

Cross-infection effect of polymers of historic and heritage significance on the degradation of a cellulose reference test material



Katherine Curran^a, Alenka Možir^b, Mark Underhill^a, Lorraine T. Gibson^c, Tom Fearn^d, Matija Strlič^{a,*}

^a Centre for Sustainable Heritage, The Bartlett School of Graduate Studies, University College London, Central House, 14 Upper Woburn Place, London WC1H 0NN, United Kingdom

^b University of Ljubljana, Faculty of Chemistry and Chemical Technology, Aškerčeva 5, SI-1000 Ljubljana, Slovenia

^c Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, United Kingdom

^d Department of Statistical Science, University College London, Gower Street, London WC1E 6BT, United Kingdom

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ABSTRACT

The cross-infection effect of 105 polymer samples was studied, using cellulose as a reference test material. In total 14 polymer types were studied, comprising “modern materials” commonly found in historic and artistic collections including: cellulose acetate (CA), cellulose nitrate (CN), poly(vinyl chloride) (PVC), polyurethane (PUR) and a selection of specialised packaging materials used in art and heritage conservation. Polymer samples were placed in glass vials containing a piece of the cellulose reference and vials were sealed before being heated to 80 °C for 14 days. The cross-infection effect on the reference cellulose was measured using viscometry to calculate the degree of polymerisation relative to that of a control reference and a classification system of the cross-infection or preservation effect is proposed.

Solid phase micro-extraction (SPME)-GC/MS was used to detect and identify the emitted volatile organic compounds (VOCs) from a select number of polymer samples. CN was identified as the polymer with the most severe cross-infection effect while others e.g. polycarbonate (PC) had no effect or even a beneficial effect. Acetic acid was found to be the most characteristic emission detected from the most severely cross-infecting materials.

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1. Introduction

Polymer degradation can be both infectious and cross-infectious, resulting in the spread of degradation within a sample and/or between samples composed of the same or different materials. Infections are spread via reactive species, such as radicals or volatile organic compounds (VOCs). For example, a pro-degradant cross-infection effect of degrading polypropylene (PP) on the degradation of both polypropylene (PP) and polybutadiene samples has been observed, although the reactive species were not identified [1,2]. Recent work has modelled infectious polymer degradation using stochastic methods, similar to those used for studying the spread of infectious diseases in human populations [3,4].

The phenomenon of cross-infectious material degradation is well-known within the heritage sector, having been observed as early as the 1890s [5]. The effect on cultural heritage collections of

VOCs released during the degradation of materials used in display and storage is a particular area of concern and new materials are routinely tested to assess their potential hazards [6,7]. Historic objects themselves can display a cross-infection effect and it has recently been demonstrated that the degradation of historic paper can be accelerated by reactive species emitted from both iron gall inks and from the paper itself [8,9].

The cross-infection effect of “modern materials” has also been observed. Within a heritage context, “modern materials” refers to synthetic and semi-synthetic polymers produced from the mid-nineteenth century onwards, incorporating vulcanised rubber, Bakelite and cellulose derivatives in addition to more recent industrial materials such as poly(vinyl chloride) (PVC) or polyethylene (PE). A wide range of VOCs are known to be emitted from modern materials ([10,11], this issue) One well-documented cross-infection effect is “vinegar syndrome”, whereby the release of acetic acid vapour from degrading cellulose acetate (CA) objects, such as cinematic film, accelerates the degradation of other CA-based objects in the vicinity [12]. The emission of NO₂ from

* Corresponding author. Tel.: +44 (0) 20 3108 9036.

E-mail address: m.strlic@ucl.ac.uk (M. Strlič).

Table 1
Plastic objects used in degradation experiments.

Entry	Sample no.	Object	VOCs analysed by SPME-GC/MS	Notes
Cellulose acetate and derivatives				
1	HS34	Transparent ResinKit	Yes	Cellulose Acetate Propionate
2	HS35	Transparent ResinKit	Yes	Cellulose Acetate Propionate
3	HS45	Transparent ResinKit	Yes	Cellulose Acetate Propionate
4	HS91	Ladybrush doll	Yes	Cellulose Acetate
5	HS166	Black spectacles frame	Yes	Cellulose Acetate Propionate
6	HS250 ^a	Orange plastic sample	No	Cellulose Acetate Butyrate
7	HS251 ^a	Transparent plastic sample	Yes	Cellulose Acetate
8	HS331	Imitation tortoiseshell sample	Yes	Cellulose Acetate (Rhodoid)
Cellulose nitrate				
9	HS2	Cream-coloured jewellery box	Yes	
10	HS3	Imitation tortoiseshell jewellery box	No	
11	HS104	Vanity set	Yes	
12	HS232	Cream-coloured box	Yes	
13	HS248 ^a	Ruler	Yes	
14	HS249 ^a	Ruler – degraded	Yes	
15	HS266	Brown box	Yes	
16	HS270	Comb	Yes	
17	HS271	Cigarette case	Yes	
Poly(vinyl chloride)				
18	HS5	Doll	No	
19	HS61	Transparent ResinKit	No	
20	HS62	Transparent ResinKit	No	
21	HS153 ^a	White and grey tile	Yes	
22	HS157 ^a	Transparent film	Yes	
23	HS321	White plastic sample	No	
Poly(vinyl chloride)/Poly(vinyl acetate)				
24	HS132	Vinyl record	Yes	
25	HS136	Vinyl record	Yes	
26	HS137	Vinyl record	Yes	
27	HS138	Vinyl record	Yes	
28	HS149 ^a	Green plastic mould	Yes	
29	HS154 ^a	Vinyl record	Yes	
Polyurethane				
30	HS69	Elastomeric ResinKit	No	
31	HS201 ^a	Artificial leather	No	Thermoplastic Polyurethane (TPU) Elastomer
32	HS202 ^a	Artificial leather	No	Thermoplastic Polyurethane (TPU) Elastomer
33	HS206 ^a	Foam	No	Thermoplastic Polyurethane (TPU) Elastomer
34	HS244 ^a	Yellow foam	Yes	Polyurethane Ether
35	HS245 ^a	Black foam	Yes	Polyurethane Ester
36	HS316	White foam	No	Polyurethane Ether
37	HS317	Grey foam	No	Polyurethane Ester
38	HS328	Colourless transparent plastic sample	No	Thermoplastic Polyurethane Ester
39	HS329	Colourless transparent plastic sample	No	Thermoplastic Polyurethane Ether
Rubbers				
40	HS30	Red baking cup	Yes	Silicone Rubber
41	HS67	Elastomeric ResinKit	No	Acrylonitrile-Butadiene Styrene
42	HS92	White swimming cap	No	Polyisoprene Rubber
43	HS150 ^a	Rubber cookie	No	Styrene-butadiene Rubber
44	HS214 ^a	Degraded yellow rubber sample	No	Polyisoprene Rubber
45	HS216 ^a	Soft yellow object	Yes	Polyisoprene Rubber
46	HS268	Pipette bulb	Yes	Polyisoprene Rubber
47	HS269	Brown doll's head	No	Polyisoprene Rubber
Styrene-Butadiene Copolymers				
48	HS43	Transparent ResinKit	No	
49	HS144 ^a	White cup	No	
Polystyrene				
50	HS4	Pink box lid	No	
51	HS25	Transparent box	No	
52	HS32	White ball (foamed Polystyrene)	No	
53	HS36	Transparent ResinKit	No	
54	HS37	Transparent ResinKit	No	
55	HS38	White ResinKit	No	
56	HS145	Green plastic bowl	Yes	
57	HS168	Record duster	No	
58	HS300	Black plastic sample	Yes	High-impact Polystyrene
59	HS312	Extruded Foam	No	
60	HS322	Transparent, rigid plastic sample	No	
Polycarbonate				
61	HS12	Transparent sheet	No	
62	HS52	Transparent ResinKit	No	
63	HS143 ^a	Green bottle	Yes	
Polyesters				
64	HS50	Transparent ResinKit	Yes	Polyethylene terephthalate Glycol-modified

(continued on next page)

Table 1 (continued)

Entry	Sample no.	Object	VOCs analysed by SPME-GC/MS	Notes
65	HS207 ^a	Yellow bracelet	Yes	Unsaturated polyester
66	HS302	White, rigid plastic sample	Yes	Polybutylene terephthalate
67	HS324	Green board	Yes	Fiberglass
Polyethylene				
68	HS13	Doll	No	
69	HS15	Doll	No	
70	HS28	Black sheet	No	
71	HS56	White ResinKit	No	Low Density Polyethylene (LDPE)
72	HS57	White ResinKit	No	High Density Polyethylene (HDPE)
73	HS80	White ResinKit	No	Medium Density Polyethylene (MDPE)
74	HS147 ^a	Green bottle lid	Yes	
Polypropylene				
75	HS58	White ResinKit	No	Polypropylene copolymer
76	HS60	White ResinKit	Yes	Polypropylene with BaSO ₄
77	HS68	Grey ResinKit	No	Polypropylene – glass filled
78	HS70	White ResinKit	Yes	Polypropylene – flame retardant
Phenol formaldehyde				
79	HS22	Black box	No	
80	HS239 ^a	Black box	Yes	
81	HS320	Imitation wood – light brown	Yes	
Poly(methyl methacrylate)				
82	HS8	Hard, transparent sheet	No	
83	HS44	Transparent ResinKit	Yes	
84	HS187	Earrings	No	
85	HS210 ^a	Transparent purple object	Yes	

^a All samples in Table 1 are part of the Historic Plastic Reference Collection from the Centre for Sustainable Heritage (CSH) at UCL. However those marked^a were originally provided by the European Community's Seventh Framework Programme funded project POPART. The identification of these samples was performed as part of the POPART project. All other samples were identified at the CSH using ATR-FTIR spectroscopy (see Experimental section).

degrading cellulose nitrate (CN) objects can react with moisture in the air forming nitric acid which can corrode metals [13] and the release of hydrochloric acid from PVC objects can accelerate their degradation, resulting in discolouration [14]. However, a wide-ranging study of the cross-infection effect of different “modern” polymers relevant within heritage collections has not been performed to date.

