A novel approach to the assessment of aerospace coatings degradation: The HyperTest

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ABSTRACT

Protecting an aircraft from the extremes of environments during service begins at the interface between topcoat and environment. The topcoat considered here is an aliphatic polyurethane (PU) based matte coating. This paper examines the degradation of the PU topcoat through the use of a novel HyperTest which combines ultra-violet (UV) and ozone as the degradation method. To benchmark the technique against accepted accelerated testing methods, QUV was used and samples were tested between two and 56 days. For the HyperTest, samples were degraded at increments between one to 120 min. X-ray photoelectron spectroscopy (XPS) determined that 56 days of UV exposure was equivalent, in terms of the extent of the chemical degradation of the topcoat, to one to two minutes of UV/ozone (UV/O₃) exposure. There was a significant increase in carbonyl component with increasing oxygen concentration for samples treated with the HyperTest, whereas no clear degradation trend was observed for the samples exposed to UV alone. After 60 min of UV/O₃ exposure a steady-state mechanism is established as the oxidative decomposition of the PU coating. The proposed degradation mechanism of the PU topcoat, through UV/O₃ exposure, is the reaction of atomic oxygen with the polymer matrix/binder through hydrogen abstraction producing a hydroxyl group. This further decomposes to produce a carbonyl component observed in the XPS analysis. The products of degradation are simple volatile molecules such as CO₂ and H₂O for both testing methods used here. However, the efficient nature of the HyperTest, requiring only minutes to degrade samples as shown here, proves it to be a viable complementary technique to established methods of laboratory accelerated testing.

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1. Introduction

The topcoat of an aircraft is the first form of protection against the environment and must maintain its high performance properties even at extremes of temperature, humidity and ultra-violet (UV) exposure. Therefore, it is desirable to understand and examine the degradation phenomena associated with topcoat performance in order to develop an evidence based approach to maintenance painting. There are many ways in which coating degradation can be accomplished, examples of the various methods used are in abundance within literature and vary from natural exposure through to a number of well-developed accelerated test methods [1,2]. Natural exposure of coatings is the placement of coated panels in an atmosphere typical of, for instance, urban, coastal, sub-tropical or sub-Saharan environments. This is, however, time-consuming and to observe significant degradation this method requires months or even years of exposure. Additionally, it is unlikely that it will mimic the varied extreme environments an aircraft coating can experience, particularly at high altitudes. Thus a variety of accepted laboratory acceleration test procedures have been developed by the coatings industry. Although accelerated methods are only loosely related to field behaviour they do provide useful indicators of the class of performance that can be expected. For this reason, they often feature in specifications provided by customers which vendors are expected to meet with their products. These methodologies include salt spray, QUV and prohesion exposure, which all are carried out to appropriate national or international standards [3,4]. They are commonly used in an attempt to understand the effects of different environments and can be used either synergistically or in isolation. With the latter applied to understand the individual role a degradation method may have on the degradation phenomena of a coating. The effect of UV radiation is notably the acute cause and initiation of degradation [5]. As an aircraft crosses the tropopause into the stratosphere the level of ozone (O₃) rises significantly and the combination of UV and O₃ degradation is seldom addressed in current accelerated degradation

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approaches. However, it may contain vital information in determining the degradation pathway of a topcoat. In order to examine this, a novel exposure method has been developed. A commercial UV/ozone (UV/O₃) desktop cleaner, originally intended for scanning electron microscopy (SEM) sample preparation, was used to provide an extremely accelerated exposure test. The device uses UV/O₃ exposure and allows the control of the time and pressure to which the sample is exposed. As this method in not traditionally used, the duration of exposure required, in order to observe degradation, is not yet standardised. In order to benchmark such an approach against standard test methods, UV exposure through a QUV chamber has been used. In an attempt to relate one method to the other, X-ray photoelectron spectroscopy (XPS) was employed to perform surface chemical analysis of the coating in order to determine the mechanism that gives rise to the degradation phenomena that occur.

