, 186.

free tissue.[19]

More recent studies indicate a more proactive approach, targeting the slowing of plasticiser migration, which subsequently slows dehydrochlorination and the accompanying discolouration and deformation. Yvonne Shashoua's experiments with PVC plasticised with DEHP demonstrate the use of sealed storage enclosures to create an equilibrium between the PVC-P and the environment, thus decreasing plasticiser loss.[20] Two investigations by Adeline Royaux et al. show that wrapping PVC-P sheets in silk paper (compacted silk fibres in paper-like form) slows plasticiser migration without accelerating colour change.[21] Both studies found that polyethylene (PE) storage materials accelerate PVC-P degradation, which Yvonne Shashoua theorises is due to PE acting as an adsorbent for the plasticiser.[22] Royaux et al. additionally tested poly(ethylene terephthalate) (PET) wrapping, which was found to accelerate PVC-P discolouration and adhere to PVC-P over time. Shashoua notes in one study that DEHP is highly soluble in PET, making it inadvisable to store PET in contact with DEHP-plasticised PVC,[23] but elsewhere recommends the use of Mylar® envelopes made from

[19] See Morgan, *Conservation of Plastics*, 29; Sharon Blank, 'An Introduction to Plastics and Rubbers in Collections', *Studies in Conservation* 35, no. 2 (1990), 54–5, https://doi.org/10.1179/ sic.1990.35.2.53 (accessed 20 July 2021).

[20] Shashoua, 'Inhibiting the Deterioration'; Yvonne R. Shashoua, 'Effect of Indoor Climate on the Rate and Degradation Mechanism of Plasticized Poly (Vinyl Chloride)', *Polymer Degradation and Stability* 81, no. 1 (2003), https:// doi.org/10.1016/S0141-3910 (03)00059-4 (accessed 3 July 2019).

[21] Royaux et al., 'Long-Term Effect'; Adeline Royaux et al., 'Conservation of Plasticized PVC Artifacts in Museums: Influence of Wrapping Materials', *Journal of Cultural Heritage* 46 (2020): 131–9, https://doi.org/10.1016/j. culher.2020.07.002 (accessed 20 July 2021).

[22] Shashoua, 'Effect of Indoor Climate'.

[23] Shashoua, 'Inhibiting the Deterioration', 60.

PET for storage of PVC-P.[24] It appears that further investigation is needed into the use of PET for PVC-P storage.

Temperature manipulation also affects degradation rates, with cool storage (10–20ºC) shown to slow the chemical degradation of PVC-P. However, freezing (-30ºC) increases the risk of deformation and condensation, and should therefore be avoided.[25]

4 The case study artwork *Chinese Bible*

Chinese Bible is a performance installation artwork by contemporary Chinese artist Yang Zhichao and comprises of 3000 notebooks and diaries.[26] From 2005 the artist bought and read second-hand notebooks from markets in Beijing, from which he then made a recorded performance of himself washing the covers of each book. *Chinese Bible* was first exhibited in 2009 at the China Art Archives Warehouse in Beijing, where the books were installed flat on a large rectangular elevated podium. Later exhibitions took place in Hong Kong, Singapore, Perth, and Sydney.[27]

Dating from between 1949 and 1999, the collection of notebooks is significant not only as an artwork, but also as an historical archive of everyday life after the Chinese Civil War, during the Cultural Revolution and into the post-Mao generation. The archival nature of this artwork is particularly relevant when considering the extensive cataloguing needed to manage 3000 unique

[24] Shashoua, Conservation of Plastics, 201.

[25] Yvonne Shashoua, ‘Modern Plastics: Do They Suffer from the Cold?’, *Studies in Conservation* 49, supp. 2 (2004): 91– 5, https://doi.org/10.1179/sic.2004.49. s2.020 (accessed 27 July 2022).

[26] Claire Roberts, Zhichao Yang, and Ye Sang, *Yang Zhichao: Chinese Bible,* trans. Jeff Crosby and Lina Wang (Paddington, NSW: Sherman Contemporary Art Foundation, 2015), 11–2.

[27] For details of the work as described in the exhibition at the Art Gallery of New South Wales, see https://www. artgallery.nsw.gov.au/collection/works/ 231.2015/#about (accessed 27 July 2022).

books.[28] In the process of condition reporting and cataloguing the artwork, conservators at the Art Gallery of New South Wales (AGNSW) found that the notebooks displayed a wide variety of sizes, structures, paper types, and covering materials. Approximately 1000 of the notebooks were found to have plastic covers of various types.

As part of a collaborative project for managing plastics degradation in Australian museums, a survey focusing on the polymer identification and condition of the plastic-covered books was conducted by the authors. In a sample of 100 books, all but one of the plastic covers was identified as PVC-P using Fourier transform infrared (FTIR) spectroscopy with attenuated total reflection (ATR).

Slip-on PVC-P covers were found to be one of the most common plastic covers amongst the wide variety of structures in *Chinese Bible*. Slip-on covers in *Chinese Bible* have the form of a continuous exterior sheet attached to two interior sheets, creating two pockets that fit onto the covers of the enclosed paper notebooks. Some covers have a raised texture across the interior pockets or along the borders of the interior pockets, while others are entirely smooth. Most covers have a single base colour, such as red or green, and many have embossed or printed designs. As for the enclosed paper notebooks, some of the paper text blocks are machine sewn and some are adhesive bound. The outer layer of the paper notebooks are plain cards made to be inserted into the plastic covers, many of which are attached to endpapers.

[28] See Sarah Bunn, ‘Performing Parts: Exploring the Installation of Chinese Bible as Artwork and Archive’ (presented at the 10th AICCM Book, Paper & Photographic Materials Symposium, Melbourne, 20–23 November 2018); Susannah Smith, ‘A Feat of Biblical Proportions’, *Look*, Jan–Feb 2019, Art Gallery Society of NSW at the Art Gallery of NSW, 60–1.

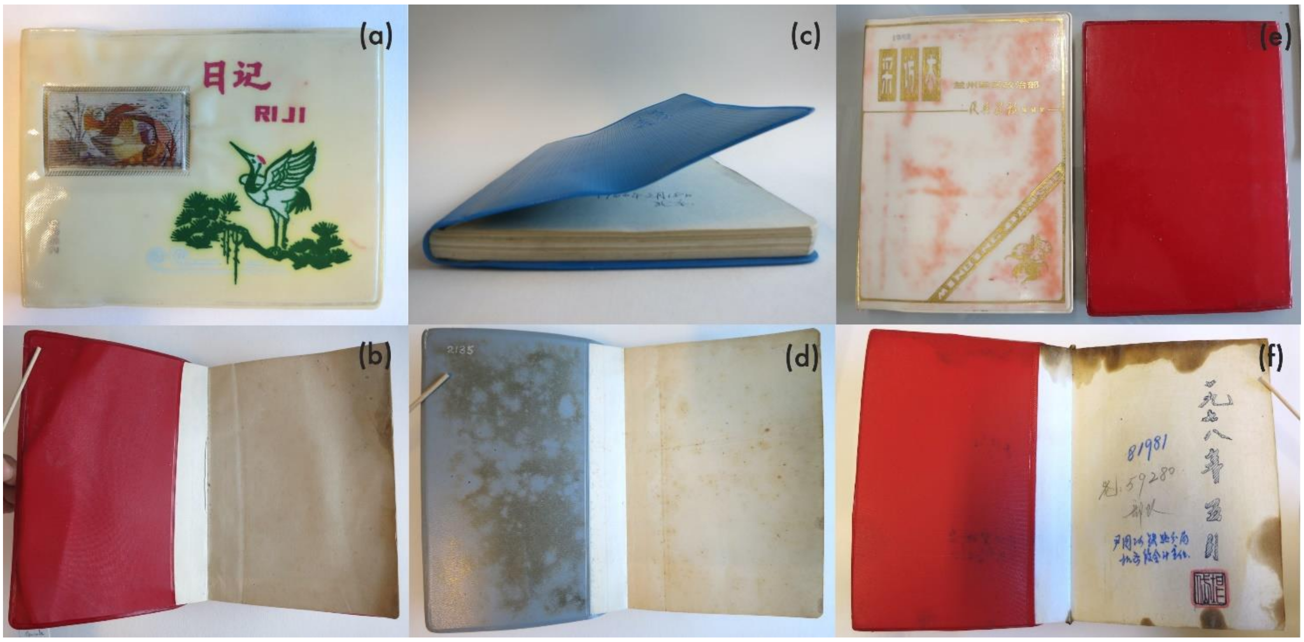


Fig. 2. Examples of degradation signs observed in Chinese Bible. Plasticiser migration of the PVC-P cover leading to: (a) shrinkage and cockling of cover; (b) shrinkage of cover leading to warping and creasing of enclosed paper notebook; and (c) warping and lifting of the front cover. Discolouration patterns such as: (d) dispersed brown-black discolouration of the surface found on interior pocket of the cover, along with yellow-brown discolouration of the facing paper which is more advanced in areas in contact with the cover; (e) colour transfer between adjacent covers; and (f) selective colour transfer of ink media from paper to cover.