In this paper, the cross-infection effect of 105 polymer samples was studied. This included 14 polymer types, chosen to reflect materials known to be both problematic and common in heritage collections, based on surveys from the recent EU FP7-funded project “Preservation of Plastic Artefacts in Museum Collections (POPART)” [15], other surveys from museums such as the Victoria and Albert (V&A) Museum, the British Museum and the Science Museum (London) and literature relating to unstable plastics in museum collections [16–20]. A selection of packaging materials used in the display or storage of heritage objects was also studied.

The test method used is based on one recently proposed for studying the cross-infection effect of VOC emissions from various materials on organic heritage material [21] and involved exposing a piece of reference paper made of pure cellulose to the test material in a sealed vessel for 5 days at 100 °C. For the current work, a lower temperature of 80 °C and a longer test period of 14 days was used. Assessment of the impact of VOC emissions from the tested material was measured using viscometric analysis to determine the degree of polymerisation (DP) of the exposed reference cellulose. This method is also similar to the Oddy test, which has been used extensively in heritage institutions since the 1970s to test the suitability of materials for use in storage and display [6,7,22–24]. The Oddy test involves exposing a piece of the test material to silver, lead and/or copper metal coupons at 60 °C for 28 days, followed by visual assessment of metal corrosion. It should be noted, however that although the setup of both tests is similar, the sensitivities of cellulose and metals to VOCs such as organic acids are quite different.

The test method used in this work has the advantage of a shorter test period than the standard Oddy test and the use of

viscometry provides a quantitative method of comparing the impact of VOC emissions on different organic materials. Cross-infection effect was defined here as the effect of emissions from a degrading polymer sample on the degradation of cellulose exposed to those emissions as measured by viscometry. As paper made of pure cellulose is susceptible to both oxidative and hydrolytic degradation, this test enables the potential for both kinds of degradation to be assessed, and for both negative as well as positive effects to be evaluated.

More fundamentally, the mechanistic processes which cause the cellulose to depolymerise were probed by assessment of the vapour phase environment using SPME-GC-MS analysis of the headspace above plastic samples both at room temperature, and following heating at 80 °C for 14 days. Polymer types shown to initiate and exacerbate degradation processes under the chosen test conditions are presented, highlighting potential hazards that need to be considered when storing or displaying susceptible objects close to the emitting material types. In addition, examination of VOCs emitted by specialised materials used in conservation for the storage and display of objects allowed their suitability for use in heritage institutions to be tested.

2. Materials and methods

2.1. Source, description and characterisation of polymer samples tested

Polymer samples tested were selected due to their ubiquity in museum environments and comprised 14 different polymer groups including 8 cellulose acetate (CA) and cellulose acetate derivative samples, 9 cellulose nitrates (CN), 6 poly(vinyl chloride)s (PVCs), 6 PVC/poly(vinyl acetate) (PVAc) samples, 10 polyurethanes (PURs), 8 rubbers: polyisoprene rubber (IR), silicone rubber (SR), acrylonitrile butadiene styrene (ABS) rubber and styrene-butadiene rubber (SBR), 2 styrene-butadiene copolymers, 11 polystyrenes (PS), 4 polycarbonates (PC), 3 polyesters, 7 polyethylenes (PE), 4 polypropylenes (PP), 3 phenol formaldehyde (PF) samples and 4

poly(methyl methacrylate)s (PMMA). Several different samples of the same polymer type were used in order to incorporate a range of material formulations, porosities and states of degradation. The samples were collected from 3 different sources: the Historic Plastic Reference Collection (HPRC) at the Centre for Sustainable Heritage, University College London, the SamCo collection from the European Community's Seventh Framework Programme funded POPART project [25], and the RESINKIT™ company, Woonsocket, RI, USA. These 85 objects are listed in Table 1. Packaging samples were provided by the British Museum (London), the Library of Congress (Washington), the UCL Petrie Museum (London) and from English Heritage (London) (Table 2). Standard construction materials such as medium density fibreboard (MDF), laminated wood and corrugated cardboard were also tested.

Prior to studying VOC emissions, most samples were analysed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) using a Bruker Alpha FTIR Spectrometer with an ATR Platinum Diamond single-reflection module #CFBFA32D. 24 scans were collected over the wavenumber range 4000 to 375 cm⁻¹ with a resolution of 4 cm⁻¹. The exception was the samples provided from the POPART SamCo reference collection as they had been previously characterised using FTIR, Raman spectroscopy and pyrolysis GC/MS giving an unambiguous identification of the samples' polymer type [25].

2.2. VOC emission set-up

To study the cross-infection effect of the polymer samples, a piece of the test material (500 ± 15 mg) and a piece of reference cellulose (250 ± 10 mg; Whatman filter cellulose No. 1, Maidstone) were placed inside Schott glass vials (nominal volume 100 cm³) (21 801 24 09, retrace code: 00797355). Two different sheets of cellulose were used and the starting degree of polymerisation (DP) of each sheet was measured using the method described below and found to be 2600 and 2700. Separate controls were run for each sheet of cellulose used, and the appropriate control matched to the reference cellulose in order to calculate DP/DP_{cont} values (see below). The pH of the cellulose was determined using a Mettler Toledo SevenGo pro™ pH/ORP/Ion meter SG8 with both a 51340288

InLab® 413 SG electrode and a 51343153 InLab® Solids electrode and was found to be 5.4 for both sheets. Polymer samples were cut from the objects and a single piece was used if possible.

The cellulose was pleated and allowed to stand vertically, without touching the plastic sample. The vial volume was measured to be 132 cm³, giving a material/volume ratio of approximately 5.7 mg cm⁻³ [21]. The glass vials were sealed and left for 14 days at 80 °C in a fan-assisted Carbolite oven. A control experiment was also set up which involved using a sealed vial with reference cellulose only, held at 80 °C for 14 days.

2.3. Analysis of reference cellulose by viscometry

At the end of the heating period, the DP of the cellulose was determined using the standard viscometric method (ISO 5351:2004) [26].

DP values were calculated from the intrinsic viscosity using the Mark-Houwink-Sakurada equation: [27]

$$DP^{0.85} = 1.1[\eta] \quad \text{where } [\eta] \text{ is the intrinsic viscosity of the cellulose sample.}$$

The final extent of cellulose degradation was described as a percentage value by comparing the DP of each reference cellulose with the DP of the control cellulose i.e. DP/DP_{cont} × 100%.

2.4. Analysis of VOC emissions in the headspace above selected plastic samples

To assess the VOC emission profile above selected polymer samples, 2 pieces from an object (100 ± 5 mg) were placed inside 2 sets of 20 cm³ Chromacol headspace vials (20-HSV T229) before being sealed with a Chromacol 18-mm magnetic screw cap with 1-mm silicone/PTFE liner – not prefitted (18-MSC-ST101). Note that for one sample (HS207) a sample mass of 120 ± 5 mg was used on account of that object's rigidity and small size. The vials were either stored for 14 days at 80 °C (Set 1) or for 7 days at room temperature (Set 2) to mimic degraded sample VOC emissions and sample emissions under ambient conditions respectively. Whether or not a

Table 2

Materials from heritage institutions and additional non-plastic materials used in degradation experiments.

Entry	Sample name	VOC profile analysed by SPME-GC-MS	Manufacturer/Distributor	Notes
1	Tyvek®	Yes	Purchased from Preservation Equipment Ltd.; Produced by DuPont®	White polyethylene sheet
2	Polyester film	No	Purchased from Preservation Equipment Ltd.	Similar to Melinex®
3	Plastazote®	No	Produced by Zotefoams PLC	White polyethylene foam
4	Plastazote®	No	Produced by Zotefoams PLC	Grey polyethylene foam
5	Plastazote®	No	Produced by Zotefoams PLC	Black polyethylene foam
6	Ethafoam™	No	Produced by Dow®	White polyethylene foam
7	Polyweld®	No	Purchased from Conservation by Design Ltd.	Inert polyester pocket
8	Correx®	No		Polypropylene
9	Coin Holder	No	Purchased from Prinz Publications (UK) Ltd.	Lindner LR Coin Capsule; Product code 2251017. Polystyrene
10	Storage box	No	Unknown	Polystyrene
11	Stewart box lid	Yes	Unknown	Polyethylene box lid
12	Corrugated foam	Yes	Unknown	White polyethylene foam
13	Sample bag	No	MacFarlane Group Self-seal bags, product code 001170	Polyethylene bag
14	Ragboard unbuffered	No	From Alphasag™ Artcare™	White ragboard
15	Ragboard buffered with Zeolite CR-SPZ	No	From Alphasag™ Artcare™	White ragboard
16	Acid-free Cardboard	No	Purchased from Preservation Equipment Ltd.	Code: 613-4001
17	Acid-free tissue	No	Purchased from Conservation by Design Ltd.	Item no. PAAFTP1000
18	Corrugated cardboard	No	Unknown	
19	MDF	Yes	Unknown	
20	Laminated wood	Yes	Unknown	

Table 3
Results of triplicate experiments using five polymer samples.