2. Experimental

The commercial aerospace topcoat investigated in this work is primarily made from an aliphatic polyurethane (PU) system. The backbone of the PU system is derived from the reaction of an aliphatic isocyanate (hexamethylene diisocyanate biuret) with a flexible polyol. The PU topcoat was prepared according to manufacturer’s instructions for spray application onto clean aluminium panels and allowed to cure forming an aliphatic matte PU topcoat, with a topcoat thickness between 35 and 40 µm.

The topcoat was exposed to UV radiation (UVA 340 at a nominal wavelength of 340 nm) within a QUV accelerated weathering test chamber for 2, 5, 7, 14, 28, 42 and 56 days. The topcoat was also exposed to UV/O₃ using a Hitachi High Technologies Zone SEM Cleaner, intended for cleaning organic detritus from samples prior to examination by SEM. The variables of the zone cleaner which are user controllable include the distance between the sample and the lamp, the gas pressure and the duration of exposure. The pressure and distance are known to have the greatest effect on the extent of oxidation of surface hydrocarbon material (i.e. the general detritus when the device is used for its original purpose) during treatment. The samples were exposed, at a reduced pressure of approximately 350 Torr, for 1, 2, 5, 10, 15, 30, 60 and 120 min. Exposing the samples for minutes rather than days was established as it conforms to the functionality of the zone cleaner system and in addition to this, preliminary results suggested accelerated degradation within this time.

The Zone Cleaner contains a mercury UV lamp light source at wavelengths (λ) of 185 and 254 nm. A working distance of 2 cm, between the sample and the UV source, was used throughout. In the Zone Cleaner the long UV wavelength at 184 nm dissociates naturally occurring molecular oxygen (O₂) into atomic oxygen (O³P), the atomic oxygen is then able to react and form ozone (O₃). The shorter wavelength at λ = 254 nm photo-dissociates ozone back into molecular oxygen and atomic oxygen, creating a small cycle. The shorter wavelength is also able to penetrate the sample surface and break the hydrocarbon bonds, creating excited molecules or free radicals. They are then oxidised by the atomic oxygen to form simple molecules such as CO₂, which are removed by vacuum [6].

The aliphatic PU topcoat was examined as received in order to determine the original state of the coating, with no exposure by XPS. The UV and UV/O₃ exposed samples were also examined with the same techniques, enabling an understanding of any changes occurring chemically.

For XPS, a Thermo Scientific Theta Probe spectrometer was employed using a monochromated Al Kα radiation with a spot radius of 400 µm. Pass energies of 200 eV for survey spectra and 50 eV for high resolution spectra were used. Spectral analysis, including quantification of the high resolution spectra, was performed using Thermo Avantage v5.8 software.

3. Results

3.1. Analytical strategy

The results described here enable an understanding of the chemical changes to the surface. Three sets of samples were analysed; unexposed PU topcoat, QUV exposed PU topcoat (exposed from 2 to 56 days) and UV/ozone exposed PU topcoat (exposed from 1 to 120 min). The unexposed and exposed XPS spectra (survey spectra and high resolution spectra) are all shown together for ready ease of comparison. Quantitative surface chemical analyses and the results of the peak fitting of the high resolution C1s spectra are shown in Tables 1 and 2 respectively.

3.2. XPS analysis

3.2.1. Unexposed PU topcoat

XPS survey spectrum of the as received unexposed coating, shown in Fig. 1a, identifies the C1s (75.6 at.%) O1s (18.1 at.%) and N1s (6.4 at.%) photoelectron peaks along with their equivalent Auger peaks. From the high resolution spectra (Fig. 2a) of the C1s

