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Quantitative spectroscopic analysis of weathering of polyester-urethane coatings

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ABSTRACT

Transmission FTIR analysis of polyester-urethane coatings (PUC), that were degraded under different accelerated laboratory weathering conditions, are compared. The aim of this comparison is to deepen our insight into the chemical pathways of weathering of polyester-urethane coatings. We monitored the chemical changes for different environments, such as aerobic or anaerobic conditions as well as wet or dry conditions, in order to increase our insight into the effect of each individual stress factor, i.e., photons, oxygen, temperature and water, on the chemical pathways of weathering.

We showed that the degradation of urethane groups proceeds via photo-oxidative pathways and that the ester groups mainly degrade via photolytic reactions. The ester bond scission accelerates after an initially-slow-rate stage of weathering in the presence of urethane groups. This is due to an increase in the optical absorptivity of the coating as a result of degradation under anaerobic conditions, as shown before. By means of a kinetic analysis using a combination of FTIR and UV–Vis spectroscopy results (obtained before), we found that a first-order kinetic model can perfectly describe the rate of ester bond scission during the weathering and that the increase in the rate of reaction is due to the increase in the light absorptivity of the coating as a result of degradation. Finally, using the interference fringes of FTIR spectra, we showed that evaporation and water-caused removal of degraded material cause a particularly pronounced decay in the thickness of the coating. In the absence of water spray, the material loss takes place in the same period as urethane groups decompose and stops afterwards, even though the ester bond scission proceeds with higher rates. This supports the hypothesis of photo-oxidative pathways for the urethane group decomposition and photolytic mechanisms for ester bond scission. Dark experiments showed that PUC coatings are highly resistant to hydrolysis and thermal degradation.

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1. Introduction

Polymeric coatings are designed for different applications and, accordingly, have to fulfill different requirements. Among these, clearcoats, the external layers of automotive and aerospace coatings, are designed to be resistant against environmental stress factors, i.e., UV light, oxygen, temperature and water [2]. Exposure to these stress factors for prolonged time leads to macroscopic failure of these coatings, such as cracks. Accordingly, a keen interest

exists in understanding the long-term performance of these coatings. Sophisticated experimental methods such as FTIR and UV–Vis spectroscopy [3–8], ESR [9] and mass spectroscopy [10,11] techniques are used to chemically characterize the degradation processes involved [12–18]. In addition to the experimental techniques, simulation methods are also employed to study chemical evolution of coatings as a result of degradation [19,20].

Chemical changes in the coating due to the weathering, such as chain scission, cross-linking and oxidation, lead to changes in physical properties of the coating, i.e., T_g , moduli, hardness and oxygen and water diffusivities. The changes in these properties have been investigated at macro- [21,22] and micro-scales [23–25] for different systems. Weathering builds up internal stresses in the

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coatings which eventually lead to (micro) cracks and mechanical failure [26]. Therefore, understanding the mechanisms of weathering is the key factor to understand the relation between chemical and physical changes of the coating due to weathering.

Due to the fact that clearcoats are designed to be highly resistant to environmental stress factors, outdoor experimental degradation tests are rather time-consuming. Therefore, faster artificial degradation setups, which are designed to mimic real outdoor conditions with higher intensity of the stress factors, are used.

Considering that each stress factor in photo-degradation triggers specific changes in the material, applying all stress factors at the same time, significantly complicates studying the mechanisms of weathering [27]. However, in order to mimic the real outdoor condition one needs to expose the material to all of them at the same time. So, to keep this study as close as possible to the real outdoor condition and at the same time, to be able to identify the role played by each stress factor (light, temperature, oxygen and water), we first conducted an artificial weathering experiment which has water (spray), oxygen and daylight, all together. Thereafter, a set of controlled experiments was conducted in which individual stress factors come into play in a systematic way, e.g., dark hydrolysis and dry anaerobic or aerobic weathering conditions.

2. Experimental

2.1. Material

A model OH-functional polyester poly (neopentylisophthalate) or PNI (provided by DSM Resins) with a hydroxyl value of 100 (theoretical molecular mass 1144 g/mol, degree of polymerization 4.4), non-cross-linked or cross-linked with hexamethylenediisocyanurate trimer or HDT (provided by Perstorp), are used in this study, see Fig. 1.

2.2. Coating preparation

Polyester-urethane coatings (PUC) were prepared using solution coating application. PNI is dissolved in 1,3-dioxolane at 70 °C, after cooling down to room temperature, HDT was added to the solution at an NCO:OH ratio of 1.05 and then stirred for 5 min at room temperature before application using spin coating. Thereafter, coatings were dried and cured in a convection oven at 120 °C for 1 h.