Polymer type	Sample no.	Mean DP/DP _{cont} (±Std Dev)
Cellulose acetate	HS331	91.1 ± 1.3%
Cellulose nitrate	HS270	41.6 ± 1.6%
Poly(vinyl chloride)	HS321	100.5 ± 1.9%
Polyurethane	HS69	97.4 ± 0.4%
Polystyrene	HS38	98.9 ± 0.4%

sample was analysed using SPME-GC/MS is indicated in Tables 1 and 2

VOC extraction was performed at room temperature using a DVB/CAR/PDMS SPME fibre (50/30 µm) (Supelco, 57298-U) with adsorption times of 1 min for Set 1 (held at 80 °C for 14 days) or 60 min for Set 2 (held at room temperature for 7 days). One exception was the CN samples which were analysed for 10 s and 1 min respectively on account of their very intensive emissions.

Additional analysis was performed on several PVC/PVAc and CN samples using 50 ± 5 mg of material that had been ground using an

Everise Rotary Tool (Code: N60GR) and then held in a headspace vial at room temperature for 7 days. Extractions were performed at room temperature using a DVB/CAR/PDMS SPME fibre (50/30 µm) and an adsorption time of 60 min. The results were weighted using an external standard (MISA Group 17 Non-Halogenated Organic Mix 2000 µg/cm³ in methanol; 48133 Supelco, diluted 1/50 in methanol). 1 cm³ aliquots of the diluted standard were analysed at room temperature using the DVB/CAR/PDMS SPME fibre (50/30 µm) with an adsorption time of 20 s.

The analytes were recovered from the fibre using a Perkin Elmer Clarus 500 gas chromatograph equipped with a Combipal PAL System (CTC Analytics) autosampler coupled to a Perkin Elmer Clarus 560D mass spectrometer. A VOCOL column (Supelco, 20% phenyl-80% methyl-polysiloxane) was used (60 m in length and 0.25 mm diameter) to separate the VOCs using an oven programme as follows: initial temperature of 50 °C (hold for 5 min), ramp rate of 10 °C/min to 100 °C, then 5 °C/min to 200 °C, then 2 °C to 220 °C, which was held for 20 min. The carrier gas was helium with a constant flow of 1 cm³ min⁻¹. The injector temperature was 250 °C and the injector

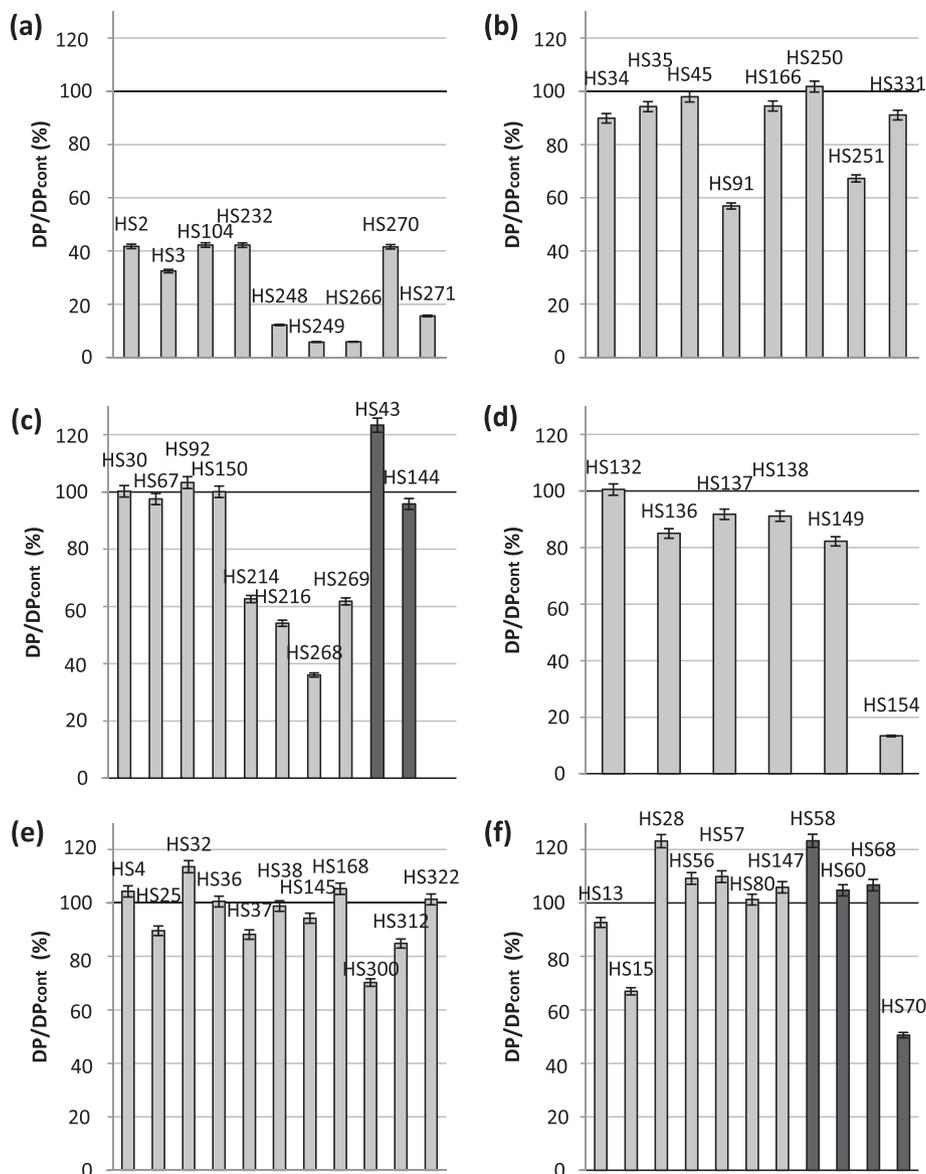


Fig. 1. DP/DP_{cont} of reference cellulose exposed to: (a) Cellulose nitrate, (b) Cellulose acetate and derivatives, (c) Rubbers (light grey bars) and hard plastic Styrene–butadiene copolymers (dark grey bars), (d) Poly(vinyl chloride)/poly(vinyl acetate) copolymers or blends, (e) Polystyrene, (f) Polyethylene (light grey bars) and Polypropylene (dark grey bars).

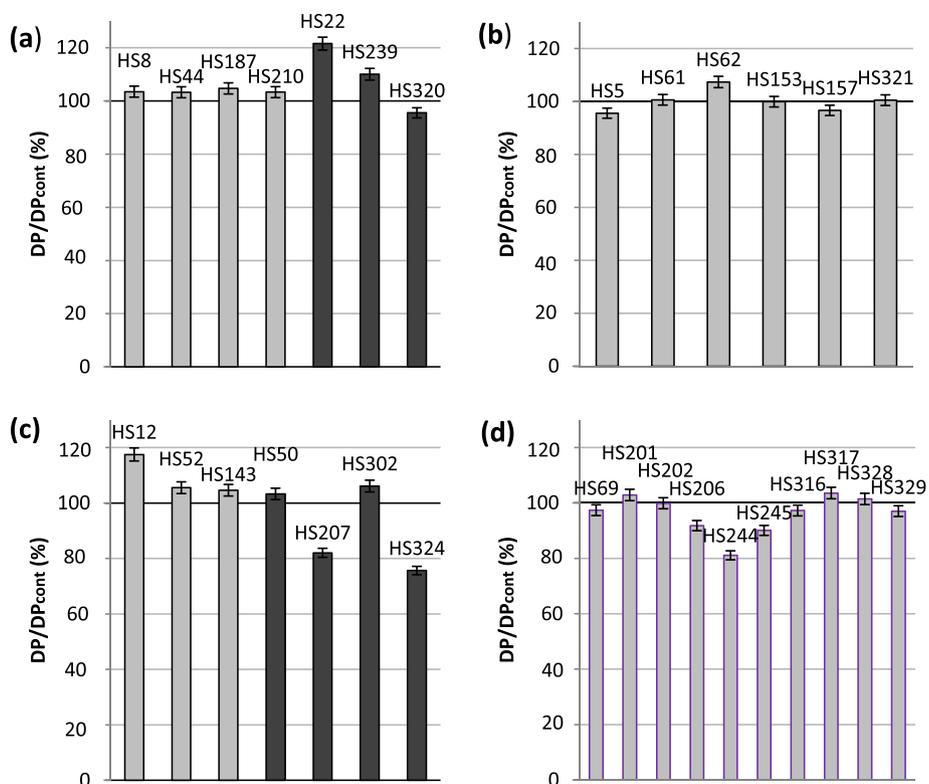


Fig. 2. DP/DP_{cont} of reference cellulose exposed to: (a) Poly(methyl methacrylate) (light grey bars) and Phenol formaldehyde (dark grey bars), (b) Poly(vinyl chloride), (c) Polycarbonate (light grey bars) and Polyester (dark grey bars), (d) Polyurethanes.

was used in splitless mode with a 1 min injection. A split flow of 20 cm³ min⁻¹ was applied for 4 min to flush out the injector and splitless mode was then used for the rest of the programme.

For analysis of the external standard the following programme was used: Initial temperature of 50 °C (hold for 5 min), ramp rate of 10 °C/min to 100 °C, then 5 °C/min to 150 °C, hold for 5 min. The carrier gas was helium with a constant flow of 1 cm³ min⁻¹. The injector temperature was 250 °C and the injector was used in splitless mode with a 1 min injection. A split flow of 20 cm³ min⁻¹

was applied for 4 min to flush out the injector and splitless mode was then used for the rest of the programme.

The interface and source temperatures were 200 °C and 180 °C. Mass spectra were collected in the electron ionisation (EI) mode at 70 eV and recorded from m/z 45–300 with a scan time of 0.4 s and an interscan delay of 0.05 s. VOC peak identification was performed using the NIST 2005 Mass Spectra Library V2.1.

