Preventive conservation research for plastics on open display

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ABSTRACT Decisions regarding the long-term display of artefacts within historic collections rely on an intimate knowledge of materials behaviour. Deterioration rates may be greatly reduced by careful control of the environment. However, this is not always possible where objects are presented as part of an historic interior, outside of the museum environment. The physical response of Delrin panels has been determined and its implication for allowable relative humidity fluctuations assessed. Degradation and stability vary through the polymer classes, with some synthetic and semi-synthetic types posing particular problems. This illustrates the need for positive identification and characterisation of these polymers. However, the nature of such materials can restrict sampling, particularly where repeated, periodic condition monitoring is desired. It is for this reason that the use of non-invasive, vibrational spectroscopy techniques is finding increasing application within the heritage sector. The ability to quickly identify modern materials enables museum professionals to make informed long-term action plans and more immediate remedial conservation plans.

Monitoring of rubber objects has been undertaken and the results have informed the preventive conservation of this material as part of historic interiors.

KEYWORDS monitoring, environment, dimensional change, analysis, NIR, FTIR, Raman

Introduction

The UK devolved government agency English Heritage is charged with the care of two sites presenting large contemporary collections in original contexts. Plastic materials form a significant proportion of these collections. The options for preventive conservation are limited by the nature of the sites, public access and the necessity to preserve the historic fabric of the buildings as well as their contents. As both sites are underground, mechanical ventilation is required. These high supply air volumes, combined with the porosity of the 'building' envelopes and percolation of rainwater into the surrounding fabric, limit the degree of climate control that can be achieved.

Secret Wartime Tunnels, Dover

The Secret Wartime Tunnels present a Second World War collection in two levels of chalk tunnels underneath Dover Castle. The very high thermal mass of the chalk keeps temperatures low throughout the year, despite a mechanical ventilation system. The close proximity to the sea and porous nature of the chalk leads to an environment with very high and fluctuating relative humidity (RH). Representative data for a period of two months are shown as Figure 1. The high salt and water levels in the chalk mean that mechanical dehumidification leads to unacceptably rapid fabric deterioration of the tunnels. Experiments have shown that still conditions lead to high RH levels in the tunnels and that a rigid ventilation regime can reduce RH. This also ensures full mixing of the air, eliminating high RH spots and retarding the mould germination which is a significant risk at the high levels of RH experienced, even with the ventilation running.

The presentation of the Secret Wartime Tunnels exhibition includes over a hundred plastic social history objects. The largest concentration of plastics is in a series of XB10 telephone cabinets located in the telephone exchange. As well as numerous internal components and hundreds of plastic-coated wires, the exchanges are clad in a structural red plastic material. This was tentatively identified as Delrin a commercial acetal resin, in a student MA project. This identification was performed with Fourier transform infrared (FTIR) spectroscopy and remains tentative due to lack of reference spectra and experience.