5 Degradation of *Chinese Bible*

While most of the *Chinese Bible* notebooks were found to be in a good to fair condition, several examples of advanced PVC-P degradation were observed (see **Fig. 2**), summarised here under four categories:

1 *Deformation* (**Figs. 2a-c**): Shrinkage and warping were observed in varying degrees in the covers. In some cases, the shrunk cover was placing stress on the enclosed notebook, leading to warping and creasing of the paper cards. In one example, the cover shrinkage was so extreme that the text block protruded beyond the cover along the bottom and opening edges of the book. Additionally, there were signs of embrittlement in many covers, evidenced by cracks and losses along the edges.

2 *Discolouration* (**Fig. 2d**): PVC-P discolouration appeared in dark glossy patches, and only occurring on the interior pockets in direct contact with the text block. In some cases, the paper areas in direct contact with the plastic showed more advanced discolouration compared to the rest of the page. Based on these discolouration patterns, it was suspected that interaction between the PVC-P and paper accelerated degradation in each other, known as a cross-infection effect. The release of acids by both PVC-P and cellulose-based paper during ageing supports this hypothesis.[29] However, one study had found no cross-infection between PVC-P samples and cellulose paper.[30]

3 *Colour transfer* (**Figs. 2e-f**): Storing and displaying the books in stacks appeared to result in colour transfer between some covers, resulting in generalised but uneven staining. Additionally, selective transfer of written media from the first leaf of the notebook onto the inside pocket was observed. Only certain inks were found to have this offsetting effect, most likely due to being soluble in the plasticiser.

4 *Tackiness*: Adjacent covers had a tacky grip between them, particularly for the books under the greatest weight at the bottom of stacks. When separating the books, the covers produced a loud creaking noise, like the noise heard when peeling adhesive packing tape from a roll.

6 Investigating the storage of *Chinese Bible*

Although it is recommended that PVC-P be stored separately from other materials, it was not

[29] Cf. Chandru J. Shahani and Gabrielle Harrison, ‘Spontaneous Formation of Acids in the Natural Ageing of Paper’, *Studies in Conservation* 47, supp. 3 (2002): 189–92, https://doi.org/10. 1179/sic.2002.47.s3.039 (accessed 1 May 2022).

[30] Katherine Curran et al., ‘Cross-Infection Effect of Polymers of Historic and Heritage Significance on the Degradation of a Cellulose Reference Test Material’, *Polymer Degradation and Stability* 107 (2014): 294–306, https:// doi.org/10.1016/j.polymdegradstab. 2013.12.019 (accessed 28 July 2022).

possible to separate the covers from their notebooks for *Chinese Bible*. Aside from the need to preserve the original meaning of the artwork by maintaining the physical integrity of each book, the physical process of removing the covers for storage is likely to cause further damage to the books that are already in fragile condition. Additionally, re-applying the covers for future installation may be impossible, since the PVC-P covers are prone to shrinkage. Furthermore, refitting 1000 book covers with the appropriate level of care in each future display iteration presents an impractical time commitment.

For these reasons, introducing interleaving materials was proposed as a potential preservation strategy. Interleaving materials are an established method for reducing contact with the surface of paper materials, particularly when the surface is sensitive to contaminants or contains fragile media.[31] Introducing interleaving materials is therefore likely to reduce discolouration, colour transfer, and cover adhesion in *Chinese Bible* if these are caused by physical contact between the relevant surfaces. Additionally, adding a barrier layer around the PVC-P was hypothesised to slow plasticiser migration. In summary, interleaving materials have the benefit of being a familiar technique in collection settings and appear to be a viable solution accounting for access needs, time commitment, object condition, material types, and maintaining the original meaning of the artwork *Chinese Bible*.

As there was no literature available on the use of interleaving materials for PVC-P book covers, an experiment was formulated to simulate and test the proposed strategy along with the potential interleaving material candidates. Results are envisioned to be applicable to other collections of bound paper materials covered in PVC-P, such as albums, textbooks, and notebooks, where PVC-P is in close contact with paper, and for which it has been determined that the cover should not

[31] See, for example, Society of American Activists, 'Interleaving', *Dictionary of Archives Terminology*, https://dictionary. archivists.org/entry/interleaving.html (accessed 11 August 2021).

be removed due to significance or preservation reasons. The technique is relatively quick, which is beneficial in large collections of bound materials such as libraries and archives.

Table 1. Materials used for notebook samples, interleaving, and ageing set-up.

Name	Material	Details
Notebooks	Paper, adhesive	Unbranded A5 80-page adhesive bound notebook with paper board covers
Covers	PVC-P film	180mm width clear adjustable slip-on book cover
Buffered tissue	Paper	20gsm, from 1016mm roll
Mylar	PET film	100µm thick, A5 enclosures with short side opening, 25 pack
Hollytex	PET non-woven textile	3257 .0029” thick, from 1193mm roll
Weights	Ceramic	Johnson tile, 200 x 200 x 6.8mm, plain white, gloss finish
Supports	Paper board	Corrugated board, single wall, grey/white, from 1750 x 1050 sheet
Ink	Ballpoint pen ink	Paper Mate® InkJoy 100 1.0M

Note: Details from supplier websites. See also Materials and suppliers section.

Methods

1 Sample materials

To simulate the slip-on PVC-P cover structure, book models were assembled from commercially acquired adhesive-bound notebooks and clear adjustable PVC-P slip-on covers. All materials were purchased in 2019 in metropolitan Melbourne, Australia (see **Table 1** and the Materials and suppliers section). There are many obvious differences in the manufacture of the book models compared to the books in *Chinese Bible*, such as the covers being clear rather than coloured, which may introduce uncertainty in applying the results to *Chinese Bible*. However, this combination of materials was the most practical for achieving consistent samples within resource limitations.

The composition of the purchased covers was confirmed to be PVC plasticised with DEHP, identified using pyrolysis-gas chromatography-mass spectrometry (Py-GCMS) (see testing protocol in Appendix). Py-GCMS is a destructive technique, so rather than sampling the artwork, testing was performed on a donated book from a personal collection, dating from 1978 with a matching manufacturer and design to some of the books in *Chinese Bible*. The donated book was identified as PVC predominantly plasticised with DEHP, along with smaller amounts of diisobutyl phthalate (DIBP) and dioctyl sebacate (DOS). The purchased cover materials were considered a reasonable match with *Chinese Bible* for the purposes of this experiment.

Three commonly used collection storage materials were chosen for testing as interleaving materials: buffered tissue, Mylar® and Hollytex®. All three are readily purchasable in Australia and made of chemically stable materials.[32] Mylar® and Hollytex® are PET in the form of stretched film and non-woven textile respectively. Hollytex® is permeable to liquids, vapours and gases, while Mylar® is not. Both permeable and non-permeable forms of PET were tested to determine whether allowing the ventilation of acidic gases or reducing plasticiser migration would be more beneficial to the composite object. PET is currently used as a housing and interleaving material at AGNSW for both paper- and PVC-based items, so experimental results are also applicable to the storage of other collection items.

Table 2. Experimental ageing parameters, all at 50±5% relative humidity for 130 days.

Simulation	**Interleaving**	**Temperature (°C)**
Non-interleaved control	None	70±2
Interleaving type 1	Buffered tissue	70±2
Interleaving type 2	Mylar®	70±2
Interleaving type 3	Hollytex®	70±2
Natural ageing control	None	20±3

2 Sample preparation

Samples were prepared in triplicate for five ageing sets: a non-interleaved control, three interleaving material types, and a room temperature control (see **Table 2**). Set numbers were labelled onto the

[32] Cf. Janet Pasiuk, 'Safe Plastics and Fabrics for Exhibition and Storage', *Conserve-O-Gram* 18, no. 2 (2004), https://www.nps.gov/museum/ publications/conserveogram/18-02.pdf (accessed 20 October 2021).

paper covers with graphite pencil, and PVC-P covers were labelled with graphite pencil on a loose paper slip. Interleaving materials were cut into 130 x 190mm sheets, the size of the books with an additional 5mm margin to ensure maximum coverage. To test the ink offset effect, two lines of ballpoint ink were drawn on the last page. When closed, one line is in contact with the PVC-P cover and the other with the paper board of the notebook cover.

To simulate storage conditions in boxes, two books were stacked on top of each other, and ceramic tiles used to simulate the weight of additional books. The total weight of the tiles per stack was approximately 1.5kg, limited by the shelf clearance of the ageing chamber. Archival corrugated blue boards were used as supports, the same material used for some of the existing storage boxes. Interleaving sheets were cut and placed loose between the PVC-P cover and other surfaces: between the cover and paper, between books in the stack, and between books and the support board (see **Fig. 3a**). A non-interleaved control was included for comparison. Samples were photographically documented before and after ageing.