It should be noted that all comparisons of chromatograms are semi-quantitative and no calibration was attempted. Therefore,

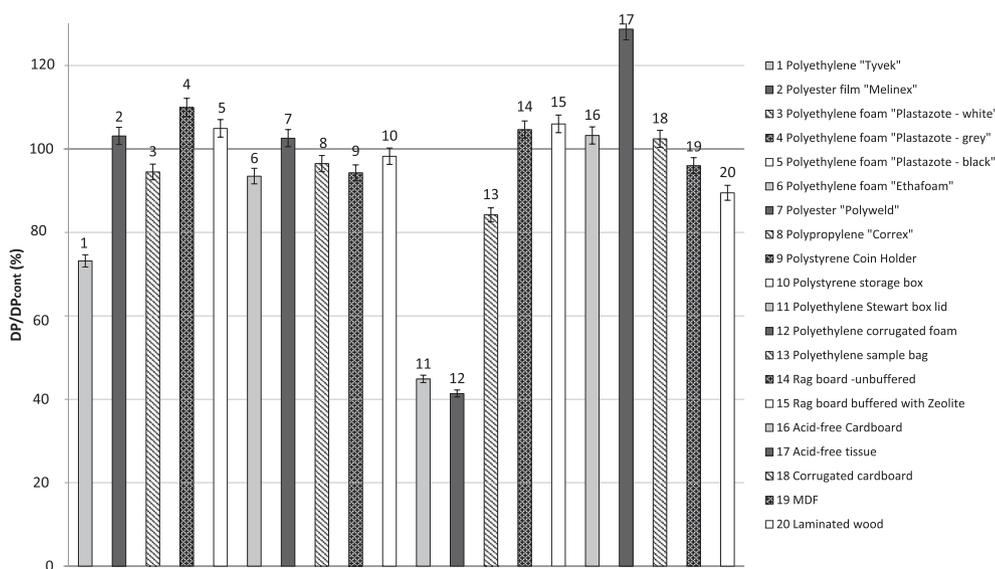


Fig. 3. DP/DP_{cont} of reference cellulose exposed to plastic and other materials collected from museums and heritage institutions and additional non-plastic materials.

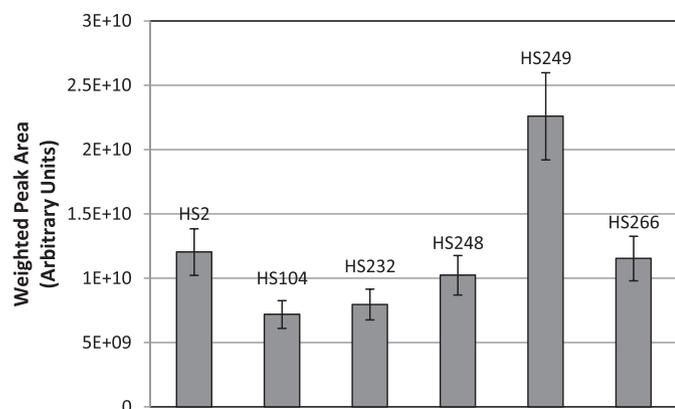


Fig. 4. Detected camphor emissions from 6 of the CN samples studied.

while the peak areas of specific analytes may be compared between chromatograms, quantitative comparison between dissimilar compounds cannot be made.

XCMS Online version 1.0.32 (XCMS version 1.30.7 and CAMERA version 1.15.5) from the Scripps Center for Metabolomics and Mass Spectrometry was used for retention time alignment, peak detection and peak integration and to construct a data table containing peak areas, retention times and m/z values which was imported into Minitab 16 (State College, PA) for further analysis [28].

3. Results

3.1. Viscometric analyses of reference cellulose exposed to polymer samples

To test the precision of the degradation experiments, triplicate experiments were run for one sample from each of 5 of the 14 polymer types studied in this work at 80 °C for 14 days. The mean and standard deviation values of the DP/DP_{cont} of the reference cellulose were calculated and are given in Table 3. The precision

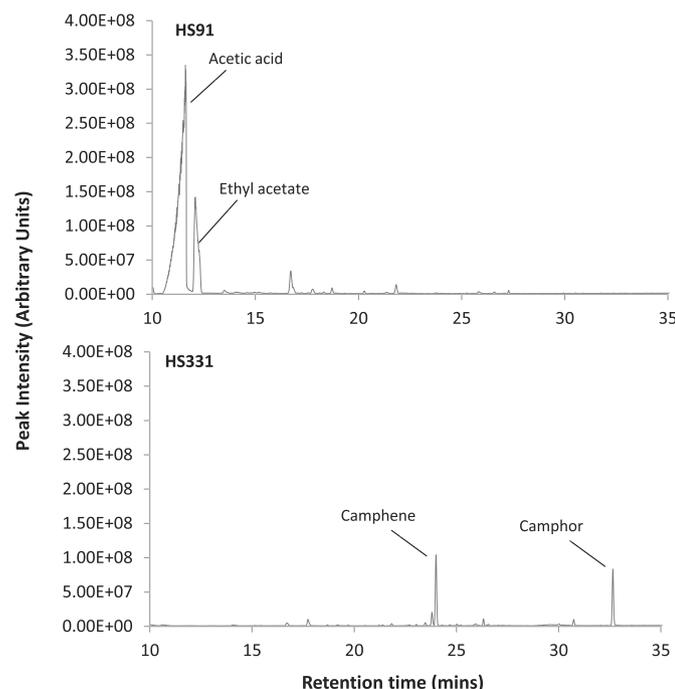


Fig. 5. SPME-GC/MS chromatograms of CA samples labelled HS91 (top) and HS331 (bottom).

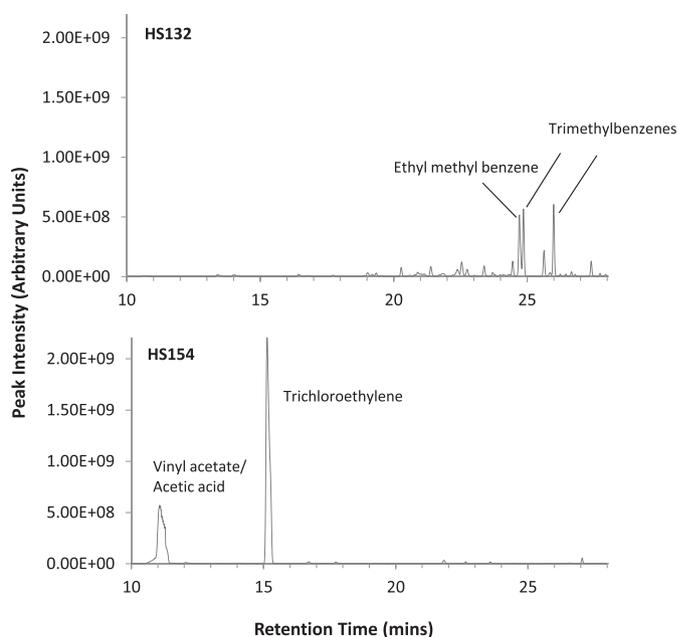


Fig. 6. Chromatograms showing results of SPME-GC/MS analysis of two PVC/PVAc samples: HS132 (top) and HS154 (bottom) heated to 80 °C for 14 days.

(Std Dev <2%) allowed for statistically significant comparisons to be made between DP/DP_{cont} values for reference celluloses exposed to different plastics.

The results of the viscometric analyses of reference celluloses exposed to plastic samples at 80 °C for 14 days are summarised below and grouped to illustrate where at least one sample had a significant or severe cross-infection effect ($DP/DP_{cont} = 55\text{--}75\%$ or $DP/DP_{cont} < 55\%$, see Section 4 below), (Fig. 1) or where no samples had a severe cross-infection effect (Fig. 2). Fig. 3 summarises the results of the plastic and other packaging materials collected from museums and heritage institutions and additional non-plastic materials. In all figures, the error bars show $\pm 2\%$, the maximum standard deviation value calculated from triplicate experiments (see Table 3).

3.2. SPME-GC/MS analysis of the headspace above plastic samples

In order to investigate the reasons for the observed effects, the headspace above certain plastic samples (see Tables 1 and 2) was analysed using SPME-GC/MS. This was performed after heating the samples to 80 °C for 14 days, in order to mimic the conditions used for the degradation experiments and identify VOCs responsible for

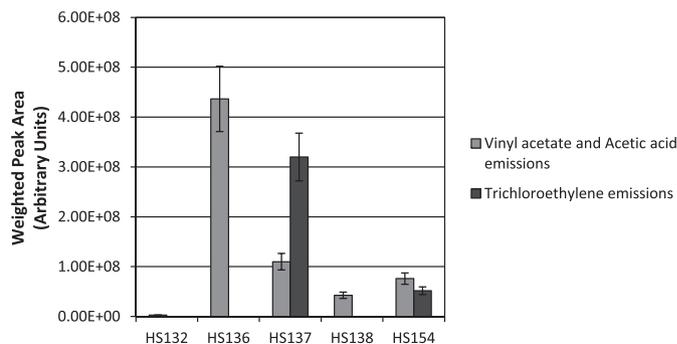


Fig. 7. Emissions of vinyl acetate, acetic acid and trichloroethylene from PVC/PVAc objects studied as part of these experiments.

the observed degradation of cellulose. Analysis was also performed after enclosing the samples in vessels at room temperature for 7 days, to ascertain whether the same VOCs are emitted under ambient conditions. Degradation of polymer samples for SPME-GC/MS analysis was run as a separate series of experiments in Chromacol headspace vials rather than Schott vials, to enable rapid analysis of VOC emissions.