| Table 1 | Surface composition by XPS (in atomic%) of the PU coating samples examined in this work. |
|---------|-------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| Elements | C | O | N | Na | Si | S | Ba | Mg | Al | K | Ca | F | Ti |
| Unexposed | 75.6 | 18.1 | 6.4 | | | | | | | | | | |
| UV exposed | 77.0 | 15.3 | 7.7 | | | | | | | | | | |
| 2 days | 79.0 | 13.5 | 7.6 | | | | | | | | | | |
| 5 days | 78.6 | 15.5 | 5.4 | 0.2 | 0.3 | | | | | | | | |
| 7 days | 75.8 | 16.7 | 6.7 | 0.3 | 0.3 | 0.3 | | | | | | | |
| 14 days | 78.7 | 13.6 | 7.7 | | | | | | | | | | |
| 28 days | 74.3 | 16.6 | 7.6 | 0.3 | 0.5 | 0.3 | 0.05 | | | | | | |
| 42 days | 75.8 | 16.7 | 6.7 | 0.3 | 0.3 | 0.3 | | | | | | | |
| 56 days | 75.8 | 16.7 | 6.7 | 0.3 | 0.3 | 0.3 | | | | | | | |
| UV/O₃ exposed | | | | | | | | | | | | | |
| 1 min | 75.5 | 15.9 | 7.0 | 1.5 | | | | | | | | | |
| 2 min | 69.6 | 19.2 | 9.5 | 1.7 | | | | | | | | | |
| 5 min | 68.1 | 20.1 | 10.3 | 1.6 | | | | | | | | | |
| 10 min | 64.2 | 21.7 | 11.7 | 0.2 | 1.9 | | | | 0.1 | 0.2 | | | |
| 15 min | 61.5 | 22.5 | 14.3 | 0.2 | 1.5 | | | | 0.1 | 0.3 | | | |
| 30 min | 59.1 | 22.0 | 14.6 | 0.9 | 1.2 | 0.5 | 0.1 | 0.3 | 0.2 | 0.4 | 0.2 | | |
| 60 min | 48.5 | 28.4 | 13.9 | 1.5 | 2.1 | 1.3 | 0.3 | 0.5 | 0.4 | 0.6 | 2.4 | 0.3 | 0.2 |
| 120 min | 46.3 | 30.7 | 13.4 | 0.9 | 3.8 | 1.2 | 0.5 | 0.8 | 0.8 | 0.3 | 0.5 | 0.4 | 0.3 |
region it is clear there are many contributions to the peak envelope. The assignments of the peaks were based on the fact that it is an aliphatic polyurethane coating derived from hexamethylene diisocyanate (HDI) biuret and polyol [7,8]. The assignments include C–C (285.0 eV), C–N (285.9 eV), C–O (286.4 eV), C=O (288.1 eV) and NCO (289.0 eV) which represents the urethane linkage. The N1s high resolution spectrum was fitted with two peaks due to the slight asymmetric nature of the peak. The peak at 399.8 eV is representative of C–NH2 group. The peak at 400.4 eV is considered to represent NCO which is consistent with a nitrogen component within a PU organic matrix (Fig. 3a). The O1s envelope has been fitted with 3 peaks representing C–O, NCO and C=O at 531.6, 532.3 and 533.5 eV respectively (not shown here), which is also consistent with a polyurethane system. It is worth noting that multiple analyses were carried out and the coating gave consistent results irrespective of position, confirming the lateral homogeneity of the topcoat.

3.2.2. QUV exposed PU topcoat

The PU samples which were exposed to UV exhibited small changes from the as received (unexposed) sample with the emergence of silicon, sodium and sulphur as seen from the survey spectra (Fig. 1b–c), which show the extremities of the QUV treatment at 2 and 56 days exposure. The high resolution Na1s peak at a binding energy of 1071.5 eV was fitted with a single peak. This is representative of an ionic sodium compound, as sodium is highly reactive and therefore elemental sodium is seldom observed in XPS. The sulphur 2p (not shown here) was fitted with two peaks, S2p3/2 (168.7 eV) and S2p1/2 (169.9 eV) (Δ = 1.2 eV). The sulphur peak is shifted to higher binding energy compared to elemental sulphur (S2p3/2, 161.3 eV) and is indicative of a metal sulphate [7]. As the sulphur appears with sodium this suggest they may be linked and therefore represent sodium sulphate environment. However it is well known that there are many components within a coating system, such as many inorganic pigments and fillers; this includes BaSO4 (although at such an early stage of degradation the exposure of barytes is unlikely as no Ba3d peak – which has a significantly higher photoelectron cross-section than S2p – is observed in the spectra) which could be beginning to emerge with UV exposure. After two weeks of UV exposure a Si2p peak is observed, peak-fitting establishes binding energies of the spin orbit splitting of the 2p as Si2p3/2 (102.5 eV) and Si2p1/2 (103.6 eV: Δ = 1.1 eV). This binding energy is representative of an aluminosilicate or siloxane [7], both are plausible based on binding energy considerations but the absence of aluminium in the analysis indicates the latter assignment is correct. The high resolution spectrum of the carbon 1s peak envelope after 56 days of UV exposure, shown in Fig. 2b, was fitted using the same protocol as the unexposed PU sample. This indicates that with UV exposure there is little change in the functionality of the C 1s peak and there is no introduction of new chemical environments. These results are indicative that the in terms of UV degradation, after eight weeks of QUV exposure, the PU topcoat is comparatively unaffected, retaining its original surface chemistry.