Small samples were removed from break areas to confirm the identification of the main plastic type. FTIR spectra were
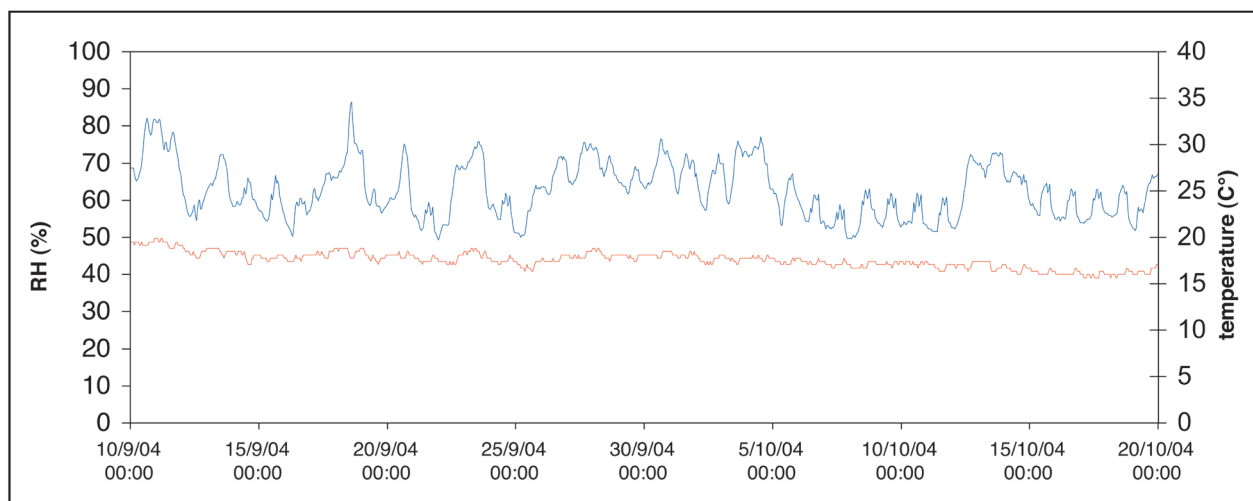
Figure 1 Temperature and relative humidity in the telephone exchange at the Dover Secret Wartime Tunnels.
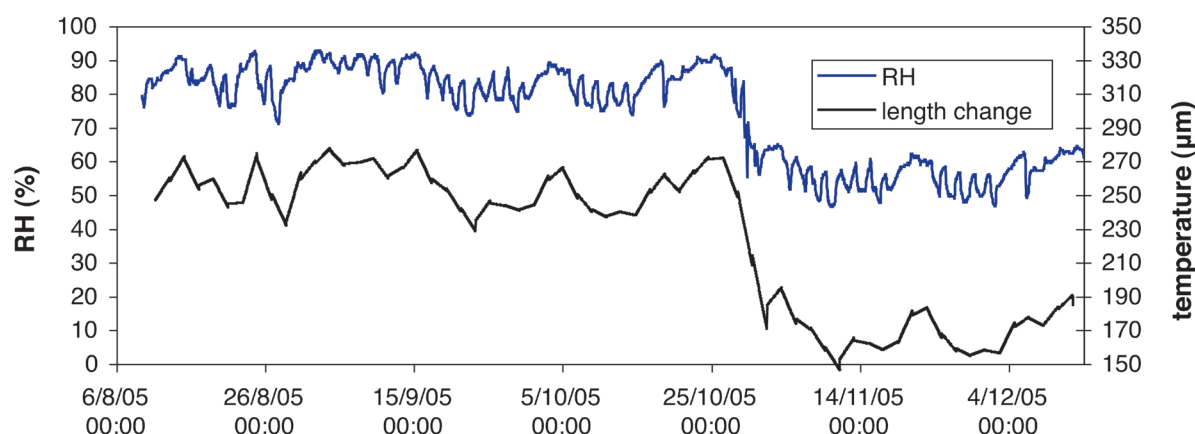

Figure 2 Length response to RH of Delrin in the telephone exchange.

collected using diamond attenuated total reflectance (ATR) (Durascope on a Perkin Elmer 2000). These were compared to spectra from a sample of Delrin obtained commercially and matched to the Hummel plastics library. They were found to be an excellent visual match to the Delrin samples and this material was selected as the highest match using three algorithms to compare to the Hummel library. Raman spectra were also collected using a Spectrolab R2001 spectrometer with 785 nm laser at 60 mW, again giving an excellent visual match to the Delrin samples.

Delrin was developed between 1952 and 1956 by DuPont and entered volume production in 1956. While not contemporary with presentation of the tunnels, the exchanges were sourced from Osborne House and Hinchley Wood and are of the same physical type originally used in the telephone exchange. The Osborne House exchanges date from 1962 to 1965, explaining the use of a post-1956 plastic in their construction.

Examination of the exchanges in 2003 indicated that several of the side panels had undergone plastic deformation and some of the front panels had cracked. Little has been reported in the conservation literature about the physical deformation of plastics and this was investigated further. The reaction time of the plastic sheeting was of particular interest as the ventilation system causes magnified daily fluctuations in RH

in the telephone exchange. If the reaction time is significantly greater than 24 hours then these fluctuations would have little effect.

One 2 cm piece of Delrin had become detached and its physical response to RH was measured. A frame was made to clamp the piece to a GTX1000 linear variable differential transformer (LVDT). The LVDT is capable of converting very small displacements into a voltage signal. The LVDT output was recorded with a SR008 voltage logger, recording any change in the piece's length. The RH in the chamber was controlled with glycerol solutions (Miner and Dalton 1953) between 30 and 98%. The RH was continuously monitored using a Rotronic hygroclip probe connected to a Meaco radiotelemetry system, calibrated to NAMAS accredited saturated salts covering this RH range. The reaction time, fitted as an exponential, was found to be approximately 72 hours. In order to confirm the assumption that the large daily variations were of little significance, the measuring rig was placed in the telephone exchange for a 12-month period. The length was found to follow the long-term variation in RH and not to follow the daily variations, confirming the previous reasoning (see Fig. 2). Autocorrelation analysis yielded a maximum correlation between the length and RH changes of 70 hours (Chatfield 1984).