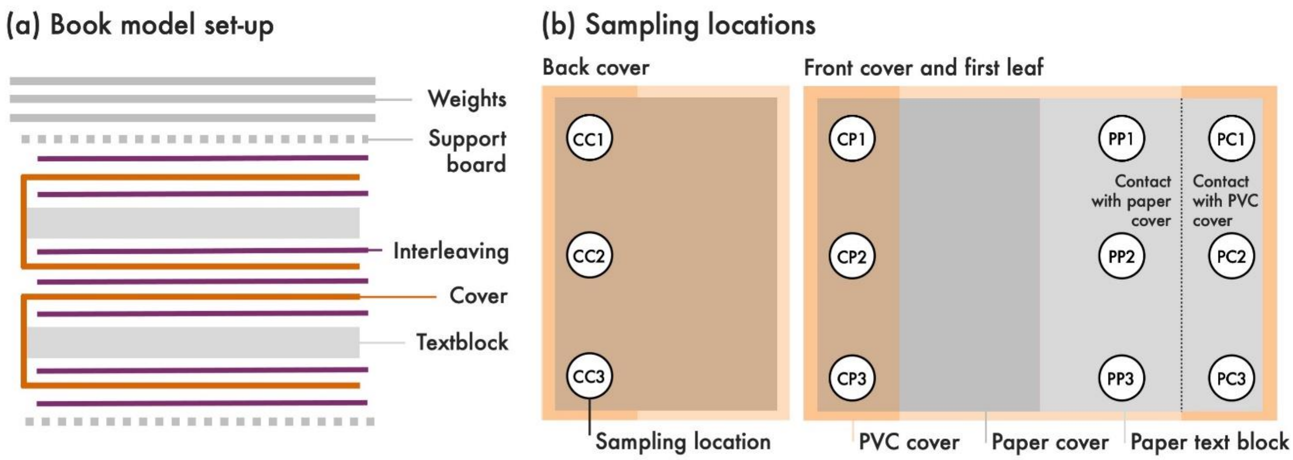


Fig. 3. (a) Set-up of materials used to model book stacks during the ageing experiment; (b) four analysis areas for colourimetry and ATR-FTIR, each area sampled in triplicate to make 12 analysis sites. *CC*: exterior of PVC-P cover in contact with adjacent PVC-P cover; *CP*: interior pocket of PVC-P cover in contact with first leaf of paper text block; *PP*: first leaf of paper in contact with paper board; *PC*: first leaf of paper in contact with PVC-P interior pocket.

3 Thermal ageing

To allow for all materials to reach moisture equilibrium with the atmosphere, samples were first allowed to pre-acclimatise at 50±5% relative humidity (RH) and 20±3°C for four weeks in the laboratory workspace. Next, the three interleaving types and non-interleaved control were aged in a Labec M-HG Series Temp Humidity Chamber with ventilation. Humidity was controlled at 50±5% RH to approximate conditions at an AGNSW storage site, and samples aged at 70±2ºC to replicate settings used in a previous PVC-P ageing study aiming to simulate museum environments.[33] The natural ageing control sample was left in the laboratory workspace at 20±3°C and 50±5% RH. A trial experiment found that changes could be observed after about 100 days, but the samples in this experiment were aged for 130 days due to COVID-19 safety restrictions delaying sample analysis.

Table 3. Analytical techniques used to assess changes before and after ageing.

Parameter	Degradation pathway(s)	Technique	Instrument
Colour	Paper hydrolysis, dehydrochlorination	Colour change	BYK colour photo-spectrometer
Infrared absorbance	Plasticiser migration and dehydrochlorination	ATR-FTIR	Bruker alpha with ATR module
Weight	Plasticiser loss	Weight change	Analytical balance
Colour transfer	Offsetting	Visual examination	None
Deformation	Plasticiser loss and dehydrochlorination	Visual examination	None
Tackiness	Plasticiser migration and physical pressure	Visual examination	None

4 Analytical techniques

Before and after ageing, samples were analysed using visual examination techniques, ATR-FTIR spectroscopy, colourimetry, and weight change (see **Table 3**). Data were averaged across the triplicate samples in each ageing set-up, with measurements conducted on the top book of each stack. Analysis was conducted in two sampling areas of the PVC-P cover and two areas of the paper text

[33] Shashoua, ‘Inhibiting the Deterioration’.

block, of which one is in contact with PVC-P and one in contact with paper when the book is closed (see **Fig. 3b**), making a total of 12 analysis sites.

Colour change was measured using a pre-calibrated BYK Gardener Spectro-Guide Sphere colour spectrophotometer (10º standard observer, D65 tungsten illuminant) in CIE2000 L*a*b colour space. Colour difference (DE_{00}) was determined between before and after ageing samples, and each measurement was averaged from 10 readings to ensure repeatability.

ATR-FTIR spectroscopy was conducted on the same 12 analysis sites using a Bruker ALPHA FTIR instrument, a Platinum-ATR module with a diamond window, and OPUS 7 software. Measurements were made in the 4000–400cm^{-1} range, at a resolution of 4cm^{-1}, with 32 co-added scans in absorbance mode.

For weight analysis, PVC-P covers and paper notebooks were separately weighed in grams to four decimal places, with an AND GR-200 analytical balance.

After ageing, samples were additionally examined using a BX-51 Olympus optical microscope equipped with a DP70 camera. Images were captured with DPControl and DPManager software.

Results

1 Colour change

The most obvious aesthetic change in the PVC-P covers was discolouration. Across all aged samples, the interior PVC-P pocket in contact with the paper (*CP*) was found to have discoloured at a faster rate compared to the exterior cover in contact with another cover (*CC*), like in *Chinese Bible*. *CC* changed from colourless to orange-brown, while *CP* changed from colourless to reddish-brown with a spotted pattern (see **Fig. 4**). Observed changes are consistent with the discolouration patterns described in the literature.[34] Discussion of the possible causes of discolouration, namely dehydrochlorination and microbiological staining, is addressed later in the discussion of other analytical techniques. The ΔE_{00} of the PVC-P covers for all three interleaved samples were not statistically different from the non-interleaved control, when taking a ΔE_{00} of 1.5 as the accepted threshold of perceptible colour difference (see **Table 4**).[35] This indicates that interleaving did not significantly impact the rate of PVC-P discolouration.

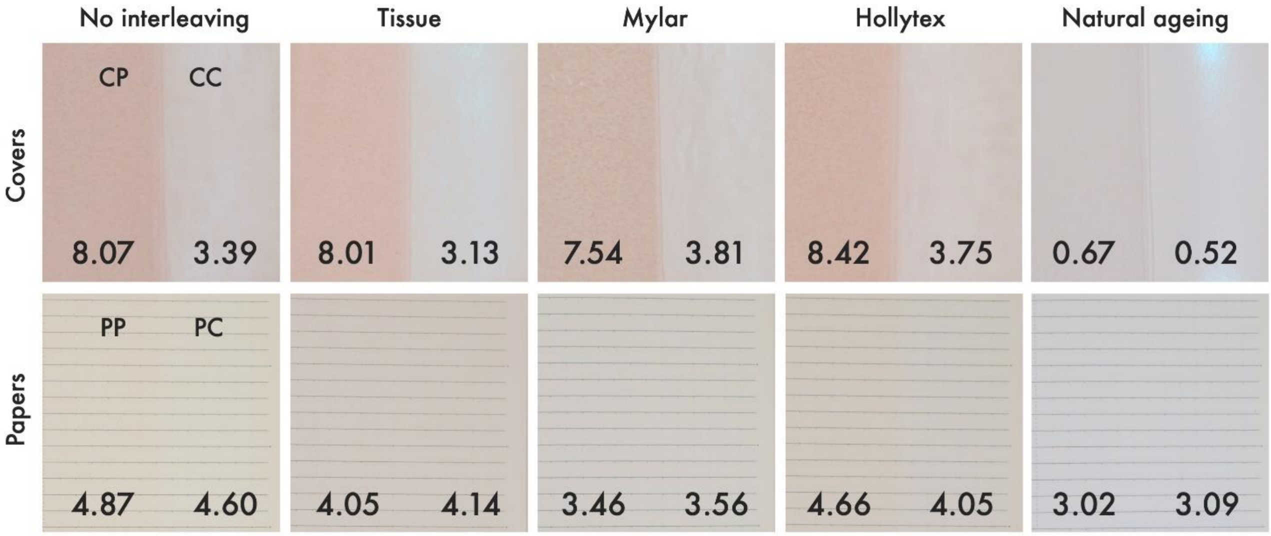


Fig. 4. A representative image and ΔE00 value of each sampling location after ageing. *CC*: exterior of PVC-P cover in contact with adjacent PVC-P cover; *CP*: interior pocket of PVC-P cover in contact with first leaf of paper text block; *PP*: first leaf of paper in contact with paper board; *PC*: first leaf of paper in contact with PVC-P interior pocket. Note that *CP* areas are double layered with *CC* and appear darker. Across the samples, there are negligible differences in ΔE_{00} values between the interleaved and non-interleaved samples.