3.2.3. UV/ozone exposure PU topcoat

UV/O3 exposed PU topcoat samples were produced at times of one to 120 min in the Zone Cleaner. The survey spectra after one, 30 and 120 min of UV/O3 exposure is shown in Fig. 4, and the quantitative surface analyses are collated in Table 1 with other XPS data. One minute maintains the dominance of the carbon, nitrogen and oxygen with the emergence of silicon (Si2p) at 102 eV. After 30 min of exposure there is a rise in sodium concentration and the Ba 3d doublet at ca. 790 eV becomes a well-defined component in the spectrum at a concentration of 0.1 at%. At 120 min there are multi-

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Table 2

<table>
<thead>
<tr>
<th>Carbon species</th>
<th>UV/O3 Treatment Time/minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>C=O</td>
<td>72.8</td>
</tr>
<tr>
<td>C–N</td>
<td>13.8</td>
</tr>
<tr>
<td>C–O</td>
<td>6.2</td>
</tr>
<tr>
<td>C=O</td>
<td>1.9</td>
</tr>
<tr>
<td>N=O</td>
<td>5.3</td>
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Fig. 1. XPS survey spectra of (a) unexposed PU topcoat and QUV exposed PU topcoat after exposure times of (b) 2 days and (c) 56 days.
ple peaks representative of the inorganic components of the coating (mainly pigmentation and extenders) such as Ti 2p (458 eV), Mg 1s (1305 eV), Al 2p (73 eV), P 2p (135 eV) and K 2p (293 eV), as well as a rise in the oxygen species. Although the gradual evolution of the inorganic species is seen in the data of Table 1, a clearer appreciation is obtained by a systematic inspection of the XPS survey spectra. Fig. 5a shows the XPS survey spectra of specimens for all the UV/O\textsubscript{3} exposure times, each sample showing the gradual increase of bulk components (pigments) as well as oxygen and a decrease in carbon with treatment time. There are many low intensity photo- electron peaks which appear within the binding energy 0–200 eV (shaded area in Fig. 5a). In order to better appreciate the variation of these minor features as a function of UV/O\textsubscript{3} time, this region of the survey spectrum for all samples is shown enlarged in Fig. 5b. Some of these features are low intensity orbitals of elements with main transitions elsewhere in the spectrum (e.g. Ba and Mg), however this region of the spectrum is rich in information relating to inorganic compounds. Such elements feature relatively low photoelectron cross-sections and expansion of this low energy region makes relative differences between the spectra much more readily discernible. The major peaks of four elements relevant to this work, identified as Al 2p, Si 2p, P 2p and S 2p are observed to develop with increasing UV/O\textsubscript{3} treatment. Sulphur and phosphorous appear after 30 min and aluminium after 60 min.

The C 1s high resolution spectra of samples treated with UV/O\textsubscript{3} for one and 120 min are presented in Fig. 2b–c. These spectra show the significant changes occurring to the surface of the PU topcoat with extended UV/O\textsubscript{3} exposure. The carbonyl peak (C\textequiv O) at 288.2 eV exhibits the most significant increase, whilst the aliphatic carbon reduces by some 20% relative to the total carbon, (Table 2), after 120 min treatment time. Quantifying these changes, the total carbon concentration falls by approximately 30% of its original value (Table 1), whilst the oxygen concentration increases by 12 at% and the exposure of the inorganic compounds become evident, as a result of intense treatment in the Zone Cleaner.