In order to perform transmission FTIR measurements, an IR-transparent substrate is needed. We used silicon wafers (p-doped, Anadis Instruments Benelux B.V., Almere, The Netherlands), cleaned by UV-ozone treatment (Novascan PSD-UVT) and coated

with our solution (30 m% of PNI) by spin coating (Laurell WS-650SX-6NPP/LITE) for 30 s, at 4000 or 2000 rpm depending on the desired thickness.

2.3. Artificial weathering

A Ci65A Weather-Ometer (Atlas MTS), equipped with xenon arc lamps and borosilicate inner and outer filters, was used as the first artificial weathering machine. Exposure was carried out at a black standard temperature (BST) of 65 °C, with a total cycle time of 2 h that was composed of a 102 min dry cycle at 40–60% relative humidity (ISO 11341, cycle-A with daylight filters) and an 18 min wet cycle with water spray (ISO 4892-2, cycle 2). The exposure time of each weathered sample is defined by the moment at which it is removed from the equipment. Samples were not re-exposed after removal.

A Suntest XXL+ (Atlas MTS), equipped with xenon lamps (NXe1700) and daylight inner and outer filters was used, as the second artificial weathering machine. Two exposure cells were made (Equipment and Prototype Center at TU/e, Eindhoven) in order to have two exposure conditions in a single run of the Suntest XXL+, see Fig. 2. Cells were made of aluminum alloy with a top window of fused silica which has been sealed by a silicon rubber O-ring. Each cell had an inlet and an outlet tube to purge it by a desired gas. One cell was constantly purged by dry air and the other one by dry nitrogen during exposure. The BST was set to 45 °C outside the cells, which approximately corresponded to a BST of 65 °C inside the cells. Samples made for transmission FTIR measurements were re-exposed after removal. Samples were reshuffled every 500 h in order to provide a uniform irradiance of light for all of them.

Dark experiments were performed to rule out the effects of hydrolysis and thermal degradation in the absence of light. Samples were placed in a dark oven and other samples soaked in demi-water in the same oven at 60 °C. The exposure times of the samples was set to be the same as the accumulative time of samples in the WOM exposed to dry and wet cycles, respectively. Samples were dried in a convection oven for 3 h prior to each measurement and re-exposed after each measurement. Table 1 summarizes the information about all weathering tests.

2.4. Analytical methods

UV–Vis spectra were studied using an Ocean Optics USB4000 spectrometer. This spectrometer was calibrated for measuring absolute values of photon fluxes. For this purpose, a cosine corrector was placed next to the samples in the weathering machines and the collected light was transferred to the spectrometer using an optic

Fig. 1. Chemical structure of the cross-linked PNI.

Fig. 2. Suntest air and nitrogen cells.

Table 1
Weathering conditions in different apparatus.

	Irradiation [W/m ²] (300–400 nm)	Relative humidity	Atmosphere	Temperature [°C]
WOM	54.12 ± 1.5	Water spray/40–60%	Air	BST = 65 T ≈ 45
Suntest	37.87 ± 0.5	< 5%	Air/nitrogen	BST = 65 T ≈ 45
Dark oven	0	Dry air or soaked in water	–	T = 60

fiber. The reported value is an average of 1000 scans and each scan time was 100 ms.

Transmission FTIR measurements were performed on a Varian 670-IR spectrometer. The internal chamber was purged with dry nitrogen for 30 min prior to measurements in order to remove water vapor and carbon dioxide from the chamber. The spectrum of a bare silicon wafer was used as the baseline. Transmission infrared scans were performed on the samples with a spectral scan range from 4000 to 400 cm⁻¹ with a 2 cm⁻¹ resolution. For each measurement 50 spectral recordings were averaged.

3. Theoretical background

3.1. General scheme of the chemistry

Photo-oxidation chemistry of polymers is highly complicated [28] and largely studied. Extensive studies have been devoted to this area and valuable results have been obtained.

In general, the initiation step (photolysis) of photo-degradation of polymers which contain chromophore groups in their repeating units is triggered by excitation of the chromophore by photons. In our system, for virgin material, aromatic and carbonyl groups are good candidates for being excited by absorbed photons. Note that as a result of weathering reactions, other chromophores can also form. Considering a certain quantum efficiency, the absorbed photon can break a chemical bond and two radicals form. For aromatic polyesters, it has been reported in many papers [10,29–32] that a Norrish type I photo-cleavage, as depicted in Fig. 3, is the main initiation step along paths a, b or c. In our case urethane bonds could be another candidate for the photolysis reaction. However, according to Wilhelm and Gardette [33] this mainly occurs in the presence of short wavelengths UV light ($\lambda < 254$ nm) that is not present in either WOM or Suntest light spectra, see Fig. 7. Therefore, the most plausible initiation mechanism for our coating is Norrish type I.