[34] Cf. Waentig, *Plastics in Art*, 246–9.

[35] See Jonathan Ashley-Smith, Alan Derbyshire, and Boris Pretzel, 'The Continuing Development of a Practical Lighting Policy for Works of Art on Paper and Other Object Types at the Victoria and Albert Museum', in *13th Triennial Meeting, Rio de Janeiro, 22–27 September 2002* (London: James & James, 2002), https://www. icom-cc-publications-online.org/2181/ The-continuing-development-of-apractical-lighting-policy-for-works-ofart-on-paper-and-other-object-typesat-the-Victoria-and-Albert-Museum (accessed 20 October 2021).

Table 4. Results of colourimetry and ATR-FTIR assessments, showing mean±standard deviation.

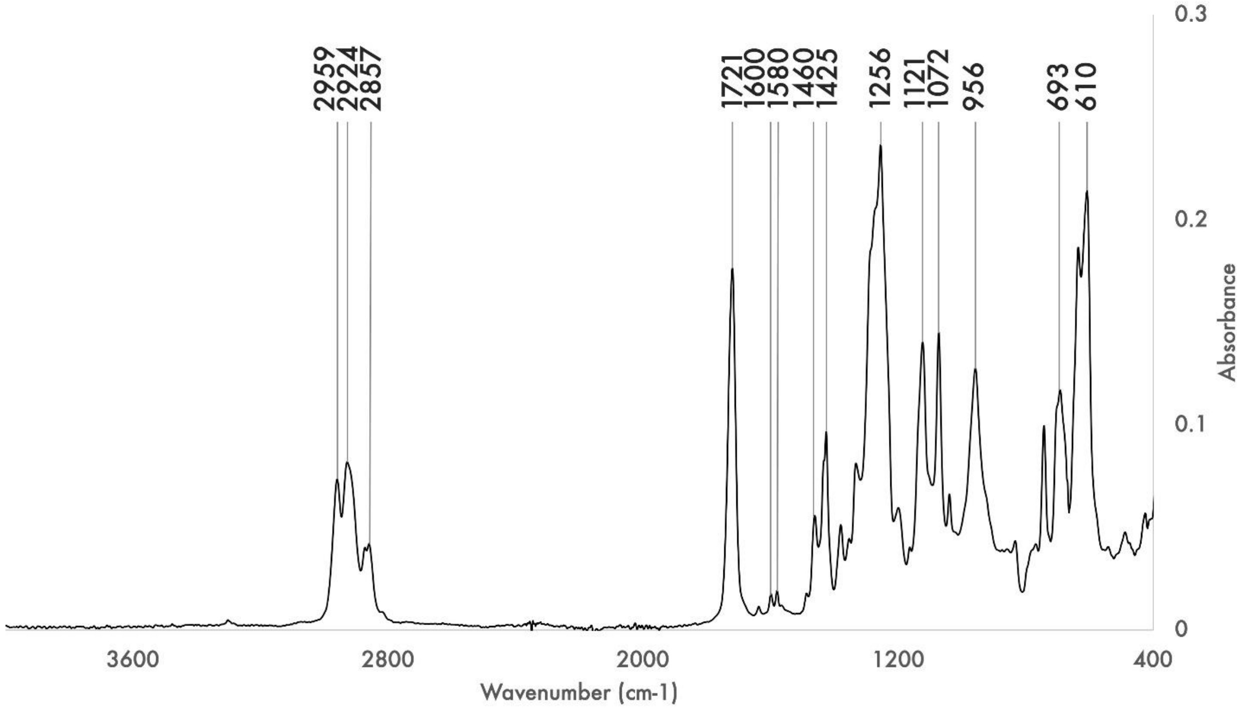
Parameter	Location	No interleaving	Tissue	Mylar®	Hollytex®	Natural ageing
Colour change (ΔE_{00})	*CP*	8.07±0.36	8.01±0.39	7.54±0.27	8.42±0.30	0.67±0.13
	CC	3.39±0.21	3.13±0.14	3.81±0.25	3.75±0.27	0.52±0.21
	PP	4.87±0.10	4.05±0.18	3.46±0.12	4.66±0.18	3.09±0.20
	PC	4.60±0.83	4.14±0.55	3.56±0.14	4.05±0.11	3.02±0.25
IR change in covers (%)	*CP*	20.86±4.99	13.61±8.63	47.92±13.51	21.72±8.79	−4.76±0.63
	CC	59.60±5.17	49.42±8.59	47.58±9.02	50.60±7.44	−2.65±0.39
IR change in papers (%)	*PP*	10.51±41.20	5.35±6.69	7.40±10.38	19.03±12.00	−0.12±9.08
	PC	9.20±26.27	18.14±12.72	21.60±14.29	17.69±12.05	−5.27±36.73

Notes: IR change is reported as the percentage change in the ratio of absorbance at bands 1460:1425cm^{-1}, and the percentage change of absorbance at 1425cm^{-1}, for the covers and notebook papers respectively

In the paper notebooks, a difference could be observed between the area in contact with the plastic (*PC*) versus the paper boards (*PP*). In the non-interleaved sample, the PVC-P cover appeared to have a preserving effect on the paper, as seen from how *PC* is less discoloured than *PP* (see **Fig. 4**). Note that this is not the same pattern seen in the *Chinese Bible* books and may be due to the low-quality paper of the sample book models. Further testing with different paper types may reveal a better approximation of the books in the *Chinese Bible* case study. Averaged colour changes were below a ΔE_{00} of 1.5, indicating the negligible impact of interleaving materials on the rate of paper discolouration.

Table 5. Summary of FTIR-ATR band assignments for PVC-P and paper samples.

Spectra

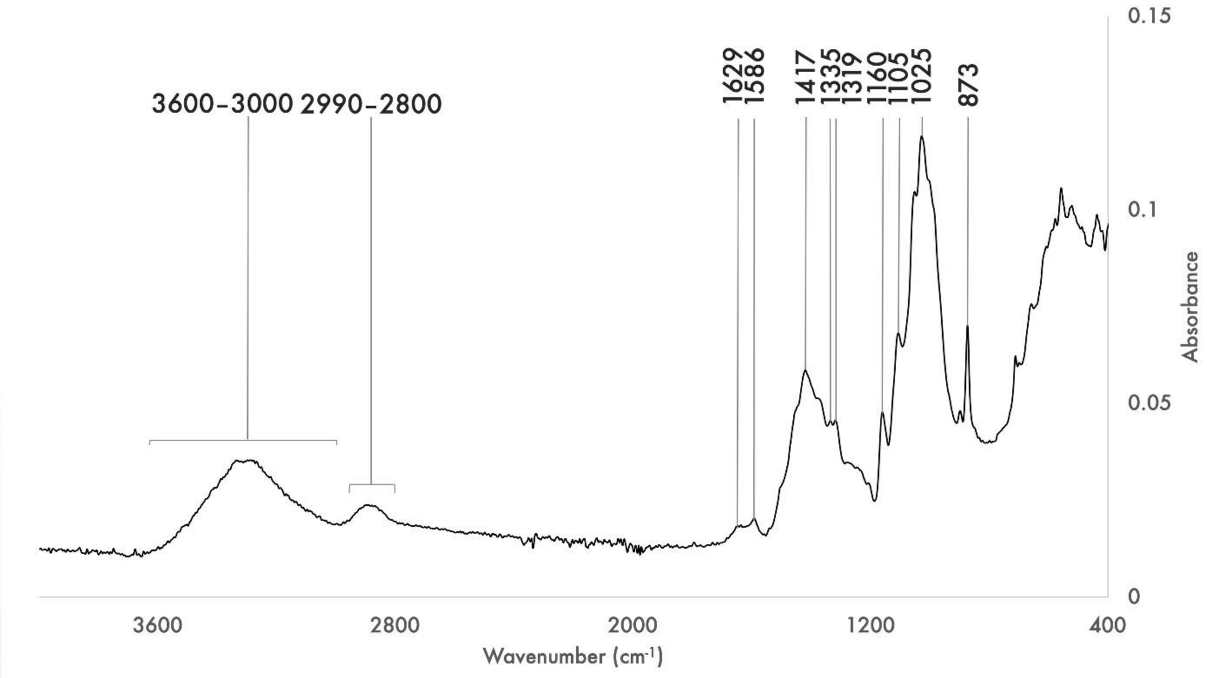


Example spectrum of PVC-P cover before ageing

Wavenumber (cm^{-1})	Assignment	Compound
2959, 2924, 2857	C–H stretching	DEHP
1721	C=O stretching	DEHP
1600, 1580	C=C stretching	DEHP
1460	C–H bending	DEHP
1425	C–H bending	PVC
1256, 1121, 1072	C–O stretching	DEHP
693, 610	C–Cl stretching	PVC

Table 5. (cont.) Summary of FTIR-ATR band assignments for PVC-P and paper samples.