The high resolution N 1s spectra of the PU coating with UV/O\textsubscript{3} exposure of 1, 30 and 120 min are shown in Fig. 3. These spectra indicate the development of a new nitrogen environment with increasing treatment time, these developing features are indicative of an azo group type functionality (398.9 eV) and an amide functionality on the higher binding energy side.

4. Discussion

The results show a clear difference in the degradation of the PU topcoat when exposed to UV radiation through the use of a QUV chamber versus exposure through the novel approach applied here, using a commercial UV/O\textsubscript{3} desktop cleaner. XPS has provided an insight into the chemical changes occurring at the surface of the PU topcoat with accelerated testing particularly by The Hypertest.

The XPS results of the unexposed PU topcoat exhibit the chemical environments consistent with a PU resin. However within a topcoat system it is expected that there may be organic additives which primarily segregate to the outermost surface of the coating, such as hindered amine light stabilisers (HALS) and UV absorbers. These have been identified in a separate study by time-of-flight secondary ion mass spectrometry (ToF-SIMS) [9]. It is clear that, although XPS is a highly surface sensitive technique, the presence
of organic additives is not apparent through XPS, as it does not provide detailed molecular information.

UV exposed samples show little change when the survey spectra of the unexposed, UV exposed for two days and UV exposed for 56 days are compared. After 56 days the emergence of sulphur, sodium and silicon is seen but they are in low concentrations. The atomic concentrations of all the elements (Table 1) observed through XPS analysis shows slight fluctuations with UV exposure, however no clear trend is observed. What is evident is that these elements are not typical of an unexposed surface and are compo-
The use of the UV/O₃ desktop cleaner as a hyper degradation accelerated test method (The HyperTest) proved to be highly effective, showing significant degradation to the coating. The exposure of the inorganic components becomes evident after only 30 min of exposure which is greater than the amount of inorganic components seen after 56 day under UV radiation.

The XPS surface concentrations of Table 1 show a significant decrease in the atomic concentration of carbon and increase in oxygen with time for samples exposed to UV/O₃. The 12% rise in oxygen can be accounted for by the presence at the surface of inorganic components which contain oxygen, such as MgO, BaSO₄, and TiO₂, as a result of severe binder degradation, in addition to the oxidation of the organic components observed in the C₁s spectra. This is clearly evident when comparing the C₁s peak of the as-received surface (Fig. 2a) with that recorded after 120 min of UV/O₃ treatment (Fig. 2d).

The photoexcitation and oxidation of the PU resin through UV/O₃ exposure, produces an overall decrease in the atomic concentration of carbon (from 75.6 to 46.3 at.%). However within the C₁s peak envelope there is a decrease in the aliphatic carbon as well as an increase of the carbon-oxygen functionality (Table 2) in
the form of C=O, C=O and C(=O)–N (at binding energies of 287 eV, 288 eV and 289 eV respectively). The carbonyl increase in the C 1s peak envelope is a defining factor of the change of the PU surface with increasing UV/O3 exposure.

The increase in the carbonyl component of Fig. 6 shows a correlation with the increase in oxygen concentration. As the oxygen concentration rises so the rate of formation of the carbonyl component is greater than the rate of degradation of polymer matrix. However, the sigmoidal fit of the data in Fig. 6 shows that after 60 min of UV/O3 exposure (or at 40% O/C), the growth in the carbonyl functionality is seen to plateau. This suggests a steady state mechanism is achieved, whereby there are two competing processes, one; the oxidation of the PU surface and the other; the decomposition of the PU proceeding with similar kinetics.