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Royal Observer Corps Bunker, York

The bunker was decommissioned in 1991 and taken into care by English Heritage. It was opened to the public in 2005. The contents had been largely dispersed, and the bunker is presented with contemporary material from store or purchased on the open market. The composition of the great majority of the items was unknown and the bunker now contains well over 300 plastic objects, some of which have over 30 different components. In order to manage the conservation, both preventive and interventive, identification of the plastics was urgently required. Three techniques were used, all based on vibrational spectroscopy.

In an initial study, a series of 50 small samples was taken from objects of particular significance or representative of groups of example telephones and chairs. This provided an overview of the types of materials to be found within the collection. The samples were analysed using FTIR on a Perkin Elmer 2000 using a Durascope with diamond ATR. This technique is well established for application within the heritage field and is not described in detail. Its primary drawbacks relate to its time-consuming nature and the need for sampling (Keneghan 1995; Garside and Wyeth 2003; Buzio *et al.* 2004; Shashoua and Johansen 2005). Although non-destructive, the technique is usually invasive and therefore object sampling may be limited to certain discreet regions, thus reducing the representative nature of the analysis. The more recent ATR method of collecting spectra has several benefits for this type of work:

- it requires minimal sample preparation;
- the sample size can be relatively small;
- controlling the force applied to the sample gives good reproducibility of spectra, improving both the search efficiency and quantification;
- it can cope well with higher absorbing and scattering samples, such as carbon black fillers.

Two portable near infrared (NIR) reflectance spectrometers were subsequently employed providing non-invasive characterisation across the collection. NIR spectra are produced by the absorption of radiation at higher wavenumbers than those found in more conventional mid-IR spectroscopy ($12800–4000$ cm^{-1} compared to $4000–400$ cm^{-1} respectively).

The higher energy vibrations excited are high frequency overtone and combinations of fundamental modes seen in the mid-IR, and are generally dominated by vibrations of molecular bonds with hydrogen, which are notably anharmonic. This makes NIR spectroscopy particularly applicable to the study of organic polymeric material. The complexity of the spectra can preclude simple band assignments. However, the spectra are still characteristic, and comparison with a suitable spectral reference set usually allows for ready identification of unknowns.

A Perkin Elmer Fourier transform Spectrum One NTS with an Axiom fibre optic probe attachment was applied in conjunction with a Manfrotto articulated arm for accurate positioning of the analysis area. Spectra were recorded in absorbance with a wavenumber resolution of 8 cm^{-1}, a scan speed of 1 cm^{-1}.s^{-1} over a spectral scan range of $12000–4000$ cm^{-1} and scan accumulation

of 32. This set-up can achieve sampling depths in the region of a few millimetres, making this a non-contact method of analysis with the possibility of depth sensitivity. One aim was to exploit this characteristic for the non-invasive identification of foam padding under a number of seat covers held within the collection. Polyurethane-based foams have been used extensively in furniture manufacture. Differences in stability have been found with certain types, undergoing oxidation or hydrolysis reactions over time (Garside and Lovett 2006; Kessler and Van Oosten 2005). Unfortunately, on this occasion, depth sampling was not possible due to the tight, heavy weave of the upper fabric. It was, however, possible to identify the upper textile material as a polyester/elastomer blend (Fig. 3), which is of importance for collections care due to the fact that rubbers, both synthetic and natural, are known to suffer significant degradation with age. Further problematic materials identified within the bunker include cellulose acetate laminates to documents and polyvinyl chloride table tops, fire exit signs and cable covers.

Materials identification was made possible by spectral matching using Grams7 Spectral ID software to a custom library of over 300 reference samples of synthetic polymers. In the majority of cases matching was performed using the first derivative least squares algorithm, where unknown spectra are matched to the closest match held within the database. In some cases the complicated nature of the spectra and spectral interferences can produce poor correlation and false positive results. It is not possible to apply the analysis as a black box method therefore all assignments were accompanied by visual comparisons and the application of first or second order derivatives.

The second NIR spectrometer utilised for comparative purposes was an ASD LabSpec 2500 dispersive NIR instrument with confocal fibre optic probes. Spectra were recorded in reflectance with a wavelength resolution of 3.3 cm^{-1} over a spectral range of $28570–4000$ cm^{-1} and averaged over 20 scans. Data acquisition was in the region of 2 seconds. The smaller dispersive system allowed ready manoeuvring within the tight confines of the bunker. Coupled with the confocal optics, analysis of inaccessible components, such as the inner fly wheels and cogs of a number of teleprinters, was possible.