Spectra



Example spectrum of notebook paper before ageing

Wavenumber (cm^{-1})	Assignment	Compound
3600–3000	O–H stretching	cellulose
2990–2800	C–H stretching	cellulose
1629, 1586	O–H bending	water
1417	O–C–O stretching	$CaCO_3$
1335, 1319	C–H bending	cellulose
1160, 1105, 1025	C–O bending	cellulose
873	O–C–O bending	$CaCO_3$

2 FTIR spectroscopy

ATR-FTIR spectroscopy was used to evaluate chemical changes in the samples. Interpretation of the spectra was carried out by recognising characteristic absorbance bands linked to functional groups (see **Table 5**).[36] A strong, sharp band at 1719cm^{-1} is assigned to C=O bond stretching, along with several strong bands at 1256, 1121, 1072cm^{-1} assigned to C–O bond stretching. Together, these

[36] Cf. Barbara H. Stuart, 'Chapter 4. Organic Molecules', in *Infrared Spectroscopy: Fundamentals and Applications* (Chichester, England: John Wiley & Sons, 2004), 71–93.

indicate the ester group found in DEHP.[37] Weak bands at 1600 and 1580cm^{-1} indicate aromatic C=C stretching, also found in the structure of DEHP. Although DEHP signals dominate the spectra, bands attributed to the PVC polymer are principally observed in strong bands at 693 and 610cm^{-1} assigned to C–Cl bond stretching.[38]

Spectra of the aged and unaged samples of the covers were overlaid and compared (see **Fig. 5**). Changes fall into several categories:

1. The appearance of a sharp medium band at 3297cm^{-1} together with two medium bands at 1564cm^{-1} and 1634cm^{-1} suggest the presence of amine (N–H) groups in the aged samples. Previous literature attributes these bands to an unknown additive or reaction with additives on the surface of the PVC-P.[39] An alternate explanation is that these are caused by by-products of microorganisms. This is supported by the appearance of red discolouration which has been linked in the literature to an amine-containing pigment called prodiginine produced by the microorganism *Streptoverticillium rubrireticuli*.[40] This would also explain the strengthened alkane C–H stretching bands at 2916 and 2848cm^{-1}.
2. There is a weak indication of minor dehydrochlorination of the PVC polymer. This is indicated by a small decrease in absorbance at 605cm^{-1}, assigned to the C–Cl bond, along with the appearance of a medium band at 1552cm^{-1}, partially disguised by the amine band at

[37] Cf. Adeline Royaux et al., ‘Aging of Plasticized Polyvinyl Chloride in Heritage Collections: The Impact of Conditioning and Cleaning Treatments’, *Polymer Degradation and Stability* 137 (March 2017): 11, https://doi.org/10. 1016/j.polymdegradstab.2017.01.011 (accessed 19 April 2018).

[38] Cf. Rijavec, Strlič, and Kralj Cigić, ‘Plastics in Heritage Collections’, 1001.

[39] Royaux et al., ‘Aging of Plasticized’, 17.

[40] Nancy N. Gerber and Donald P. Stahly, ‘Prodiginine (Prodigiosinlike) Pigments from *Streptoverticillium Rubrireticuli*, an Organism That Causes Pink Staining of Polyvinyl Chloride’, *Applied Microbiology* 30, no. 5 (1975): 249, https://www.ncbi.nlm.nih.gov/pmc/articles/PMC187276/ (accessed 20 October 2021); Waentig, Plastics in Art.

1564cm^{-1}, which is associated with C=C bonds in alkenes. Alkenes are produced during dehydrochlorination in the formation of the polyene structure.

3 A decrease in ester groups is indicated by the decreased C=O band at 1721 cm^{-1} and in the C–O bands in the 1300-1000cm^{-1} region. This is consistent with the loss of DEHP plasticiser.

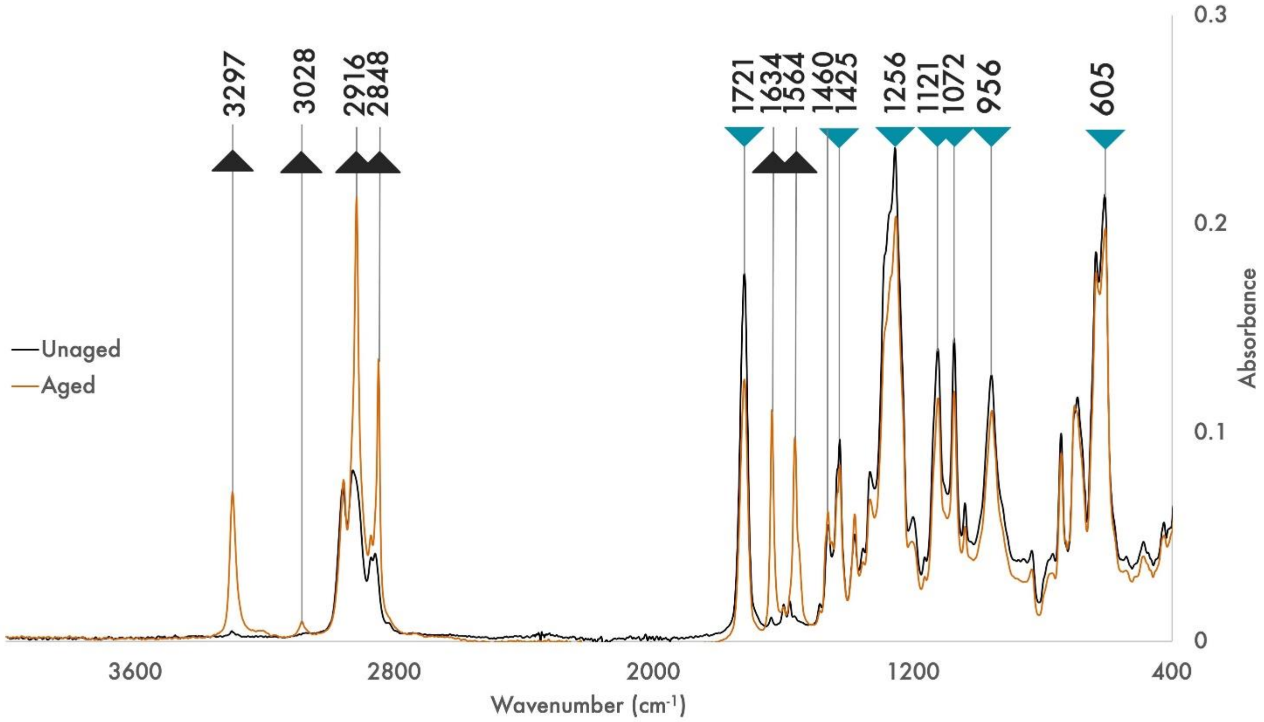


Fig. 5. Overlaid FTIR-ATR spectra of the aged and unaged PVC-P cover in a non-interleaved sample, with arrows indicating increases or decreases in absorbance at relevant bands. Similar changes were observed across all aged samples.

To quantify plasticiser migration to the surface, a comparison of the ratio of the absorbance units of the bands at 1460 and 1425cm^{-1}, assigned to DEHP and PVC respectively, were used as an indicator of DEHP content (see **Table 4**).[41] A one-way analysis of variance (ANOVA) followed by a

[41] Stuart, *Infrared Spectroscopy*, 122.

Tukey's honesty significant difference (HSD) test were performed to compare the effect of interleaving materials on IR change:[42]

1 In *CC*, the test showed that there was statistical difference in IR change between at least two interleaving materials (F (3, 32) = 4.34, $p = 0.01$). Tukey's HSD test for multiple comparisons found that the mean value of weight change was significantly different between tissue-interleaved samples and non-interleaved samples ($p = 0.04$, 95% C.I. = 0.34, 30.02), as well as between Mylar®-interleaved samples and non-interleaved samples ($p = 0.01$, 95% C.I. = 2.18, 21.86). There was no statistical difference between Hollytex® and non-interleaved samples.

2 In *CP*, the test also showed that there was statistical difference in IR change between at least two interleaving materials (F (3, 32) = 22.69, $p = 4.62 \times 10^{-8}$). Tukey's HSD test found that the mean value of weight change was significantly different between Mylar®-interleaved samples and non-interleaved samples ($p = 5.28 \times 10^{-6}$, 95% C.I. = 14.96, 39.17). Note that weight change is greater in the Mylar®-interleaved samples. There was no statistical difference between tissue or Hollytex® and non-interleaved samples.