As the propagation step, the radicals resulting from the initiation step can undergo oxidation (in the presence of oxygen) and hydrogen abstraction reactions. Oxidation reactions result in polymer peroxy radicals (Fig. 4, reaction a) which can undergo hydrogen abstraction reactions that give rise to polymer hydroperoxides (Fig. 4, reaction b). An excited chromophore can transfer

Fig. 4. Examples of propagation reactions for PUC.

energy to a hydroperoxide group that is eventually decomposed to a polymer oxy radical and a hydroxyl radical. This radical can undergo another hydrogen abstraction reaction or form a carbonyl group as a result of the cage effect (Fig. 4, reaction c). As an example, Fig. 4 shows one of the possible chemical pathways that our material might take in the propagation step.

In the termination step, two radicals simply recombine. A few examples of plausible termination reactions for our coating (partly shown to be present by mass spectroscopy techniques for PNI [11]) are shown in Fig. 5.

Having outlined these general pathways of the chemistry of weathering, by performing FTIR analysis as described in Section 4.2, we will make a clearer picture of the chemical pathways of weathering of the coating.

3.2. Interference fringes

Transmission FTIR was used to monitor the formation and disappearance of different chemical moieties in the coating during

Fig. 3. Possible initiation Norrish type I photo-cleavages of the ester group of PUC.

Fig. 5. Examples of termination reactions for PUC.

Fig. 6. Transmission FTIR spectrum of a virgin and fully degraded sample after WOM testing.

weathering. Fig. 6 depicts the IR spectra of the virgin ($t_{\text{exp}} = 0$ h) and fully degraded (in the WOM with $t_{\text{exp}} = 4600$ h) material. The immediate observations are shortening and broadening of the peaks, generally indicating degradation of the material.

Moreover, a quasi-sinusoidal baseline can be seen in both spectra. This quasi-sinusoidal baseline occurs as a result of strong interference of the light reflected from the top surface of the coating and the coating-substrate interface [34,35]. Croll and Skaja used these fringe spacings between successive maxima or minima, to calculate the change in the thickness of a coating during photodegradation [36]: For a specific coating at a specific wavenumber, there is a linear relation between the spacing of the fringe and the thickness of the coating, reading

$$\Delta\nu = \frac{1}{2dn} \quad (1)$$

where ν is the wavenumber, $\Delta\nu$ is spacing of the fringe, d is the thickness and n is the refractive index of the coating. The refractive index of a material, n , is defined usually as a complex number

$$n = n_0 + ik \quad (2)$$

where the real part, n_0 , indicates the change in the velocity of the

Fig. 7. Photon flux of the WOM, Suntest and Florida sunlight.

light when it propagates through the material and the imaginary part, k , is related to the decay of light intensity due to adsorption [37]. Therefore, even on the assumption that n_0 is constant as a function of wavenumber (in the IR-Vis range), the period of these fringes is not constant over the whole range of the spectrum due to the significantly different amount of absorption at different wavenumbers. This indicates that knowing n_0 , one can calculate the thickness of the coating only within a range of wavenumbers with no absorption (e.g., 2100–2800 cm^{-1} for our coating). However, the assumption of a sinusoidal pattern of the baseline for the whole range of the spectrum is rather flawed. Hence, baseline corrections for such a spectrum seem somewhat ambiguous. Therefore, in order to study the evolution of a chemical moiety in the system, instead of applying any general baseline correction following by peak integration, the baseline for each individual peak in each individual spectrum is defined by a line that connects the absorbance values at the integration limits.

3.3. FTIR band assignments

Although the infrared spectrum of the polyester-urethane is quite complicated, a chemical assignment for the major contribution to certain vibrational bands is still possible. Table 2 shows the band assignments of the desired chemical moieties and the corresponding (lower and upper) integration limits employed by us.

As the internal standard we use the isocyanurate ring vibration (at 765 cm^{-1}) because of the good stability of this chemical moiety during photodegradation [38] (this vibration is wholly related to the ring of the isocyanurate ring while the peak at 1726 cm^{-1} also contains other carbonyl contributions). Then, we normalize the area of each individual peak based on the area of the internal standard (in the same spectrum), i.e., $\Sigma(t_{\text{exp}})/\Sigma(t_{\text{ref}})$. Therefore, we can compare the relative area of each peak corresponding to a specific chemical moiety $\Sigma(t_{\text{exp}})/\Sigma(t_0)$ for different exposure times, where $\Sigma(t_0)$ is the same peak area for the virgin material.