Problems were encountered when importing the LabSpec spectra in the appropriate format to use with the standard library. Therefore a restricted library was built from spectra of a variety of plastics subsequently recorded with the LabSpec 2500.

The primary limitations of the near IR technique include:

- high absorbance by dark samples;
- poor scattering of some translucent samples;
- high specular reflectance from polished surfaces.

It was notable that for clear plastics the confocal probe gave the best results. While the Fourier transform NIR spectrometer has inherently better spectral resolution and lower noise in the $4500–4000$ cm^{-1} region, for the purposes of material identification the dispersive instrument, if accompanied by an appropriate reference library, appears sufficient. Furthermore the LabSpec is more portable and could allow analysis of small and less accessible samples. However, the Fourier transform spectrometer may prove an advantage when applied to
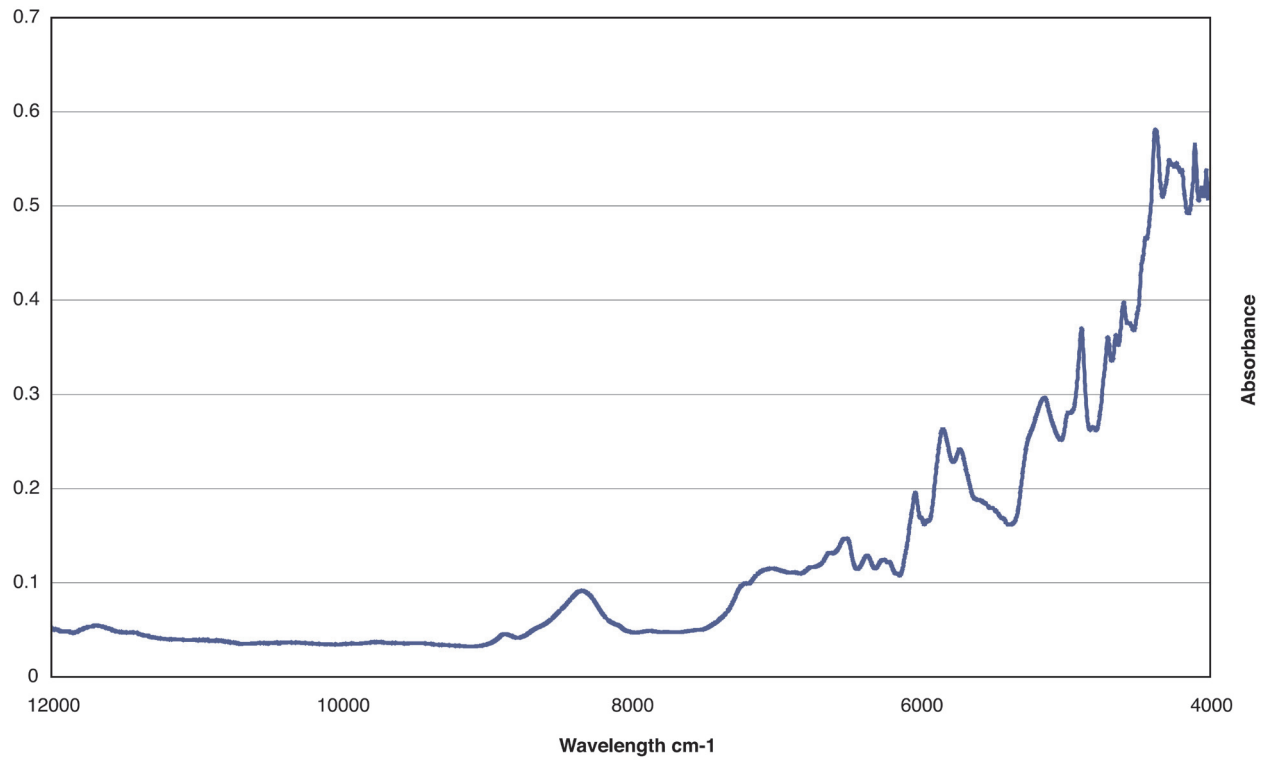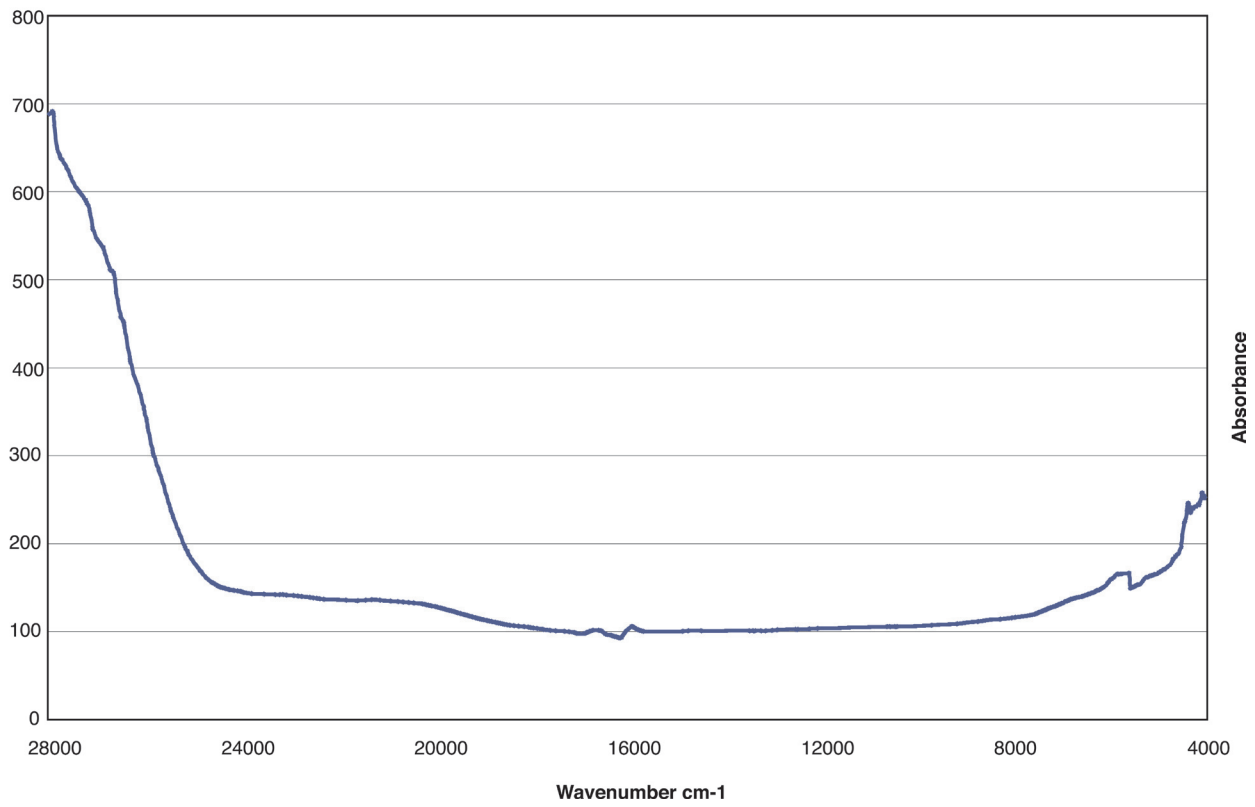
Figure 3 NIR spectra of a textile chair.