In the case of some PVC/PVAc and CN objects, SPME-GC/MS analysis was also performed on samples that had been homogenised by grinding. Grinding the material was found to provide more reproducible results, enabling more accurate comparison between samples. The results of this analysis are shown in Figs. 4 and 7.

It should be noted that not all VOCs are detectable using this method and that some VOCs which are likely to have played a role in cellulose degradation (e.g. NO₂ emissions from CN, HCl emissions from PVC or formic acid emissions which could come from several of the materials) will not have been observed.

4. Discussion

For the purposes of this discussion, the following classification is proposed. Taking into account the general uncertainty of the method, any observed effect in the interval of DP/DP_{cont} = 95–105% could be classified as ‘no effect’. With reference to previous work on the subject [8,21], materials could be classified with respect to their cross-infection or preservation effect in the following way:

1. Preservation effect: DP/DP_{cont} > 105%
2. Neutral: DP/DP_{cont} = 95 – 105%
3. Moderate cross-infection: DP/DP_{cont} = 75 – 95%
4. Significant cross-infection: DP/DP_{cont} = 55 – 75%
5. Severe cross-infection: DP/DP_{cont} < 55%

It should be noted that until this research, no materials have been observed to have as large a cross-infection effect as DP/DP_{cont} < 55%, so it seems useful to establish this category of materials that are best avoided as storage materials or else (if representing heritage or artwork objects) stored individually in order not to affect other objects in their vicinity.

Materials with a known preservation effect are either those that sustain hypoxic conditions or that remove volatile degradation products [8]. Other such materials may have antioxidative or acid-neutralising properties. Identification and quantification of this beneficial category is enabled by the test method used here. Such effects have also been observed with the more widely used Oddy test referred to in the introduction, although these are not quantified. For example, it was shown that sample HS43 which contains the antioxidant butylated hydroxytoluene (BHT) had a preservation effect (see later section).

It is interesting to note that the categories defined here do not correspond strictly to observed degradation effects on the reference cellulose such as brittleness or discolouration. For example, while the most brittle and discoloured reference celluloses are those exposed to polymers with DP/DP_{cont} < 55%, some of the reference celluloses exposed to polymers in this category display no visible discolouration or detectable change in brittleness. None of the reference celluloses exposed to polymers from the other categories were found to be brittle and most show no discolouration. However, 2 of the reference celluloses exposed to samples in the “neutral” category (DP/DP_{cont} = 95 – 105%, HS92 and MDF) show slight discolouration. There is a clear distinction between the degradation measured in this work, and “damage” detectable by visual observation. The advantage of using DP measurements is that degradation can be detected before it is so advanced as to prevent a material being touched or read. It is also worth noting

that the mechanisms of depolymerisation and discolouration are not the same.

It is very important to clarify that effects observed at 80 °C cannot be easily extrapolated to behaviour at room temperature. Degradation reactions which occur under the test conditions may not be significant at room temperature. In some cases, polymer samples may also have been heated above their glass transition temperatures (*T_g*), which will change the way in which VOC emissions will diffuse through and be emitted from the material. The test used in this work provides a rapid means of identifying materials which may have a cross-infection effect within heritage collections. It may produce false positive results, although this is a better outcome than the retention of infectious materials in a collection. In this way it is similar to the traditional Oddy test.

4.1. Polymers with a severe or significant cross-infection impact

4.1.1. Cellulose nitrate (CN)

All 9 CN samples showed a severe cross-infection effect on the reference cellulose, see Fig. 1(a), with DP/DP_{cont} values ranging between 6 and 42%. It is known that NO₂ is emitted from CN samples during degradation [13] and converted to nitrous and nitric acids which may catalyse glycosidic bond hydrolysis in the cellulose [29]. SPME-GC/MS analyses of the headspace above 2 CN samples (HS270 and HS271) held at room temperature or at 80 °C for 14 days detected high amounts of camphor and smaller amounts of camphene, eucalyptol and nitromethane. Camphor was not thought to contribute significantly to the cross-infection effect. No correlation was found between the levels of camphor emitted and the impact on cellulose. The detected levels of camphor from ground samples of 6 of the CN objects studied are shown in Fig. 4. It can be seen that, although objects HS249 and HS266 exhibit similar cross-infection effects (DP/DP_{cont} = 5.8% and 5.9% respectively), they emit significantly different levels of camphor. In addition, objects HS2 and HS266 exhibit different cross-infection effects (DP/DP_{cont} = 41.7% and 5.9% respectively), however the detected levels of camphor are very similar. In addition, samples with a neutral cross-infection effect such as HS331 (CA) and HS44 (PMMA) were also found to emit camphor.

It is therefore proposed that the presence of nitrous and nitric acids were the main initiators of cellulose degradation. The reference celluloses in several of the CN environments suffered significant physical changes, becoming yellow/brown in colour and very fragile to the touch.

4.1.2. Cellulose acetate (CA) and CA derivatives

Two CA objects (HS91 and HS251 – see Fig. 1(b)) had a significant cross-infection effect, likely due to the emission of acetic acid vapour [12,30–32]. Acetic acid is known to catalyse the hydrolysis of cellulose glycosidic bonds, and has been shown to accelerate cellulose degradation [29]. Other plastics composed of CA or its derivatives, such as cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB), had a very small impact on the DP of the exposed cellulose, potentially due to lower organic acid emissions. To test this hypothesis, SPME-GC/MS analyses of the headspace above 2 objects, HS91 (DP/DP_{cont} = 56.9%) and HS331 (DP/DP_{cont} = 91.1%) held at 80 °C for 14 days, confirmed that under these conditions HS91 emitted a relatively high concentration of acetic acid vapour whilst HS331 emitted almost no acetic acid vapour (Fig. 5).

Object HS91 was also shown to emit acetic acid vapour at room temperature and emissions of acetic acid or propionic acid vapours have been detected at room temperature from objects composed of CA or CAP respectively (objects HS34, HS35, HS45, HS166, HS251, HS331) using SPME-GC/MS analysis. These results demonstrate that at room temperature, emissions of organic acid vapours from

such objects would present a potential hazard to heritage material stored or displayed alongside them. This supports previous observations of deteriorating organic materials, metals and plastic objects stored in the vicinity of degrading CA objects. Previous studies have also highlighted the contribution of acetic acid vapour emissions to observed degradation [12,29].

4.1.3. Rubber

Several rubber (i.e. elastomers based on IR, SR, ABS rubber and SBR) and two hard styrene-butadiene copolymer samples (HS43 and HS144) were studied.

The cross-infection effect of rubber samples varied considerably, with noticeable differences observed between different types of rubber (Fig. 1 (c)). Samples of SR (HS30) and SBR (HS150) had little to no influence on the reference cellulose, however samples of IR (HS92, HS214, HS216, HS268, HS269) displayed varying effects; with some samples accelerating the degradation of cellulose quite considerably. Related materials such as samples HS144 and HS43, hard styrene-butadiene copolymers, displayed little impact and arguably HS43 had a preservation effect on the reference cellulose ($DP/DP_{\text{cont}} = 123.4\%$). The reason for this may be the migration of the antioxidant butylated hydroxytoluene (BHT), which was detected from HS43 using SPME-GC/MS analysis to the cellulose sample, inhibiting oxidation of the cellulose. In general, the cross-infection effect of a commodity material is likely to be influenced by the presence or absence of antioxidants and other additives which can either accelerate or retard VOC emissions from the polymer and also migrate to the reference material, inhibiting or promoting its degradation. From a conservation perspective, this raises an ethical question as to whether such migration is a beneficial process which will inhibit degradation, or a source of contamination which may confuse future analysis.

The most severe cross-infection effect was observed with sample HS268, a IR object with a DP/DP_{cont} value of 36.1%. SPME-GC/MS analysis detected a wide range of VOCs in the headspace above HS268, when heated to 80 °C for 14 days. Of particular interest was the presence of acetic acid, methyl- and dimethyl-furan vapours. As previously discussed, acetic acid is known to catalyse the degradation of cellulose and recent work has shown that exposure to an alkyl-substituted furan can also accelerate the degradation of cellulose [8]. It is therefore suggested that of the analytes detected, these 3 are most likely to have contributed to the cross-infection effect of HS268. There may also be an effect from other compounds which were not detectable using SPME-GC/MS. Acetic acid, methyl- and dimethyl-furan vapours were also observed in the headspace above HS216, the second most deleterious rubber sample ($DP/DP_{\text{cont}} = 54.2\%$). Acetic acid and methyl-furan vapours were also detected from these samples at room temperature, indicating that under ambient conditions, exposure to VOC emissions from these or similar IR samples may affect the rate of degradation of cellulose, although at a slower rate than under the conditions used here.

The variation in results observed from IR samples may be a consequence of the age and overall condition of the object. The 3 objects which had the most significant impact on cellulose (HS268, HS216 and HS214) were displaying visible signs of degradation such as cracking and brittleness, while object HS92, which did not have a significant impact on the degradation of cellulose, was in good condition and likely to be a newer object.