In summary, tissue and Mylar® have a beneficial effect on decreasing plasticiser migration on *CC*, but Mylar® has a negative effect on *CP*. Note that the FTIR-ATR analysis detects only surface changes and may not account for changes in the entire substrate, as revealed in the next section on weight analysis. Future experiments may utilise cross-section FTIR microscopy for a more comprehensive indication of plasticiser changes across the entire PVC-P substrate.

Infrared spectra of the notebook paper at areas *PP* and *PC* were recorded, and characteristic bands were assigned to cellulose, calcium carbonate ($CaCO_3$) and water (see **Table 5**).[43] Spectra of

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[42] Statistics Kingdom, 'ANOVA Calculator', *Statistics Kingdom* (2017), https://www.statskingdom.com/180Anova1way.html (accessed 2 May 2022).

the papers match that of post-1960s wood-pulp papers with an alkylketene dimer (AKD) sizing, a $CaCO_3$ filler, and no coatings.[44] However, only minimal changes were observed when comparing samples before and after ageing. Percentage changes in the band at 1425cm^{-1} were taken as an indicator of paper degradation, as a strengthening of absorbance indicates a change of the cellulose polymeric structure from amorphous to crystalline due to hydrolysis.[45] No statistical significance was found between the interleaved and non-interleaved samples with ANOVA. As acknowledged in the literature, infrared spectroscopy is not ideal for the identification of paper degradation mechanisms.[46] Raman spectroscopy is recommended for future experiments to reveal more information on paper degradation.

3 Weight change

Overall plasticiser loss was determined by weight measurement to complement the infrared analysis results. A one-way ANOVA was performed to compare the effect of interleaving materials on weight change (see **Table 6**). The test showed that there was statistical difference in weight change between

[43] Cf. Vito Librando, Zelica Minniti, and Salvatore Lorusso, 'Ancient and Modern Paper Characterization by FTIR and Micro-Raman Spectroscopy', *Conservation Science in Cultural Heritage* 11 (2011): 252, https://doi.org/10.6092/issn.1973-9494/2700 (accessed 17 October 2019).

[44] Andrea Gorassini, Paolo Calvini, and Alice Baldin, 'Fourier Transform Infrared Spectroscopy (FTIR) Analysis of Historic Paper Documents as a Preliminary Step for Chemometrical Analysis', in *CMA4CH Mediterraneum Meeting 2008 Multivariate Analysis and Chemometrics Applied to Cultural Heritage and Environmen*t (Ventotene Island, Italy: CMA4CH, 2008), 3, https://www.semanticscholar.org/paper/FourierTransform-Infrared-Spectroscopy-(FTIR)-of-a-Gorassini-Calvini/15e1c52ddad6e89b9914f0e72 224fc0e51e551b1 (accessed 17 October 2019).

[45] Cf. Librando, Minniti, and Lorusso, 'Ancient and Modern Paper', 261.

[46] See Gorassini, Calvini, and Baldin, 'Fourier Transform Infrared Spectroscopy'; Librando, Minniti, and Lorusso, 'Ancient and Modern Paper'.

at least two interleaving materials (F (3, 8) = 307.85, $p = 1.33 \times 10^{-8}$). Tukey's HSD test found that the mean value of weight change was significantly different between Mylar®-interleaved samples and non-interleaved samples ($p = 4.03 \times 10^{-8}$, 95% C.I. = 0.285, 0.376). There was no statistical difference between tissue or Hollytex® and non-interleaved samples. In other words, aged covers showed approximately the same change in weight, except for the Mylar®-interleaved sample for which plasticiser loss is decreased. This is an indication that plasticiser loss is slowed with Mylar®, a beneficial effect.

When compared to infrared analysis results, it can be understood that Mylar® slows the evaporation step of plasticiser migration on the *CC* area, acting as a barrier to retain the plasticiser on the surface. Conversely, the presence of plasticiser on the surface is slightly reduced by Hollytex® and buffered tissue, but since weight loss occurs at roughly the same rate as the non-interleaved sample, it can be deduced that there is a negligible effect on evaporation. This is consistent with the fact that Hollytex® and buffered tissue are permeable while Mylar® is non-permeable.

Table 6. Summary of qualitative and weight change results, showing mean±standard deviation.

Parameter	No interleaving	Tissue	Mylar®	Hollytex®	No ageing
Weight change (g)	0.543±0.006	0.562±0.010	0.213±0.015	0.576±0.026	0.071±0.003
Offsetting	2.0±0.0	0.3±0.6	0.0±0.0	0.3±0.6	0.0±0.0
Deformation	1.0±0.0	1.3±0.6	1.0±0.0	2.3±0.6	0.3±0.6
Tackiness	3.0±0.0	0.0±0.0	3.0±0.0	0.0±0.0	2.0±0.0
Surface haze	No	No	Yes	No	No

Notes: The qualitative parameters offsetting, deformation and tackiness are ranked on a scale of 0–3, with 0 being no signs observed, and 3 being significant or noticeable signs. Weight change is for covers only, reported to the accuracy of the balance used (0.001g).

4 Offsetting

Offsetting was assessed through visual examination. As expected, the most significant offsetting was observed in the non-interleaved sample. For all samples with ink offset, the ink is transferred to the cover but not the paper board, indicating that the plasticiser is acting as a solvent (see **Fig. 6**). Between the interleaving material types, Mylar® is most effective in preventing ink offset, with all covers consistently showing no traces of ink transfer. Tissue and Hollytex® both reduce offsetting, but these covers were occasionally stained with traces of ink.

Notably, traces of the ink were found even in areas that were not directly in contact with the originally drawn ink line. This was most common in areas near the cover edges, perhaps due to the direction of plasticiser migration towards areas of greater ventilation. A similar effect was observed for the interleaving materials, which inconsistently had traces of ink including sometimes in areas which were not in direct contact with the original ink line. A future experiment may be designed with more frequent observations during the ageing period, to observe the gradual changes in ink staining.

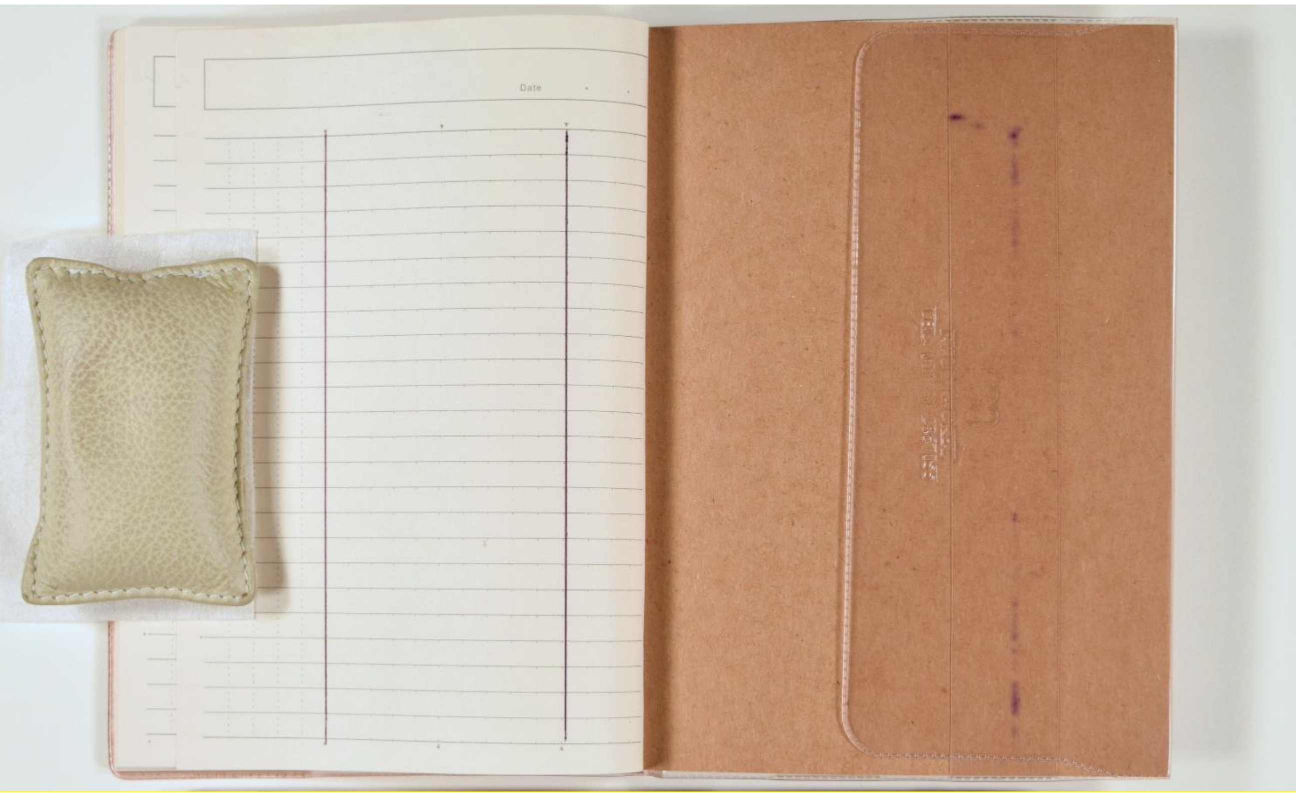

Fig. 6. Example of offsetting occurring in a non-interleaved control sample.