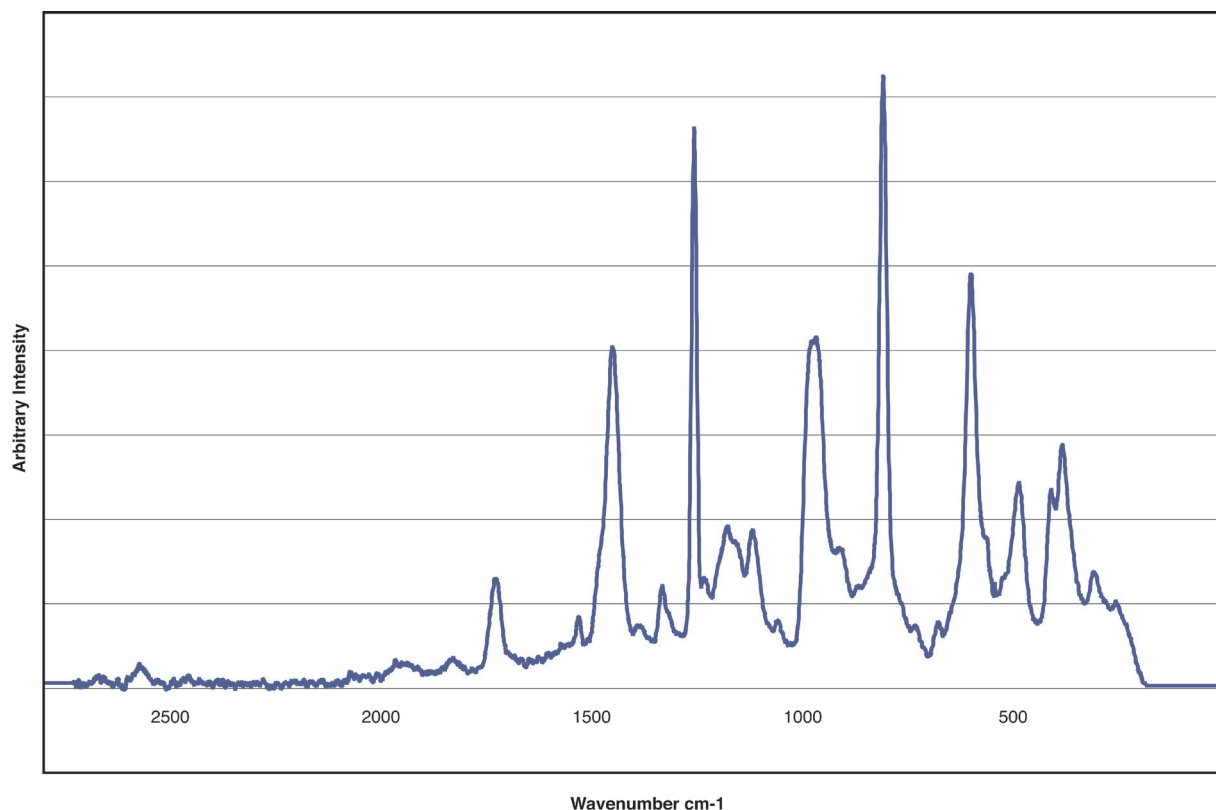**Figure 4** NIR of a clear plastic screen.