4.1.4. PVC/PVAc samples

While the majority of samples made of PVC/PVAc did not demonstrate a significant cross-infection effect (Fig. 1 (d)) with DP/DP_{cont} values above 86%, one PVC/PVAc sample (HS154) severely damaged the reference cellulose, with a DP/DP_{cont} value of 13.4%

(Fig. 1(d)). This sample was taken from a vinyl record and the observed impact was in marked contrast to that displayed by other samples of vinyl records i.e. HS132, HS136, HS137 and HS138. SPME-GC/MS analysis of the headspace above sample HS154, heated to 80 °C for 14 days, detected two major VOCs: vinyl acetate (VA) and trichloroethylene (TCE) (Fig. 6) and lower amounts of acetic acid vapour, which co-eluted with VA. Both VA and TCE are likely to be residual reagents used in the manufacture of the record, as VA is the monomeric unit used to produce PVAc and TCE a commonly used solvent and chain-transfer agent in PVC manufacture. The 2 major VOCs detected are not thought to influence the deterioration of cellulose and to support this theory, the headspace above all PVC/PVAc samples were sampled by SPME-GC-MS at room temperature, with the results given in Fig. 7. No correlation was observed between the amount of TCE or VA with cellulose degradation, indeed the polymer sample that had the most significant cross-infection effect (HS154) emitted much lower measured amounts of TCE or VA than samples with lower effects (HS136, HS137). Separating the impact of VA from acetic acid vapour was more difficult as these analytes co-eluted, however the peak shapes of the co-eluting peak in the chromatograms of HS136 ($DP/DP_{\text{cont}} = 85.0\%$) and HS154 show clearly that the amount of VA above object HS136 was much larger than that found in the headspace above HS154, suggesting that VA also does not have a significant cross-infection effect. No emissions of TCE, VA or acetic acid were detected from object HS149 (not shown in Fig. 7).

It is instead suggested that the reference cellulose exposed to HS154 was degraded by both HCl (not detectable by SPME-GC/MS) and acetic acid vapours, known degradation products of PVC and PVAc respectively [33,34]. The reason for the unusual impact of HS154 on cellulose is not known, and highlights the fact the effect of VOC emissions from real polymeric artefacts can vary significantly between similar objects.

The most significant emissions from HS132 were substituted aromatic compounds such as xylene, ethyl-methylbenzene and trimethylbenzenes (Fig. 6), which have previously been detected from other PVC objects at room temperature e.g. samples of PVC flooring [35]. The fact that this object displayed no impact on the degradation of cellulose ($DP/DP_{\text{cont}} = 100.6\%$), suggested that these aromatic species had no cross-infection effect.

4.1.5. Polystyrene

Eleven polystyrene (PS) samples used in the study showed a varied impact on the reference cellulose with DP/DP_{cont} values between 70.3 and 113.6% (Fig. 1(e)). In general, PS had a low effect on the depolymerisation of cellulose with measured DP/DP_{cont} values in most cases greater than 85%. However, HS300 (a piece of black, high-impact PS) reduced the cellulose's DP/DP_{cont} value to 70.3%. The authors were informed by the supplier that HS300 is a recycled plastic sample which may explain this result, as previous work has shown that the reprocessing of HIPS that occurs during recycling leads to progressively higher emissions of oxidative degradation products [36].

The headspace above HS300 was measured by SPME-GC/MS after heating at 80 °C for 14 days and compared to that above HS145 ($DP/DP_{\text{cont}} = 94.3\%$). The key difference in VOC emissions was the presence of acetic acid vapour in the headspace of HS300, which is likely to have contributed to the degradation of cellulose and was absent from that of HS145. It was also noted that acetic acid was detected in the headspace of HS300 at room temperature, although the measured amount was lower. Acetic acid was also not detected from HS145 at room temperature. Aromatic compounds such as styrene, ethylbenzene and 1-methylethyl-benzene were emitted from both samples, which would suggest that they do not have a negative effect on the stability of cellulose. Aromatics such as

vanillin and toluene have previously been shown to have a marginal effect on cellulose [8]. Interestingly, the total VOC emissions from HS145 appear to be much higher than those from HS300, indicating that it is the presence of specific degradative compounds such as acetic acid, rather than overall VOC emissions that results in the observed cross-infection effect (Fig. 8). The ethylbenzene and 1-methylethylbenzene peaks in the chromatogram of HS300 are too small to be visible at the chosen magnification.

4.1.6. Polyethylene (PE)

Of the 6 PE samples studied, only one (HS15, a doll) was shown to have a significant cross-infection effect on the reference cellulose, giving a DP/DP_{cont} value of 67.0% (Fig. 1(f)). All other PE samples had DP/DP_{cont} values greater than 93%, including sample HS13, which also came from a doll. Both dolls were made of flexible, pink material, although the origins and ages of the dolls are not known.

4.1.7. Polypropylene

Of the 4 polypropylene (PP) samples tested, only sample HS70 displayed a significant impact on the degradation of cellulose ($DP/DP_{\text{cont}} = 50.6\%$), Fig. 1(f). This sample contained a flame retardant. The identity of the flame retardant is not known, however “reactive” flame retardants which are incorporated into the polymer chain can affect the chemical stability of the polymer [37]. It is possible therefore that the presence of the flame retardant accelerated the degradation of HS70, resulting in a greater effect on the reference cellulose relative to the other polypropylene samples studied. These results highlight the fact that while certain polymers may in most cases not cause problems in the heritage environment, differences in formulation such as the presence of particular additives may cause particular objects to emit potentially damaging VOCs.

The contents of the headspaces above HS70 and HS60 ($DP/DP_{\text{cont}} = 104.8\%$) were measured for comparison using SPME-GC/MS analysis after heating at 80 °C for 14 days. The most significant differences between the chromatograms relate to 2 VOCs, cyclohexane and 4-methyloctane, which were both detected from HS70, however cyclohexane is absent from the headspace of sample HS60 and the amount of emitted 4-methyloctane is much lower. Other hydrocarbons such as 2,4-dimethylheptene were emitted by both samples, although higher emissions were measured from HS70.

4.2. Polymers with a preservation, neutral or moderate cross-infection effect

4.2.1. Poly(methyl methacrylate) (PMMA)

PMMA had a consistently neutral cross-infection effect ($DP/DP_{\text{cont}} = 103\text{--}105\%$, Fig. 2(a)). VOC emissions such as methyl methacrylate (MMA), 2-propenoic acid ethyl ester and camphor were detected from sample HS44, and MMA was detected from HS210 after heating at 80 °C for 14 days. Given the high DP/DP_{cont} values however, the detected volatiles were assumed not to have a cross-infection effect in this study.

4.2.2. Phenol formaldehyde

Three phenol formaldehyde samples were tested and in all cases the exposed cellulose was not significantly damaged; the lowest measured DP/DP_{cont} value was 95.5% (Fig. 2(a)). SPME-GC/MS analysis indicated that VOC emissions from HS239 were low in general, while styrene, phenol, hydroxybenzaldehyde and acetophenone were emitted from HS320 after heating at 80 °C for 14 days and measurable amounts of phenol were still detected from HS320 held at room temperature. The viscometric results suggest

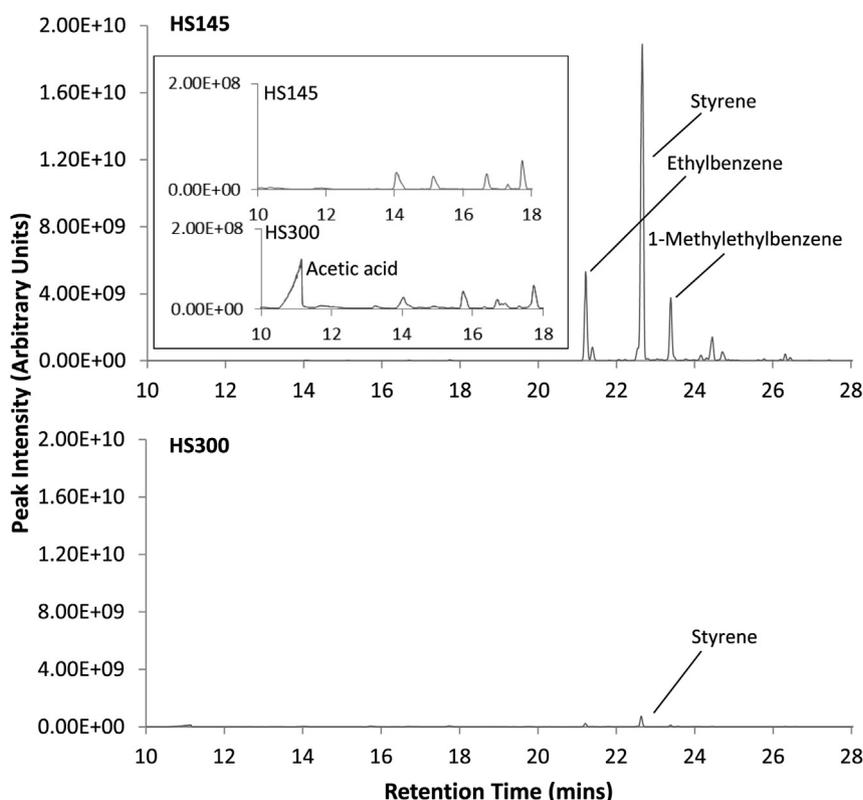


Fig. 8. Chromatograms showing overall VOC emissions detected in the headspace of HS300 (bottom) and HS145 (top) after heating at 80 °C for 14 days. Inset shows close-up of region with retention time 10–18 min.

that the emitted volatiles are not significant with respect to cellulose degradation under the test conditions. As was discussed in relation to PS, aromatics such as vanillin and toluene were previously shown to have a marginal effect on the degradation of cellulose [8].

4.2.3. PVC

Although PVC is often highlighted as a problematic material in heritage collections [14], on account of its rapid degradation, none of the 7 PVC samples studied as part of this work displayed a cross-infection effect on the degradation of cellulose ($DP/DP_{\text{cont}} = 96\text{--}107\%$, Fig. 2(b)). The VOCs emitted from 2 samples, HS153 (a grey/white tile with a $DP/DP_{\text{cont}} = 99.9\%$) and HS157 (a transparent film with $DP/DP_{\text{cont}} = 96.6\%$) were analysed using SPME-GC/MS after heating at $80\text{ }^{\circ}\text{C}$ for 14 days. Significant emissions of 2-ethylhexanol, a known degradation product of the plasticiser diethyl-hexylphthalate (DEHP) [14], were detected from sample HS153, however its presence appears to have had no impact on the reference cellulose exposed to that sample. Other compounds such as 2-ethylhexyl acetate, 2-ethylhexanal, methyl methacrylate and 2-methyl-2-propenoic acid butyl ester were also detected. No significant emissions were detected in the headspace of sample HS157.