5 Deformation

Cover deformation was assessed through visual examination. Deformation signs observed included cracking at the edges, cockled warping patterns on the interior pocket, and overall shrinkage indicated by dimensional changes and planar warping. Deformation was ranked for each sample on a scale of 0–3, with 3 being the greatest amount of deformation observed. Buffered tissue and Hollytex®, both permeable, appeared to accelerate deformation compared to the non-interleaved sample, consistent with previous studies concluding that ventilation and adsorbent storage materials are detrimental to PVC-P.[47] Mylar® had a negligible impact on the rate of deformation.

6 Tackiness

The level of tack between covers was subjectively assessed when separating the stacked books, and ranked on a scale of 1–3, with 3 being strong tackiness. As in *Chinese Bible*, physical resistance and a creaking noise were observed when separating covers with tackiness. Mylar® had a negligible impact, while buffered tissue and Hollytex® significantly decreased the tacky bond. Since tackiness is likely caused by the presence of plasticiser on the PVC-P surface between adjacent covers, this result is consistent with the results from deformation and weight that indicate greater plasticiser loss for the tissue and Hollytex® samples. However, when a Kendall's Tau test was performed to determine correlation between weight change and tackiness, no association could be confirmed (r_τ = -0.37, p = 0.09).[48] Further testing is necessary to determine the mechanisms causing tackiness.

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[47] See Shashoua, 'Inhibiting the Deterioration'; Cf. Rijavec, Strlič, and Kralj Cigić, 'Plastics in Heritage Collections'.

[48] See Patrick Wessa, 'Kendall Tau Rank Correlation—Free Statistics Software (Calculator)', *Free Statistics Software,* Office of Research and Development, version 1.2.1 (2022), http://www.wessa.net/rwasp_kendall.wasp (accessed 2 May 2022).

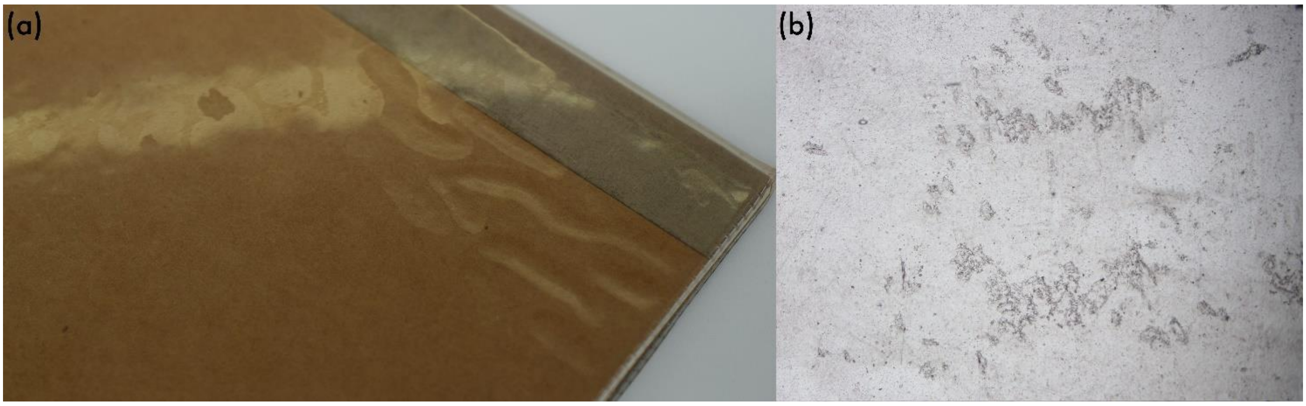

Fig 7. Details of a Mylar®-interleaved sample: (a) a blotchy white haze developed on the surface of the cover, corresponding to the shape of bubbles between the cover and paper, seen under reflected ambient light; (b) crystalline deposits seen under 40× magnification and transmitted light.

7 Surface haze

A cloudy white surface haze appeared on the Mylar®-interleaved samples. This surface haze presented as an irregularly distributed, blotchy, puddle-like pattern on all surfaces in contact with the Mylar® (see **Fig. 7a**). Bubbles between the PVC-P and paper cover were seen having shapes corresponding to the blotchy haze. Using optical microscopy, a dispersed crystalline deposit was observed on the Mylar®-interleaved samples (see **Fig. 7b**). This deposit is theorised to be crystalised phthalic acid, a degradation product of DEHP. The white haze was additionally found on the Mylar® and confirmed to match with DEHP with ATR-FTIR.

Condensation of the phthalic acid from DEHP degradation onto the non-permeable PET may have caused the blotchy pattern in the Mylar®-interleaved samples. In a previous study, an irregular surface haze was observed in oilstick screen prints wrapped in plastic sheets and identified as phthalic acid condensation.[49] Although a subtle homogenous white surface haze appeared on all samples, this blotchy pattern was the most disfiguring and had the greatest negative impact on the

[49] Im Chan, ‘The Materials, Techniques, and Conservation Challenges of Richard Serra’s Oilstick Screen Prints’, *The Book and Paper Group Annual* 32, no. 1 (2013), https://cool.culturalheritage.org/coolaic/sg/bpg/annual/v32/bpga32-05.pdf (accessed 20 October 2021).

Mylar®-interleaved samples. After several months at room temperature post-experimental ageing, the surface haze appeared less prominent on samples, although the uneven blotches persisted on the Mylar®-interleaved samples.

8 Interleaving materials

In addition to the appearance of white haze on the Mylar®, changes were observed for the buffered tissue and Hollytex®. Significant discolouration occurred in the buffered tissue which, like the paper text block, was more discoloured in areas in contact with the paper cover than the PVC-P. Additionally, a brown tide line was found corresponding to the top, bottom, and opening edges of the book. A match with DEHP was identified with ATR-FTIR spectroscopy for the darkened areas of the buffered tissue, evidencing the migration of plasticiser onto the interleaving materials. Seen under raking light, the buffered tissue was significantly cockled. Hollytex® showed less pronounced surface deformation, and unlike buffered tissue there was no tide line present. Together with the changes observed in the Mylar®, these results suggest that the plasticiser was in liquid form when in contact with the interleaving sheet, leaving evidence of plasticiser migration to the interleaving materials in the form of deformation and discolouration before evaporation to the atmosphere.

Discussion

1 Implications for interleaving materials

Results from this experiment show that the three tested interleaving materials have a mixed impact on the longevity of books with PVC-P covers (see **Fig. 8**). Aged samples showed similar deterioration signs as observed in *Chinese Bible*, including discolouration, deformation, offsetting and tackiness. All three types of interleaving materials have a positive impact on reducing offsetting, but a negative or neutral impact on other parameters. Since damage is induced by the tested materials, it is not possible to recommend them for the long-term storage of *Chinese Bible* or in the wider conservation of book with PVC-P covers.

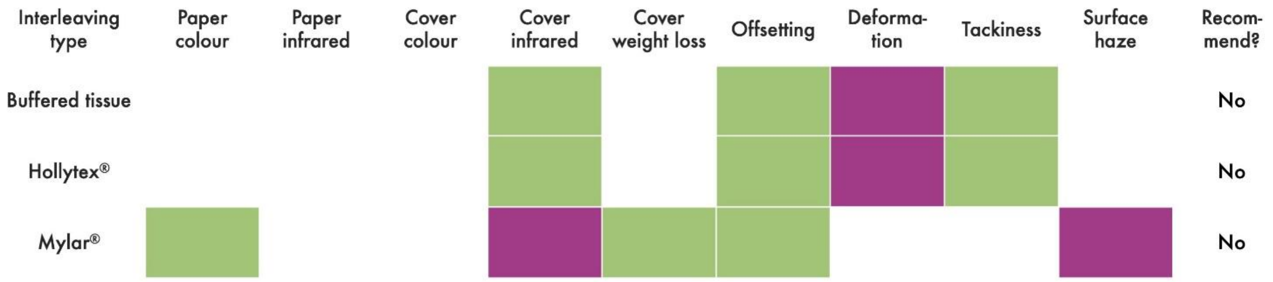

Fig. 8. Visual summary of the effect of tested interleaving types compared to no interleaving (light green = positive effect; white = negligible effect; dark pink = negative effect). Deformation included shrinkage, cracing and warping.