Figure 5 Raman spectra of a clear plastic screen.

determine small chemical changes during periodic condition monitoring.

Where sampling or identification was not possible using mid and near IR spectroscopy, the application of a portable Raman spectrometer enabled supplementary information to be gained. Raman spectroscopy results from the detection of inelastic scattering of photon energy, at lower or higher energy to that of the incident beam, Stokes and anti-Stokes scattering, respectively. The energy difference between the elastic and inelastic scattering matches the vibrational energy found in the mid-IR spectra for the same bond if it is IR active. The low incidence of inelastic scattering can produce weak Raman bands and therefore fluorescence emissions often saturate the detector. A near IR diode laser, generating pulses with a wavelength of 785 nm, and powers of 60 mW, was applied to help reduce fluorescence and increase Raman scattering. Again, a confocal system enabled analysis within small confines, with data collection from a limited plane of focus.

Of the samples studied at the bunker, approximately one-third of the spectra were saturated by fluorescence. Nonetheless, in some cases Raman did offer the opportunity to gain spectral information on samples which had proved problematic through NIR analyses or because the nature of the object prevented sample removal for FTIR–ATR analysis. One such case was the backlit screen of the lower control room in the bunker. The thick, transparent material prevented

sufficient diffuse scattering to enable successful NIR analysis (Fig. 4). However, on the application of the portable Raman system a highly resolved spectrum was gained, identifying the material as polymethyl methacrylate (Fig. 5) (Koulic *et al.* 2001).

Rubber

As previously mentioned, rubber is known to have a low stability, with its slow embrittlement reducing its durability and compromising objects formed from it. Both the Dover tunnels and the York bunker contain rubber items. The Dover tunnels have medical equipment, gas masks and machine parts, while the York bunker has predominantly machine parts and fire hoses. The deterioration of rubber is reported to be influenced mainly by temperature, ultraviolet radiation and ozone. Temperature and RH have been monitored over the past decade in the Dover tunnels. The amount of time spent in 5 °C bands is shown in Table 1 for three locations. The ventilation regime in the York bunker changed when it was opened in 2005. A year's monitoring was undertaken prior to this to assess conditions over the past decade. A continuous monitoring system has been installed. Results from both sets of monitoring in the plant room, which contains the majority of the rubber at York are included in Table 1.

Table 1 Temperature and relative humidity distributions in locations with rubber.

	Percentage time within range		
Temperature range (°C)	Dover SWT	York bunker pre-opening	York bunker after opening
<5	0.00	0.00	0.00
5.0–10.0	2.94	40.90	30.34
10.0–15.0	39.24	10.28	8.11
15.0–20.0	57.68	45.90	57.87
20.0–25.0	0.14	2.92	3.68
RH range			
0–30	0.00	0.00	0.00
31–40	0.64	8.77	11.05
41–50	11.91	47.51	47.50
51–60	31.89	38.94	32.52
61–70	20.18	4.49	5.98
71–80	15.21	0.29	2.78
81–90	11.21	0.00	0.16
91–100	8.97	0.00	0.00

Table 2 Rubber deterioration at Dover Secret Wartime Tunnels.