While the PVC polymer readily degrades thermally to yield HCl [33] (which would not be detected using the SPME-GC/MS method applied here), the presence of stabilisers in modern PVC-based objects slows their degradation significantly. The minimal impact observed on the cellulose exposed to PVC samples in this work suggests that perhaps very little or no HCl was emitted from any of them. As cellulose is susceptible to acid-catalysed degradation, a greater cross-infection effect would be expected if significant amounts of HCl were emitted from these samples.

4.2.4. Polycarbonate (PC)

The impact of VOC emissions from PC on the reference cellulose was also consistently low ($DP/DP_{\text{cont}} = 105\text{--}118\%$ for PC), Fig. 2(c). HS12, a transparent PC sheet was shown to have a preservative effect, although the reason for this is not known. PC degradation is known to result in bisphenol-A (BPA) formation, which has been shown to have radical scavenging properties [38]. BPA formed from the degradation of HS12 may therefore have inhibited the degradation of cellulose exposed to it. However, at present there is no evidence to support this suggestion. The PC sample HS302 was shown to emit tetrahydrofuran after heating at $80\text{ }^{\circ}\text{C}$ for 14 days, while emissions of heptane, dichloromethane, and small quantities of styrene, xylene and ethylbenzene were detected from PC sample HS143. SPME-GC/MS analysis of HS12 at room temperature detected only the solvent chlorobenzene.

4.2.5. Polyester

Two out of the 3 polyester samples studied were found to have a moderate cross-infection effect: samples HS207 (an unsaturated polyester; $DP/DP_{\text{cont}} = 82.0\%$) and HS324 (a fiberglass sample; $DP/DP_{\text{cont}} = 75.7\%$), Fig. 2 (c). SPME-GC/MS analyses again confirmed the presence of acetic acid after both samples were heated to $80\text{ }^{\circ}\text{C}$ for 14 days. Other VOCs emitted by both samples included aromatic compounds such as ethylbenzene, xylene and propylbenzene, which are unlikely to have contributed to the degradation of cellulose [8]. Chlorobenzene and xylene were detected from sample HS50 (PETG; $DP/DP_{\text{cont}} = 103.3\%$) after heating, however as the reference cellulose exposed to HS50 was not noticeably degraded (note that acetic acid was not detected in this environment) these compounds were not thought to influence the chemical breakdown of cellulose in the cellulose.

4.2.6. Polyurethane (PUR)

VOC emissions from some PUR samples were found to have an impact on exposed reference cellulose e.g. HS244 (a PUR ether foam, $DP/DP_{\text{cont}} = 81.1\%$) or HS245 (a PUR ester foam, $DP/DP_{\text{cont}} = 90.1\%$), Fig. 2(d). SPME-GC/MS analysis detected no significant emissions from either sample, making it likely that the reactive species responsible for the observed effect on cellulose are not detectable using this method.

4.3. Packaging materials

Of the different packaging materials used in heritage institutions, most had a low impact on the reference cellulose degradation (Fig. 3). However, two samples had a severe cross-infection effect with DP/DP_{cont} values that were comparable to those measured for some CN samples (see Fig. 1 (a)). The 2 samples were both PE-based, a foam ($DP/DP_{\text{cont}} = 41.4\%$) and a Stewart box lid ($DP/DP_{\text{cont}} = 44.9\%$). To determine why these 2 materials had such a significant impact on cellulose, the headspace was sampled after heating the plastics to $80\text{ }^{\circ}\text{C}$ for 14 days. SPME-GC/MS analysis confirmed the presence of organic acids (acetic acid, propanoic acid and butanoic acid vapours) and ketones such as 2-butanone and 2-pentanone. The organic acids were not emitted from the foam at room temperature while low amounts of acetic acid, propanoic acid and butanoic acid were detected from the Stewart box lid at room temperature.

Tyvek[®], a PE-based material used in conservation for a range of applications such as interleaving and labelling was also found to have an impact on the degradation of cellulose ($DP/DP_{\text{cont}} = 73.2\%$). Emissions of acetic acid and aldehydes e.g. hexanal were detected from Tyvek using SPME-GC/MS after heating to $80\text{ }^{\circ}\text{C}$ for 14 days, and acetic acid was also detectable from Tyvek at room temperature. Tyvek samples were wiped with de-ionised water before all experiments in order to remove the anti-static coating. These results suggest that PE-based packaging materials can have a cross-infection effect on heritage objects stored or displayed in their vicinity at ambient conditions. Degradation of PE has been shown previously to yield low molecular weight organic acids such as those detected in this work [39].

It was also demonstrated that several of the packaging materials had a beneficial effect on cellulose, such as the acid-free tissue ($DP/DP_{\text{cont}} = 128.7\%$) or the grey Plastazote ($DP/DP_{\text{cont}} = 109.9\%$).

In order to put these results into a context relevant to heritage institutions, materials such as MDF and laminated wood were also included in the study. These materials are known to cause problems when incorporated into display cases, as a result of organic acid emissions and the release of moisture [40]. It was interesting to note that exposure to both MDF and laminated wood resulted in a moderate to neutral cross-infection effect ($DP/DP_{\text{cont}} = 96.0\%$ and 89.5% respectively); these effects were much lower than those observed for CN, certain CA, IR and PS objects, among others, and for the PE foam and plastic box lid used for storage. However, it should be noted that the relative impacts of these materials under ambient conditions may be different.

4.4. Key VOC emissions contributing to a severe or significant cross-infection effect

The chromatographic data collected from the emission studies of selected samples were analysed to highlight specific VOCs that were emitted in higher quantities from plastics shown to accelerate the degradation of cellulose. 20 samples were studied, 8 that displayed a severe cross-infection effect, 2 with a significant effect, 8 with a neutral effect and 2 with a preservation effect. The most characteristic emission from plastics with a severe or significant

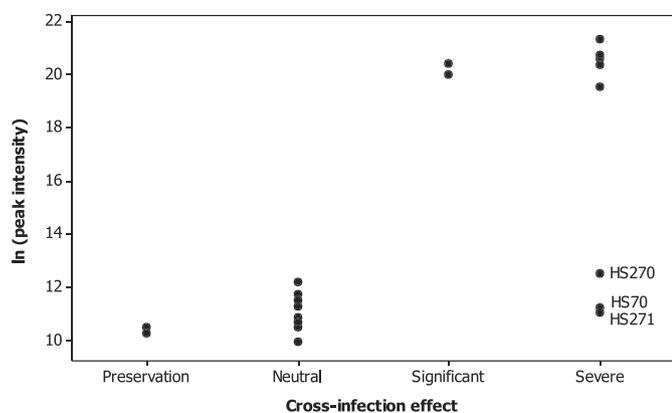


Fig. 9. Individual values plot showing how amounts of acetic acid emissions vary between samples with different cross-infection effects.

cross-infection effect was shown to be acetic acid. Out of 10 plastics with such effects, 7 had high levels of acetic acid emissions, while plastics with either a preservation or a neutral effect had low levels (Fig. 9). The remaining 3 plastics with severe cross-infection effects are two CN samples, HS270 and HS271, whose impact on cellulose may be attributed to emissions of NO₂, nitrous and nitric acids and the flame-retardant PP sample HS70, the reason for whose impact is not known.

With the exception of acetic acid vapour, there were no other VOC emissions that were found to be present in a wide selection of the plastics whose VOC emissions had accelerated the degradation of cellulose. However, analysis of the chromatographic data highlighted certain compounds shown to be emitted in high levels from certain polymers with significant or severe cross-infection effects. For example, methyl-furan emissions were detected from 2 IR samples (HS268 and HS216) shown to accelerate the degradation of cellulose while no methyl-furan emissions were detected from any of the polymers with neutral or preservation effects. As has been previously discussed, the degradation of cellulose has been shown to accelerate in the presence of an alkyl-substituted furan. In the case of both the PE foam and Stewart box lid, both of which exhibit severe cross-infection effects, propanoic and butanoic acids and ketones such as 2-butanone, 2-pentanone and 2- and 3-heptanone were found to be characteristic emissions, in addition to acetic acid. These emissions were not found to be present in polymers with a neutral or preservation effect.

In order to understand these effects in more detail and quantitatively, a calibrated setup for quantitative VOC analysis would be required. However, for the purpose of comparative assessment, the test discussed here will enable curators and conservators to rule out materials inappropriate for long term storage and to identify historic polymeric materials that could have a deleterious cross-infection effect and may thus need to be stored individually. In the future, a more detailed study of particular materials incorporating complete characterisation of the samples would certainly be of interest.