Considering the band assignments in Table 2, one can correlate the decay in the area of the band with its maximum at 725 cm^{-1} (carbonyl disubstitution on the aromatic ring) to breakage of the ester bond, either according to a) in Fig. 3 followed by the elimination of carbon monoxide, or according to c) in that figure. The vibration with the peak maximum at 827 cm^{-1} is known for C–H deformation of three adjacent coupled hydrogens on an aromatic ring (1,2 or 1,3 C=O disubstitution) [39]; therefore, the decay in this band can be partly related to the phenyl substitution as a termination reaction, see Fig. 3. The bands with maxima at 1241 and 1135 cm^{-1} are indicators of the concentration of the ester bond in the material. As show in Figs. 8–10 graphs c and d, both these vibrations show a similar trend. The peak with maximum at 1520 cm^{-1} is a reliable indication for the urethane bond in the system [33]. Carbonyl band (maximum at 1726 cm^{-1}) is also widely used as an indication of oxidation of the material. Note that the shoulder of this peak (maximum at 1689 cm^{-1}) is due to the carbonyl of the urea group in the core of cross-linker.

4. Results and discussion

4.1. Photon fluxes

As mentioned in Section 2.3, we considered different weathering conditions in order to be able to study the effect of different stress factors individually. In addition to the exposure conditions discussed in Section 2.3, it is worth noting that the spectrum of the light and the irradiance that samples are exposed to, are different for the different artificial exposure setups listed Table 1.

Table 2
Band assignments and integration limits.

Wavenumber [cm ⁻¹]	Band assignment	Lower limit [cm ⁻¹]	Upper limit [cm ⁻¹]	Ref.
725	1,3 distributed aromatic carbonyl	684	748	[39]
765	Isocyanurate core vibration	748	798	[38]
827	CH on 1,2 or 1,3 C=O disubst. arom. ring	800	846	[39]
1135	$\nu(\text{C}=\text{O}) + \nu(\text{O}-\text{CH}_2)$	1114	1156	[33]
1241	$\nu(\text{C}=\text{O}) + \nu(\text{O}-\text{CH}_2)$; $\nu(\text{C}-\text{O}-\text{C})$	1186	1270	[38]
1520	$\delta(\text{N}-\text{H}) + \nu(\text{C}-\text{N})$ (Urethane amide II)	1494	1572	[33,38]
1726 & 1689	$\nu(\text{C}=\text{O})$	1622	1826	[33]

Fig. 8. Evolution of relative absorbance of different vibrations as a function of WOM exposure time for PUC.

Fig. 9. Evolution of relative absorbance of different vibrations as a function of Suntest exposure time for PUC.

Fig. 7 depicts the flux of photons arriving at the coating surface for the WOM, Suntest and Florida sunlight (left axis) and the absorptivity spectrum of the virgin material (right axis). This figure shows that in the WOM considerably more short-wavelength photons ($290 \text{ nm} > \lambda > 300 \text{ nm}$) are present. This difference in photon flux between WOM and Suntest becomes particularly important if one takes into account the absorptivity spectrum of the coating. As can be seen, the virgin coating hardly absorbs photons with $\lambda > 300 \text{ nm}$. Therefore, one could expect a faster photo-degradation of the coating exposed to WOM conditions over the one exposed to Suntest conditions. Moreover, the coating exposed to high energy photons (existing in WOM exposure) might take different chemical pathways during the weathering process. Absorption by the polymer outside the measured range is considered as unimportant, as below 250 nm the amount of photons is negligible while radiation with wavelength above 450 nm hardly suffices for excitation.

4.2. Transmission FTIR analysis

FTIR analysis is used to study the chemical evolution of the (PUC and PNI) coatings during the degradation process. Figs. 8 and 9 depict the change in the relative absorbance ($\approx$ relative concentration) of all vibrations in Table 2 for the WOM and Suntest (air and nitrogen cells) samples as a function of exposure time, respectively. Fig. 11 shows similar vibrations for non-crosslinked PNI exposed in the Suntest air and nitrogen cells.

By quantifying the changes in the concentration of different chemical moieties, one can, to some extent, rationalize the reasons behind these changes. This, of course, can be only done based on initial assumptions about the chemical pathways of photo-degradation of the material. Our assumptions are made according to the reports in the literature about the photo-degradation mechanisms of PNI and urethane-based clearcoats [10,11,33]. Note that for each graph in Figs. 8–10, we fitted a curve (dash lines)

Fig. 10. a) Absorbed photon dose as a function of exposure time for the WOM (black dots) and Suntest air cell (red dots). b) and c) the ester d) and e) and urethane bond concentrations as a function of exposure time and absorbed photon dose for the WOM (black dots) and Suntest air cell (red dots). The lines are a guide to the eye. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

as a guide for the eye.