Comparing the kinetics of the degradation effects of the QUV chamber and The HyperTest, is not possible as the time scales and rates of degradation are not directly comparable. Therefore, in order to understand the degradative effects of both methods the relative atomic concentrations of carbon, oxygen and nitrogen were calculated. Fig. 7 reveals the change in the oxygen and nitrogen, relative to the carbon with UV exposure and UV/O3 exposure. Focusing on the relative nitrogen concentration of the UV/O3 exposed samples, as the time increases, the carbon concentration decreases and the nitrogen level increase initially, peaking at ca. 15% nitrogen. However, with QUV exposure, the relative nitrogen for all samples cluster around the one and two minutes of UV/O3 exposed samples showing no clear trend with UV exposure time. Observing in a similar manner the relative oxygen amounts for those exposed to UV/O3, there is a clear increase in the oxygen level, whereas again, the relative oxygen level of the samples exposed to UV cluster around the one and two minutes of UV/O3 exposed samples. When the data for the two methods are taken as a whole, a clear trend emerges with a linear correlation with UV/O3 exposure time followed by a clear change of gradient at ca. 60 at% carbon, equivalent to 30 min of The HyperTest exposure, whereas UV exposure results cluster at the initial stages of UV/O3 exposure. As the plot is comparing the relative carbon, nitrogen and oxygen amounts, it is a representation of the PU organic component of the coating and enables direct comparison of the two degradative methods. Through this it is clear that 56 days within the QUV chamber produces little degradative effect of the coating, suggesting much longer times within a QUV chamber would be required to observe degradative effects. Perhaps more importantly it enables an equivalence of the two methods to be established and as can be seen from Fig. 7, that 56 days QUV exposure is equivalent to 1–2 min of The HyperTest. In an effort to understand the degradation of a coating, to determine the failure point during the testing of a coating, the HyperTest method can offer results within extremely short times.

The mechanistic reaction pathway for the photo oxidative degradation of the PU topcoat is complex. A coating contains a multitude of components in order to achieve its high performing properties [10], some of which may contribute to the initiation and degradation pathways, such as organic additives and extrinsic chromophores. Therefore isolating the PU conceptually allows for a reduced dimensionality in determining the degradation pathway of the coating and is representative of the coating degradation as it is the PU which dominates the coating and controls the properties of the coating.

The ozonolysis of aryl systems are well known and well described within literature [11–13], enabling reaction mechanisms to be developed, such as the Criegee rearrangement mechanism [14]. However within an aliphatic system the reaction mechanistic pathway of ozone is somewhat unclear. Presented below is a brief review of the current view of the possible reactions, and how they can be assimilated towards a possible mechanistic degradation pathway based on the XPS data presented in this paper.

Ozone is highly versatile due to its possible resonance structures which may allow ozone to function as a nucleophile, electrophile and 1,3-dipole [11]. In the reaction between ozone and a hydrocarbon, ozone may behave as a 1,3-dipole and follow an insertion reaction as the initial reaction step [11]. However, in the presence of UV radiation, ozone can be degraded to form atomic oxygen [O(3P)] which is highly reactive [15].

Understanding the effects of UV radiation on a coating is better established [16]. UV light provides enough energy to initiate homolytic chain scission at the weakest bonds to form radicals. The radicals formed are highly reactive and propagate through the system, evolving simple molecules such as CO2 and H2O until the radicals reach termination.

Considering the environment within the ozone cleaner the wavelength at 254 nm is able to photo-dissociate bonds with dissociation energies less than 470 kJ mol−1 creating excited molecules or free radicals. These are then available to react with ozone, molec-
ular oxygen or atomic oxygen, evolving simple molecules. This combined effect of UV and ozone in the degradation of surfaces has been noted, particularly within aerospace systems and is known as photo-oxidative etching [17].

The combination of UV and ozone on a coating system then becomes more complex when determining the degradation mechanism. XPS analysis of the UV/O₃ degraded samples indicated an increase in the carbonyl component as stated. This is because of the interaction between the atomic oxygen formed through the breakdown of ozone and the hydrocarbons within the coating.