	Ozone concentration (ppb)		
	Dover external	Dover SWT	York ROC
January	9.11	1.81	0.96
March	8.56	1.67	0.88
June	12.83	2.50	1.95
October	6.63	1.06	1.35
Average (ppb)	9.28	1.76	1.28
Estimated dose (ppbd)	–	12848	<9380

FTIR spectroscopy can provide information on the deterioration of natural rubbers. The spectrum of *cis*1-4-polyisopropene shows absorption bands for *cis* alkene bonds at 830 cm^{-1} ($\delta_{C=C}$). As degradation and oxidation proceeds, absorptions appear for carbonyl bonds at 1720 cm^{-1} ($v_{C=O}$) and hyperoxides at 3435 cm^{-1} (v_{O-H}). The CH_2 and CH_3 stretching bands at 1450cm^{-1} were used as an internal reference. Rhyl Svendsen (2006) has used the CH_3 stretching bands at 2930 cm^{-1} as an internal reference. These were not used in this study as they can be affected by microbial activity, which has been observed at both sites (Linos *et al.* 2000). Several objects were monitored with FTIR spectroscopy for a variety of reasons.

A small sample was removed from a gas mask in the Dover tunnels using a scalpel to assess the state of the rubber. The exposed surface, the interior of the rubber and its cross-section were analysed using a Durascope diamond ATR accessory. The sample size was measured under the same load as applied to the Durascope using a Shimadzu TMA50 analyser. After analysis the sample was returned to the same location of the gas mask and re-measured after three years exposure. As can be seen in Table 2, no increase in deterioration was detected within the limits of the method. The instrumental errors were assessed at 8% by multiple replicates.

One of the most difficult challenges in conservation research has been the assessment of acceptable damage rates. While ATR–FTIR can provide a non-interventive method of assessing rubber's state of deterioration, the measure of deterioration is of reduced value without some way of translating it into a lifetime. Three objects were analysed from the Dover tunnels, each of which showed a wide range of deterioration states from flexible to brittle and extremely weak. The site curator's opinion was sought as to the acceptability for display purposes of a series of 10–30 areas on each object. These areas were then analysed with ATR–FTIR. Initially a non-interventive analysis was attempted by carefully positioning and supporting the object so the area of interest was resting over the ATR crystal. While this generated good quality FTIR spectra and the carbonyl absorption bands could clearly be assessed, all three objects had a fine coating of talc, which obscured the
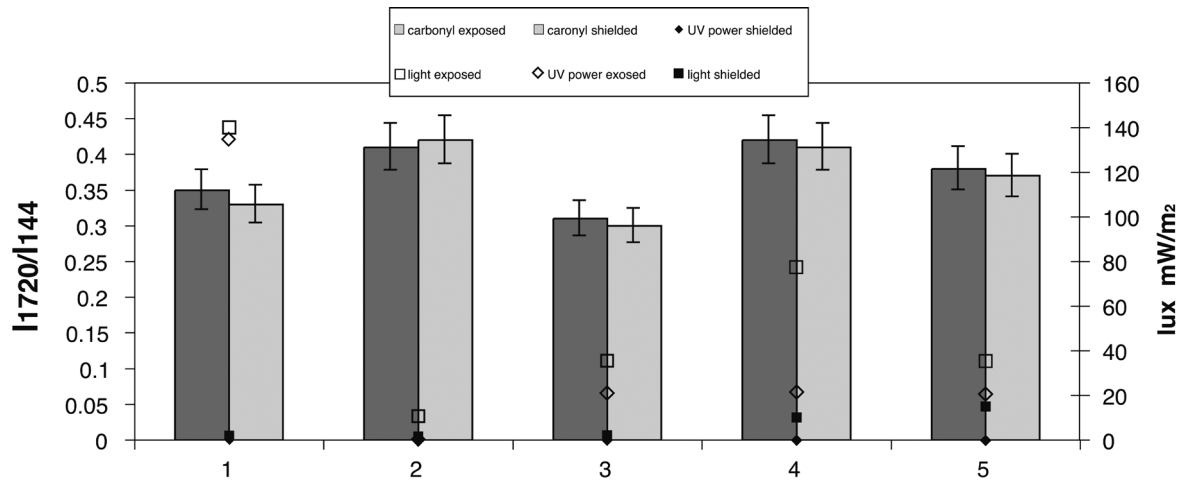
Figure 6 Carbonyl band intensities and light levels for rubbers exposed for approximately 10 years.