In Fig. 8 most of the vibrations show a decrease. Note that the highest rate among them belongs to the urethane group concentration (the axes of different graphs are in different scales). However, the vibrations at 1135 and 1241 cm⁻¹ show a slower rate initially and then a steeper decay. Therefore, the first indication from this figure is that the most sensitive chemical moiety to weathering is the urethane bond in such a way that after 2700 h all the urethane bonds are broken (for the mechanism, see Fig. 12).

In Fig. 9, for both the Suntest air and nitrogen cells, more or less the same qualitative trends are observed with the exception that the initially-slow-rate period exists for all bands and also the duration of this period for ester vibrations is around 2.5 times larger than in the WOM data. The longer initial stage of the Suntest weathering can be rationalized by the fact that the irradiance of the light in the WOM is much higher than the Suntest machine, see Table 1, therefore the degradation proceeds much faster in the

WOM. The absence of this initial stage for the 1520 cm⁻¹ band in the WOM could also be due to the fact that degradation proceeds that fast that our data sampling do not capture it. Note that, although we fitted a line on this dataset, Fig. 8 graph e, one could argue that the slope of the middle range data is larger than the initial value (more or less similar to Fig. 9, graph e).

Another interesting point about Fig. 9 is that the time span of this initial stage in all graphs except graph e, is around 2600 h. Moreover, the acceleration in urethane bond scission starts at around 1700 h. This gives rise to the idea that the photo-degradation reactions take place with small rates until the hydrogens in the α -position to the nitrogen in the urethane groups are depleted. From that stage onwards the photo-degradation proceeds faster.

To assess the effect of light intensities on the faster degradation in the WOM (as compared to the Suntest aerobic condition), one can plot the concentration as a function of number of photons

Fig. 11. Evolution of relative absorbance of different vibrations as a function of Suntest exposure time for PNI.

Fig. 12. Mechanisms of urethane bond scission.

absorbed by the material (photon dose), instead of the exposure time. This can explicitly show whether the considerable different rates of degradation in the WOM and Suntest occur as a result of different light intensities or the coating takes different chemical pathways during degradation under either conditions. However, in order to draw a valid conclusion, one has to take a few considerations into account. First, one should consider not only the number of photons emitted by the lamps in the degradation apparatus but also the light absorptivity of the material of interest during weathering. Second, since the light absorptivity of our material considerably changes by weathering [3], one cannot expect a linear relation between the number of absorbed photons and exposure time. Therefore we calculated the rate of absorption of the material, using the photon flux of the apparatus $\phi(\lambda)$ and the UV–Vis absorbance $A(\lambda, d)$ of the material at each specific wavelength and

each point in time during degradation, i.e., $r_{\text{abs}}[m^{-2} s^{-1} nm^{-1}] = \phi(\lambda)(1 - 10^{-A(\lambda,d)})$ [1]. In order to compare the number of absorbed photons as a function of exposure time for different exposures, we integrated the r_{abs} over a range of wavelength, i.e., $270 nm \leq \lambda \leq 400 nm$. Then we plotted the cumulative number of absorbed photons in the WOM and Suntest as a function of exposure time in Fig. 10a.

As can be seen in Fig. 10a, there is a considerable difference between the number of absorbed photons in the two different exposure conditions and a nonlinear relation between photon dose and exposure time is obtained. In addition, we plotted the concentrations of ester and urethane bonds during weathering in the WOM and Suntest air cell, both as a function of exposure time and photon dose (Fig. 10b and c, Fig. 10d and e). As expected, the rate of degradation in the WOM and Suntest air cell as a function of photon dose become more-or-less similar for both chemical moieties. This agrees with the above mentioned hypothesis that the differences in the degradation rates under aerobic conditions (WOM and Suntest air cell) occur because of the differences in the dose rates in different exposure conditions.

In order to confirm that the presence of this initial stage is somehow related to the urethane bond scission, we performed the same degradation experiment for non-cross-linked PNI (containing obviously no urethane group) in the Suntest air and nitrogen cells. As can be seen, no initially slow rate period is observed for these samples, see Fig. 11.

In addition to the previous observations, considering Fig. 9 graph e, one can see an enormous difference between weathering under anaerobic and aerobic conditions. Thus, this confirms that the urethane bond scission taking place in Suntest experiments, undergoes an oxidative pathway. Based on Wilhelm and Gardette's [33] suggestions, in Fig. 12 we showed the most probable mechanisms for urethane bond scission. Note that only n-substituted carbamate shows a peak at $1520 cm^{-1}$, therefore all cases in Fig. 12 lead to a decay in this vibration.