The mechanism in which atomic oxygen may react with the hydrocarbon surface is detailed below:

\[ R - \text{CH}_2 - R' + O(\text{P}) \rightarrow [R - \text{CH}^+ - R' + \cdot \text{OH}] \rightarrow R \]

\[ \text{CH(OH)} - R' \]

(1)

\[ R - \text{CH(OH)} - R' + O(\text{P}) \rightarrow R - C(\cdot) - R' + \text{H}_2\text{O} \]

(2)

Scheme (1) is the reaction of atomic oxygen with the hydrocarbon through hydrogen abstraction, forming a transition state in which the two radicals formed react rapidly to form a hydroxyl functional group. Scheme (2) shows the oxidation reaction in which atomic oxygen reacts with the hydroxyl group to produce a ketone and forms a H₂O by-product [17,18]. The degradation of the PU coating is primarily through the decrease of the carbon component via desorption of simple volatile molecules such as CO, CO₂, and H₂O. However further detailed analysis is required in order to better determine the detailed mechanistic degradation pathway. An investigation in ToF-SIMS is underway and recent developments in our in-house multi-variate analysis routines have enabled accurate definition of reactants and products of the degradation mechanism. Preliminary results have been presented [9] and once this work is complete it will be available in the public domain.

The penetration of UV and atomic oxygen within the coating is also a degrading factor [19]. The depth of penetration of UV into a coating is dependent on the energy of the UV radiation and the absorption coefficient property of the coating, thus it can vary from a few nm to several mm [20]. As a high performing topcoat the effects of UV are accounted for hence the use of UV absorbers [21]. However with the extended exposure of The HyperTest the penetration depth of UV becomes a factor as the functionality of the UV absorber diminishes. The penetration depth of atomic oxygen is also a factor in the rate of degradation of the coating, as it has a greater ability to diffuse into the coating than molecular oxygen and is more reactive. The depth of penetration of atomic oxygen is also dependent on the energy of the atomic oxygen as well as the type of coating [19]. Many studies investigating the effects of atomic oxygen on surface degradation of polymeric materials have identified differing erosion rates as a result of diverse properties of each material [22,23]. Examining the effects of the ozone cleaner as a function of depth with greater molecular detail is beneficial in determining a three dimensional degradation mechanism. The extent of erosion may be estimated qualitatively by consideration of the increase in a pigment/extender specific marker such as the Ba₃d doublert from barytes.

5. Conclusions

5. Conclusions

The application of a QUV chamber for coating degradation analysis is well established and serves for the accelerated testing of coated panels within controlled laboratory conditions. Accelerated testing of a coating is done for multiple of reasons, one of which is to assess the quality of the coating and thus help determine the possible lifetime of the coating as well as enabling comparison between coatings through a controlled method.

In order to understand the effects of degradation, it is shown here, that the coatings may require months/years of treatment to achieve significant results. However, the use of the novel approach presented here, using UV/O₃, produces a degradative effect equivalent to 56 days within the QUV chamber in only two minutes. It is proposed that such a test may have a wider applicability for the rapid screening of high performance coatings and the name of The HyperTest has been coined to describe this procedure.

The HyperTest is ideal for the coating system examined here, as it is a topcoat for aerospace purpose and therefore may better mimic the exposure an aircraft coating would experience with the combination of high UV and ozone levels. However it could also be used as a hyper accelerated laboratory test method for other coatings (not just those specified for aerospace) because of its efficient nature.

Through XPS, the major reaction of ozone with the PU coating was identified, UV/O₃ exposure produced a significant increase in the carbonyl component with increasing oxygen forming a steady-state mechanism. This is established after 60 min, between the oxidation and decomposition of the PU system. The degradation products for coatings treated with UV and UV/O₃ are, for both, simple volatile molecules which are generated following the formation of free radicals which both propagated through the coating as well as reacting with oxygen in the atmosphere. The combination of the highly reactive ozone and the UV photolysis of the coating forming excited molecules and free radicals all combine for the efficient hyper accelerated degradation of the PU coating. Understanding the details of the degradation mechanism of UV/O₃ is imperative, not only in assuring the UV/O₃ as a viable testing method but also for the detailed understanding of how a coating is degraded. Thus the lifetime of the coating will be better understood and the failure point of a coating may be developed. In order to gain a detailed mechanistic understand of what is happening at the molecular level, greater molecular specificity is required in the surface sensitive technique employed. ToF-SIMS fulfills such requirements exactly and the investigation is underway.

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