Buffered tissue and Hollytex® behaved similarly under the tested parameters, suggesting that permeability has a greater impact on efficacy than the material composition of the interleaving materials. Both minimised changes in surface DEHP content as indicated by ATR-FTIR spectroscopy and prevented tackiness between covers. However, both accelerated deformation of the covers and had a negligible effect on weight loss. This suggests that permeable interleaving materials have a minimal to negative impact on plasticiser migration, and therefore a minimal to negative impact on the preservation of PVC-P book covers.

Mylar® performed the best in preventing offsetting, and reduced weight loss in the PVC-P cover, indicating the retention of plasticiser. This is an important result as it indicates that Mylar® may be the most beneficial for the lifespan of PVC-P covers. However, the drawback is that Mylar® displayed a blotchy white surface haze across the areas in contact with the interleaving sheet. As the aesthetic appearance of the covers of *Chinese Bible* is a key component of the artwork when on display, the blotchy appearance is a significantly damaging effect. Migration or transfer of DEHP onto the PET indicated by ATR-FTIR spectroscopy is consistent with the fact that DEHP is known to be soluble in PET.[50] Despite the benefit of minimising plasticiser migration, Mylar® had a minimal impact on deformation and tackiness, and no impact on PVC-P colour change. Since the literature also indicated the negative effect of PET on PVC-P discolouration,[51] it can be concluded that PET is likely unsuitable for contact storage with PVC-P.

Interleaving materials showed traces of plasticiser transfer, causing cockling and discolouration on the buffered tissue and the appearance of surface haze on Mylar®. If these two interleaving materials are used, it is likely that the interleaving sheets would need to be periodically monitored and replaced. This is to avoid damaged interleaving materials introducing additional detrimental effects, such as cockled tissue causing paper deformation.

Although similar degradation patterns were found in the aged samples and *Chinese Bible*, one significant difference was that the discolouration pattern and FTIR spectroscopy suggested the presence of staining caused by microorganisms in the aged samples. Such staining can be transferred to the plasticiser from neighbouring surfaces or caused by the growth of microorganisms which feed on plasticiser.[52] This is a common problem observed in PVC-P, and it is likely that the humidity and heat of the ageing chamber encouraged microorganism growth. However, it is unlikely that the same environmental conditions would be found in collection storage environments, and thus the same discolouration is unlikely to occur. *Streptoverticillium rubrireticuli* is not harmful to humans, and its growth can be prevented with anti-microbial treatment of the PVC-P.[53] There are currently no studies

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[50] Cf. Shashoua, 'Inhibiting the Deterioration', 60; Leonard Sax, 'Polyethylene Terephthalate May Yield Endocrine Disruptors', *Environmental Health Perspectives* 118, no. 4 (2010): 445–8, https://doi.org/10.1289/ehp.0901253 (accessed 1 September 2021)

[51] Cf. Royaux et al., 'Conservation of Plasticized PVC Artifacts'.

[52] Gerber and Stahly, 'Prodiginine Pigments'.

[53] Cf. ASTM International, ASTM E1428-15a, *Standard Test Method for Evaluating the Performance of Antimicrobials in or on Polymeric Solids against Staining by* Streptomyce Species *(a Pink Stain*

specifically describing the cleaning of microbiological staining in PVC-P for a conservation context, but existing PVC-P cleaning techniques using detergents or diluted organic solvents for removing surface soiling and degradation products can be tested for efficacy.[54] As the *Chinese Bible* books did not exhibit this red staining, it is possible that the washing of the covers by the artist may have had preventive effects.

It was assumed during this experiment that weight loss was predominantly due to plasticiser loss rather than dehydrochlorination. This is in line with previous studies indicating the correlation between these two factors.[55] Further studies could confirm this through the measurement of acidic emissions using solid phase micro-extraction (SPME) fibres or similar methods.

Lastly, no impact on paper stability was observed in this experiment, consistent with a previous study detecting no cross-infection effect between PVC-P and paper.[56] It is possible that contemporary PVC-P formulations contain more stabilising additives, which reduce the amount of HCl produced in dehydrochlorination, in comparison to the *Chinese Bible* notebooks. This is suggested with FTIR-ATR spectroscopy of the samples used in the experiment, which showed only minor signs of dehydrochlorination. Although Py-GCMS did not reveal additives other than DEHP, it is possible that different instrumental conditions with GC-MS may reveal additional additives.

Organism) (West Conshohocken, PA: ASTM International, 2015), https://doi.org/10.1520/E1428-15A (accessed 3 September 2021).

[54] Cf. for example, Clara Morales Muñoz et al., 'A Model Approach for Finding Cleaning Solutions for Plasticized Poly(Vinyl Chloride) Surfaces of Collections Objects', *Journal of the American Institute for Conservation* 53, no. 4 (2014): 236–51, https://doi. org/10.1179/0197136014Z. 00000000040 (accessed 3 September 2021).

[55] Shashoua, 'Inhibiting the Deterioration'; Royaux et al., 'Conservation of Plasticized PVC Artifacts'.

[56] Curran et al., 'Cross-Infection Effect'.

2 Future work

The results of this investigation show that more research needs to be conducted into the storage of books with PVC-P covers. Future optimisation may focus on non-permeable materials, which performed the best in slowing plasticiser loss. Multi-layer interleaving sheets combining the properties of different materials may also be explored, such as a non-permeable sheet paired with a non-condensing layer for contact with PVC-P. Other experiments have shown the beneficial use of silk paper, which may be an additional candidate as an interleaving material.[57] Identifying and assessing strategies other than introducing interleaving materials are potential areas of further investigation, such as finding appropriate materials for lining storage boxes to reduce ventilation. This would decrease the rate of plasticiser loss that is a key factor in the stability of PVC-P.

Conclusion

Buffered tissue, Mylar®, and Hollytex® interleaving sheets lowered the probability of offsetting onto PVC-P book covers, providing some benefit in maintaining their aesthetic properties. However, all three interleaving materials introduced or accelerated chemical and physical damage, including a blotchy surface haze and cover deformation, when compared to non-interleaved samples. None of the tested materials can be recommended for use in the long-term storage of *Chinese Bible*. More research is necessary to identify a suitable strategy for preserving books with PVC-P covers. This study contributes to a better understanding of composite objects containing paper and plastic, highlighting the complexity of conserving plastic and paper composite materials in book collections.

[57] Cf. Royaux et al., 'Long-Term Effect'; Royaux et al., 'Conservation of Plasticized PVC Artifacts'.

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Dr Petronella Nel is a Senior Lecturer at the Grimwade Centre for Cultural Materials Conservation at the University of Melbourne, Australia. She has a BSc (Hons) majoring in Chemistry, a PhD in Chemistry, and an MA in Cultural Materials Conservation (specialising in objects conservation) all obtained from the University of Melbourne. She is leading a collaborative Australian Research Council Linkage Project ‘A national framework for managing malignant plastics in Museum Collections’. She is interested in developing analytical techniques for characterising materials to inform their preservation.

Appendix

1 Py-GCMS protocol

Samples were placed in a quartz sample tube and transferred into the pyrolyser (Pyroprobe 6150, CDS Analytical). Samples were flash pyrolyzed (20°C/ms) at 600°C for 20s. Pyrolysates were transferred to the gas chromatography-mass spectrometer (GCMS) via a transfer line which was kept at 300°C. GCMS settings were as follows:

- Instrument: Agilent 6890 gas chromatograph coupled with Agilent 5973N mass selective detector
- Column: Zebron ZB-5ms (30m x 0.25mm, 0.25µm), Phenomenex
- Oven temperature:
    - Hold at 40°C for 2 min

  - 40–300°C at 10°C/min
  - Hold at 300°C for 15 min
- Carrier: He at 1.0 mL/min
- Inlet temperature: 300°C
- Split ratio: 50:1
- MS scan range: m/z 25–550

Materials and suppliers

Buffered tissue, Hollytex®, corrugated board: Archival Survival, PO Box 1139, Doncaster East VIC 3109, Australia. http://www.archivalsurvival.com.au/

PVC-P covers: The Book Cover Co., 6 Azalea St, Vermont VIC 3133, Australia. https://bookcoverco.com.au/

Ceramic tiles: Bunnings Warehouse, 179 - 201 Victoria Parade, Collingwood VIC 3066, Australia. https://www.bunnings.com.au/

Notebooks, ballpoint pen: Officeworks, QV Centre Russell Street, Melbourne, VIC 3000, Australia. https://www.officeworks.com.au/

Mylar®: Zetta Florence, 197B Brunswick St, Fitzroy VIC 3065, Australia. https://zettaflorence.com.au/