As a reference exposure experiment, we also placed our coatings in a dark oven in dry and wet conditions. After 4300 h of exposure, no change in the IR spectrum was observed. Fig. 13 shows the spectra of the virgin coating and the one soaked in water at $60^\circ C$ for 4300 h. An almost identical IR spectrum was found for the sample placed in the dry condition. This confirms the high stability of the cross-linked PNI coating towards temperature and moisture stressors in the absence of light. Note that $60^\circ C$ is above the highest temperature that our samples experienced in both WOM and

Suntest machines.

So far, we observed that the photo-degradation process in the WOM and Suntest air cell show a similar chemical trend with the exception that this process is 2.5 times faster in the WOM. Moreover, for our cross-linked coating, an initial stage of weathering with slower rate has been observed and an oxidative pathway for urethane bond scission has been confirmed. In addition, we proved that in the absence of light, hydrolysis and thermal degradation are not effective.

4.3. Kinetic study of ester bond scission

In order to understand the initially slow stage of the weathering that appears in both anaerobic and aerobic conditions, one should understand the kinetics of the reactions of interest. Noting that this initial stage of weathering occurs at anaerobic condition as well as aerobic one, see Fig. 9, and having the information about the change in the chemistry of the material in anaerobic condition, provides the opportunity to study the kinetics of the weathering chemistry in a simpler condition (almost no oxidation reaction taking place). Therefore, in anaerobic condition one expects that the ester bond scission only undergoes a photolytic pathway, as indicated in Fig. 3. Suppose this reaction obeys a first-order kinetic law

$$r_{\text{ester-sciss}} = k[C_{\text{ester}}] \quad (2-3)$$

where $r_{\text{ester-sciss}}$ represents the rate of reaction, k is a constant and C_{ester} stands for the concentration of the ester bond. Moreover, having the change in the concentration of the ester bond as a function of exposure time, Fig. 9 graph d, one can assess the rate of reaction by differentiation of these data with respect to the exposure time. Fig. 14 depicts the change in the amount of broken ester bonds $(1 - \Sigma(t_{\text{exp}})/\Sigma(t_0))$ as a function of exposure time (in the Suntest nitrogen cell) and the first derivative of the fitted curve (dashed line in Fig. 14 a).

Fig. 14 graph b, shows a non-linear increase in $r_{\text{ester-sciss}}$, which is not a first-order reaction unless the reaction constant, k , changes as a function of exposure time. Of course, an increase in the optical absorptivity of the coating is expected due to the formation of, amongst others, biphenyl structures [11] as a result of termination reactions, see Fig. 5. The decay in the $827 cm^{-1}$ peak is also another indication of this reaction. Since in anaerobic condition the only stress factor which influences the ester bond scission reaction is light, studying the optical absorptivity of the coating might lead to the rationalization of our observation. A sophisticated UV–Vis spectroscopic study has been performed on samples exposed to the same weathering conditions (WOM, Suntest air and nitrogen cells) [1]. Having the UV–Vis spectra of the samples at the same exposure times as in Fig. 14, one can investigate how the change in optical absorptivity of the material effects the rate of ester bond scission. Moreover, Adema et al. [4] introduced a wavelength dependent absorptivity and showed how this changes the reaction rate of ester bond scission.

In fact, one can calculate $r_{\text{ester-sciss}}^{\text{cal}}$ (estimated rate of ester bond scission based on first-order reaction assumption) by multiplying k_{exp} by $C_{\text{ester,exp}}$. For these calculations, the authors assumed that: 1) each scission was caused by a single photon with a sufficient energy, and 2) an arbitrary quantum efficiency for the reaction was considered as a characteristic property of the scission mechanism and was kept constant during degradation. Using the Adema et al. method, the only parameter that remains unknown is the cutoff wavelength. In principle, one has to consider the cutoff wavelength, λ_{u} , in such a way that photons up to that wavelength have sufficient energy to excite the chromophores to an excited state that is susceptible to bond scission, such as their $n-\pi^*$ excited state. However,

Fig. 13. Transmission FTIR spectra of virgin coating and the sample exposed 4300 h to dark hydrolysis condition. The spectra are so similar that the difference between the virgin and degraded coating is hardly visible at this scale.