5. Conclusions

Using a collection of 105 polymer samples covering 14 polymer types, the cross-infection effect of volatile polymer degradation products on pure cellulose was studied. The results have shown the following:

- Degradation of certain polymers found commonly in heritage collections can have a significant or severe cross-infection effect, causing degradation to spread to other materials. Other

common polymers had no effect, while some displayed a preservation effect

- Cellulose nitrate was shown to be the “modern material” with the most severe cross-infection effect, likely to be the result of NO₂ emissions
- Specific samples of CA, PVC/PVAc, IR, PS, PE and PP also had a significant or severe cross-infection effect
- PMMA, PF, PVC and PC had either a neutral or a preservation effect, while polyesters and PUR samples had effects varying from moderate cross-infection to preservation
- Certain PE-based packaging materials used in heritage institutions had a severe cross-infection effect on cellulose, a result attributed to the emission of organic acids from these materials
- The cross-infection effect of real polymeric objects can vary significantly if object formulations are different, as demonstrated here by the results from PP and PVC/PVAc samples. While certain polymers may in most cases not be problematic, such differences can cause particular objects to exhibit damaging cross-infection effects.
- Acetic acid was found to be the characteristic emission detected from the most severely cross-infecting materials with significantly higher levels emitted than from materials with neutral or preservation effects. Other emissions likely to be significant are other low molecular weight organic acids, NO₂ emissions from cellulose nitrate, HCl emissions from PVC/PVAc records and methyl- and dimethylfuran emissions from natural rubber.
- The emission of specific degradative compounds such as acetic acid had a more significant effect than overall levels of VOC emissions
- Emissions of aromatic compounds such as styrene or methyl-ethylbenzene from materials such as polystyrene or PVC/PVAc appeared to have little or no impact on the degradation of cellulose. Vinyl acetate and trichloroethylene emissions also do not appear to be significant
- The presence of specific additives such as antioxidants in a polymer sample may result in that sample displaying a preservation effect

The research has also enabled the development of a cross-infection classification method, which is proposed for evaluation of the suitability of a particular packaging material or a material used for display or art and heritage objects. The results may enable curators and conservators to take better informed decisions about the choice of storage and packaging materials, and about storage of art and heritage objects themselves, that could potentially have a significant negative effect on objects in their vicinity.

More broadly, the research has shown that emissions of VOCs from polymer objects of the same base formulation may differ significantly, and that the reasons for this need to be better understood. Significant differences in the emissions of naturally pre-degraded and new samples indicate that a polymer material could have different cross-infection impacts during its lifetime. This is an area of active current research.

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References

- [1] Celina M, Clough R, Jones G. Polymer degradation initiated via infectious behavior. *Polymer* (Guildf) 2005;46:5161–4.
- [2] Celina M, Clough RL, Jones GD. Initiation of polymer degradation via transfer of infectious species. *Polym Degrad Stab* 2006;91:1036–44.
- [3] Goss BGS, Blakey I, Barry MD, George GA. Modelling of infectious spreading in heterogeneous polymer oxidation II. Refinement of stochastic model and calibration using chemiluminescence of polypropylene. *Polym Degrad Stab* 2001;74:523–32.
- [4] Goss BGS, Barry MD, Birtwhistle D, George GA. Modelling of infectious spreading in heterogeneous polymer oxidation I. Development of a stochastic model. *Polym Degrad Stab* 2001;74:271–82.
- [5] Byne LSG. The corrosion of shells in cabinets. *J Conchol* 1899;9: 172–178 and 253–254.
- [6] Oddy WA. An unsuspected danger in display. *Museum J* 1973;73:27–8.
- [7] Green LR, Thickett D. Testing materials for use in the storage and display of antiquities: a revised methodology. *Stud Conserv* 1995;40:145–52.
- [8] Strlič M, Kralj Cigić I, Možir A, de Bruin G, Kolar J, Cassar M. The effect of volatile organic compounds and hypoxia on paper degradation. *Polym Degrad Stab* 2011;96:608–15.
- [9] Strlič M, Menart E, Kralj Cigić I, Kolar J, de Bruin G, Cassar M. Emission of reactive oxygen species during degradation of iron gall ink. *Polym Degrad Stab* 2010;95:66–71.
- [10] Curran K, Strlič M. Polymers and volatiles: using VOC analysis for the conservation of plastic and rubber objects. *Stud Conserv* 2014 [in press].
- [11] Mitchell G, Gibson LT. Emissions from polymeric materials: characterised using thermal desorption-gas chromatography. *Polym Degrad Stab* 2013 [in this issue].
- [12] Allen NS, Edge M, Appleyard JH, Jewitt TS, Horie CV, Francis D. Degradation of historic cellulose triacetate cinematographic film: the vinegar syndrome. *Polym Degrad Stab* 1987;19:379–87.
- [13] Shashoua Y. Degradation of cellulose nitrate. *Conserv Plast* 2008:177–80. Oxford: Elsevier.
- [14] Shashoua Y. Degradation of plasticized PVC. *Conserv Plast* 2008:184–8. Oxford: Elsevier.
- [15] Keneghan B, van Oosten T, Lagana A, Wagenaar M, Barabant G, Balcar N, et al. In what condition are my artefacts? Case studies. In: Lavedrine B, Fournier A, Martin G, editors. *Preserv. Plast. Artefacts Museum Collect., Comite des travaux historiques et scientifiques* 2012. pp. 109–37.
- [16] Then E, Oakley V. A survey of plastic objects at the Victoria & Albert Museum. *Conserv J* 1993:11–4.
- [17] Mossman S. Plastics in the Science museum, London: a Curator's view. In: Grattan DW, editor. *Sav. Twent. Century Conserv. Mod. Mater. Proc. A Conf. Symp.* '91. Ottawa: Canadian Conservation Institute; 1991. pp. 25–35.
- [18] Calmes A. Plastics found in archives. In: Grattan DW, editor. *Sav. Twent. Century Conserv. Mod. Mater. Proc. A Conf. Symp.* Ottawa: Canadian Conservation Institute; 1991. pp. 95–102.
- [19] Shashoua Y, Ward C. Plastics: modern resins with ageing problems. In: Wright MM, Townsend JH, editors. *Resins Anc. Mod. Pre-prints Conf. Held Dep. Zool. Univ. Aberdeen. The Scottish Society for Conservation & Restoration*; 1995. pp. 33–7.
- [20] Shashoua Y. Degradation pathways for the least stable plastics in museum collections. *Conserv Plast* 2008:177–92. Oxford: Elsevier.
- [21] Strlič M, Kralj Cigić I, Možir A, Thickett D, de Bruin G, Kolar J, et al. Test for compatibility with organic heritage materials—a proposed procedure. *e-Pre-serv Sci* 2010;7:78–86.
- [22] Robinet L, Thickett D. A new methodology for accelerated corrosion testing. *Stud Conserv* 2003;48:263–8.
- [23] Bamberger JA, Howe EG, Wheeler G. A variant Oddy test procedure for evaluating materials used in storage and display cases. *Stud Conserv* 1999;44: 86–90.
- [24] Reedy CL, Corbett RA, Burke M. Electrochemical tests as alternatives to current methods for assessing effects of exhibition materials on metal artifacts. *Stud Conserv* 1998;43:183–96.
- [25] Lagana A, Keneghan B. Which plastics are in my collection? the need for a plastic reference sample collection (SamCo). In: Lavedrine B, Fournier A, Martin G, editors. *Preserv. Plast. artefacts museum Collect., Comite des travaux historiques et scientifiques* 2012. pp. 37–42.
- [26] BS ISO 5351:2004. *Pulps — determination of limiting viscosity number in cupri-ethylenediamine (CED) solution*, vol. 3; 2007.
- [27] Evans R, Wallis A. Comparison of cellulose molecular weights determined by high performance size exclusion chromatography and viscometry. In: 4th Int symp wood chem 1987. pp. 201–5.
- [28] Tautenhahn R, Patti GJ, Rinehart D, Siuzdak G. XCMS Online: a web-based platform to process untargeted metabolomic data. *Anal Chem* 2012;84: 5035–9.
- [29] Menart E, De Bruin G, Strlič M. Dose–response functions for historic paper. *Polym Degrad Stab* 2011;96:2029–39.
- [30] Shashoua Y. Degradation of cellulose acetate. *Conserv Plast* 2008:180–4. Oxford: Elsevier.
- [31] Schilling M, Bouchard M, Khanjian H, Learner T, Phenix A, Rivenc R. Application of chemical and thermal analysis methods for studying cellulose ester plastics. *Acc Chem Res* 2010;43:888–96.
- [32] Edwards HGM, Johnson AF, Lewis IR, Turner P. Raman spectroscopic studies of “Pedigree Doll disease”. *Polym Degrad Stab* 1993;41:257–64.
- [33] Grassie N, Scott G. Poly(vinyl chloride). *Polym. Degrad. Stabilisation*. Cambridge: Cambridge University Press; 1988. pp. 44–7.
- [34] Grassie N, Scott G. Poly(vinyl acetate). *Polym Degrad Stab* 1988:43–4. Cambridge: Cambridge University Press.
- [35] Lundgren B, Jonsson B, Ek-Olausson B. Materials emission of chemicals – PVC flooring materials. *Indoor Air* 1999;9:202–8.
- [36] Vilaplana F, Ribes-Greus A, Karlsson S. Chromatographic pattern in recycled high-impact polystyrene (HIPS) – occurrence of low molecular weight compounds during the life cycle. *Polym Degrad Stab* 2010;95:172–86.
- [37] Grassie N, Scott G. “Additives” and “reactives”. *Polym Degrad Stab* 1988:173–5. Cambridge: Cambridge University Press.
- [38] Kadoma Y, Fujisawa S. Kinetic evaluation of reactivity of bisphenol A derivatives as radical scavengers for methacrylate polymerization. *Biomaterials* 2000;21:2125–30.
- [39] Hakkarainen M, Albertsson A-C, Karlsson S. Solid phase microextraction (SPME) as an effective means to isolate degradation products in polymers. *J Environ Polym Degrad* 1997;5:67–73.
- [40] Thickett D, Luxford N. Development of show cases for archaeological metals in aggressive environments. In: Degrigny C, van Langh R, Joosten I, Ankersmit B, editors. *Met. Proc. ICOM-CC Met. Work. Gr. Int. Trienn. Meet*, vol. 5. Amsterdam: Rijksmuseum; 2007. pp. 105–9.