alkyl absorption bands. Small samples were removed with a scalpel and analyses conducted of the interior and cross-sections. One of the objects still showed strong silicate bands and microscopic examination revealed white inclusions through the depth of the rubber, indicating a silicate filler. A good discrimination between the brittle and flexible rubbers, as described by the curator, was achieved and it appears a value around 0.45 (I_{1720} / I_{1450}) marks the limit of 'acceptable' deterioration.

The plant room at the York bunker contains a series of four motors that ran the original air conditioning system. Each contains a rubber driving belt. The motors have not operated since the bunker was decommissioned and hence the belts have not moved. The lighting in the room means that each belt has a different irradiation and exposed and masked areas could be found on each belt. Small samples were removed from each belt from an irradiated and masked area and the light and UV levels on those areas measured. The samples were analysed as above, and results along with the light and UV levels are shown in Figure 6.

The deterioration reactions of rubber do not include hydrolysis and water vapour would not obviously be expected to play a major role in the deterioration rate. However, ozone is well known to massively accelerate the deterioration of rubber. Most materials show increased deposition velocities for ozone as their surface water layer thickens with increasing RH (Grontoft and Raychaudhuri 2004). Ryan *et al.* (1992) demonstrated this effect for a latex-based paint, with the reaction probability being 160 times greater at 91% than at 50% RH. The RH levels in the Dover tunnels reach 90% at times of the year and those in the York bunker reach 80%.

The pollutant gases ozone, sulphur dioxide, nitrogen dioxide and hydrogen chloride were measured in the telephone exchange in the Dover tunnels using diffusion tubes. The tubes were exposed for four-week periods and four measurements were undertaken equally spread over a year. The measured ozone concentrations are shown in Table 3. Ozone concentrations are generally highest in summer as the ozone originates from the reaction of nitrogen dioxide with alkyls in the presence of sunlight. The concentrations at York are lower than at Dover, probably due to the bunker's location in a quiet cul-de sac, sheltered from major road traffic. The inlets for the Dover mechanical ventilation system are located in close proximity to the Dover ferry port, with extensive ferry and heavy goods vehicle traffic. Although no diffusion tube measurements were made externally at the York bunker, a series of measurements in May 2007 with a Grey Wolf gas probe TG-501 indicated ozone concentrations below 10 ppb (the instrument's detection limit) over a two-day period. A similar series of measurements at Dover indicated instantaneous concentrations between 10 and 30 ppb. The doses were estimated for the two locations from the average ozone concentration and the dates when the rubber artefacts were thought to have been exposed. The York site dose cannot be accurately assessed as the present ventilation regime brings much more air into the bunker.

Table 3 Ozone concentrations in locations with rubber.

Sample	Surface	Depth of sample under load (μm)	I_{1720}/I_{1450}	Information depth (μm)	I_{850}/I_{1450}	Information depth (μm)
Gas mask sample 2003	Exposed	370	0.423	1.08	0.543	2.25
	Interior		0.403		0.556	
Gas mask sample 2007	Exposed	370	0.420	1.08	0.538	2.25
	Interior		0.410		0.560	

Rubber dosimeters developed by Rhyl Svendsen (2006) were exposed in the Dover tunnels and York bunker for six months. After exposure the dosimeters were assessed visually to determine the amount of surface cracking and ranked according to the system developed as part of that work. Results indicated higher deterioration rates at the Dover tunnels telephone exchange (phase 3) than in the York bunker plant room (phase 2). These correlate with the ozone concentrations measured.

Conclusion

The physical deformation of Delrin panels has been found to be insensitive to short-term RH fluctuations. This means the present method of RH control is not causing unacceptable stress on these panels. The three methods of vibrational spectroscopy allowed identification of the majority of the plastics present in the York bunker. The more portable dispersive NIR could identify many of the plastics, but its sensitivity and reproducibility are unlikely to compete with the long-term condition monitoring promised by non-interventive techniques.

Mid-IR spectroscopy remains a valuable technique and its use for rubber has been exploited. Movement has been made towards defining acceptable levels of change for display situations. Reasonable levels of illumination with decent UV filtration appear to have caused little additional deterioration to natural rubber.

Acknowledgements

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