Fig. 14. a) Change in the amount of broken ester bonds as a function of exposure time (in the Suntest nitrogen cell). b) The first derivative of the fitted curve.

as weathering proceeds, new types of chromophores can form and therefore predicting λ_u is fairly impossible. Nevertheless, one can choose a range of λ_u values, calculate the corresponding $r_{\text{ester-scis}}^{\text{cal}}$ and compare the results. Fig. 15 shows the $r_{\text{ester-scis}}^{\text{cal}}$ values with different hypothetical λ_u and the $r_{\text{ester-scis}}$ as a function of exposure time.

As shown in Fig. 15, $r_{\text{ester-scis}}$ and $r_{\text{ester-scis}}^{\text{cal}}$ are in a full agreement for $\lambda_u = 324$ nm. So far, we have shown that the increase in the absorptivity of the coating as a result of weathering, more than compensates for the decrease in the concentration of ester bonds, leading to an increase of the rate of ester bond scission. In addition, under the assumption of first-order kinetics for the ester bond scission, reproduction of the actual change in the rate of the reaction is possible. Having a match between actual rate and the estimated rate of reaction as a function of exposure time and considering the fact that in anaerobic condition ester bond scission is most likely undergoing a photolytic pathway, one can claim that for our coating – under the above mentioned weathering condition – photons with wavelength larger than 324 nm do not substantially contribute to the photolysis of the ester bonds.

By using the same method, but this time for the coatings weathered in an aerobic condition (Suntest air cell), one can investigate the degradation kinetics in the presence of oxygen. Fig. 16 depicts the actual and calculated rates of ester bond scission for different λ_u values as a function of exposure time in the presence of oxygen.

Fig. 15. $r_{\text{ester-scis}}^{\text{cal}}$ with different λ_u as a function of exposure time for the Suntest nitrogen cell.

For samples degraded in the aerobic condition, the actual and calculated rates based on the first-order kinetics model with $\lambda_u = 336$ nm match rather well at higher exposure times. However, the calculated rates based on $\lambda_u = 324$ nm show a large deviation with the actual rates as exposure time elapses.

Here we can imagine two likely scenarios: 1) the successive photons for ester bond scission in the Suntest air cell have the same range of wavelengths as samples weathered in the nitrogen cell. In this case the deviation between $r_{\text{ester-scis}}$ and $r_{\text{ester-scis}}^{\text{cal}}$ (for $\lambda_u = 324$ nm) is due to the contribution of other possible mechanisms, e.g., oxidation reactions (broadening of carbonyl peak is an indication). 2) The deviation is not due to other mechanisms for ester bond scission, but photo-oxidation reactions result in other type of chromophores in the coating that can get excited by larger wavelength photons, e.g., up to $\lambda_u = 336$ nm, as well.

It is worth noting that the samples degraded in the Suntest nitrogen cell become yellow as weathering proceeds, while the samples degraded in air cell do not. This indicates that different weathering conditions lead to the formation of different types of chromophores. Although, drawing conclusions solely based on discoloration in the visible range is far-fetched for the effects in the UV range, this turns the argument in favor of the second scenario.

So far we proved that the fast decrease in ester bond concentration coincides with a fast increase in optical absorptivity of the coating (for details on absorptivity, see refs. 1 and 3). Moreover, comparing non-cross-linked PNI and PUC FTIR results, Figs. 9 and 10, one can see that the initially-slow-rate period only occurs in

Fig. 16. $r_{\text{ester-scis}}^{\text{cal}}$ with different λ_u as a function of exposure time for Suntest air cell.

Fig. 17. Change in the thickness of material as a function of exposure time.

the presence of urethane groups. From that stage onwards, the rate of ester bond scission for PU and PNI coatings is more or less similar. Considering that the urethane group is a very good hydrogen donor, one can expect that in the beginning of the weathering process, most of the radicals formed as a result of ester bond photolysis, abstract a hydrogen from the urethane groups (most likely the hydrogen connected to the α -carbon of the nitrogen). Note that even the nitrogen gas that purges the Suntest nitrogen cell, contains a few ppm of oxygen, and therefore these radicals undergo an oxidation reaction and form hydroperoxide compounds, see Fig. 12. In addition, in agreement with previous results from Mielewski et al. [17] the concentration of hydroperoxide compounds in urethane-based clearcoats shows an initial sudden increase (after 200 h of exposure in WOM condition) and, after passing a peak, reaches a plateau (between 400 and 800 h), followed by a gradual decrease. This indicates that in the beginning of the weathering process, urethane groups use the radicals generated by photolysis of the ester bond to form hydroperoxide compounds in such a way that the rate of hydroperoxides formation is larger than hydroperoxides consumption. After a while (around 800 h of exposure in WOM condition), the concentration of urethane groups decreases and these hydroperoxides undergo β -scission reactions with a larger rate and generate even more radicals, see Fig. 12. These radicals can contribute to the formation of new chromophores, e.g., biphenyl compounds, which absorb more photons and therefore more ester bonds break.

4.4. Thickness analysis

Using interference fringes in the transmission FTIR spectra we calculated the change in the thickness of the coatings as a function of exposure time, see Equation (1). The real part of the refractive index was measured as 1.52, in the visible range, by optical profilometry measurement [4]. We also assumed that the refractive index does not change significantly as a result of weathering. Fig. 17 shows how the thickness of the coating changes at different weathering conditions. In ref. 3 we showed good agreement with independent thickness measurements, and, since we employed similar preparation techniques here (exactly the same concentration and spin rate), the thicknesses measured by UV–Vis and FTIR spectroscopy techniques for the WOM samples will be similar, e.g., $4.5 \pm 0.1 \mu\text{m}$.

For the Suntest nitrogen cell, no considerable change in thickness is observed. For the Suntest air cell and WOM conditions the thickness increases slightly in the beginning which can be due to

the reaction with oxygen. Following the initial increase, the thickness of the material reduces in both cases. However, material removal in the WOM experiment is extremely high, in such a way that after 5000 h there was almost no material left on the substrate. Comparing WOM and Suntest air cell sample thicknesses and in the same time looking at the changes in the chemistry of the material, Figs. 8 and 9, one notices that the sharp decay in thickness for the WOM experiment is not only due to the evaporation of the volatile compounds which form as a result of degradation. As an illustrative example, for instance, the coating after around 1400 h of degradation in the WOM has more or less the same FTIR spectrum as the coating exposed for 6000 h in the Suntest air cell, see Figs. 8 and 9. However, the WOM sample has lost 20% of its initial thickness while the thickness of the Suntest air cell sample has dropped only by 4%. This difference can be rationalized by the fact that in the WOM, degraded material is removed by water during wet cycles as a result of the water spray. Moreover, this material removal becomes more severe as weathering proceeds, more urethane bonds break and cross-link density drops. Note that the FTIR analysis of the extracted material shows that the material washed out is not essentially different from the degraded material. Note that the washing away of photooxidation products has been reported in the literature as well [40].

It is also worth noting that the drop in the thickness of Suntest air cell samples starts after around 2200 h of exposure and reaches a plateau after 5500 h. Looking at Fig. 9 graph e, one notices that in the same range of exposure time, a significant drop in the urethane band takes place (drops by 80%). Due to the oxidative pathway of urethane bond scission, one can explain that during this period, a considerable amount of volatile compounds, e.g., carboxylic acids, alcohols and carbon dioxide, form and evaporate from the coating. The fact that, on the one hand, this thickness decay stops by the time in which almost no urethane bond scission takes place and on the other hand, the ester bond scission proceeds even with higher rates after this time, is another confirmation of the predominantly photolytic mechanism for ester bond scission.

Finally, it should be noted that this study is not in disagreement with the current industrial practice in which the cross-linked polyester-urethane coatings are known to be highly durable: the widely spread use of HALS components in these films can be easily understood to be essential in prevention of the photo-oxidative degradation pathway of urethane bonds.

5. Conclusions

Quantitative transmission FTIR analysis of the weathering of PUC in aerobic and anaerobic as well as wet and dry conditions has been performed. The chemical moiety most sensitive to the weathering in aerobic conditions is found to be the urethane group. It shows the fastest degradation rate among all others. Comparing aerobic and anaerobic weathering results shows that urethane bond scission results from a photo-oxidative pathway. Most likely the oxidation reaction starts with hydrogen abstraction at the α -position of the nitrogen by other radicals, followed by hydroperoxide formation and β -chain scission. In contrast, the ester bond scission predominantly results from a photolytic mechanism.

The presence of urethane groups leads to a non-linear change in the ester and urethane bond concentration as a function of exposure time. For the PU coating, an initially-slow-rate period for both ester bond and urethane bond scission has been observed with the period for urethane bond scission being slightly shorter. After the urethane concentration is depleted, ester bond scission accelerates. The acceleration in ester bond scission is caused by the increase in the optical absorptivity of the coating which is most likely due to the formation of new chromophores, like biphenyl structures, that

seems to coincide with decomposition of the urethane derived hydroperoxides.

The evolution of thickness of the coating as a result of weathering, in different weathering condition, shows that both evaporation and water-caused removal of the coating result in material loss. However, the effect of water spray was found to be more pronounced. Moreover the material loss as a result of evaporation, in the absence of water spray, occurs in the period that urethane decomposition takes place and stops afterwards, while the ester bond scission proceeds with even higher rates. This confirms the photo-oxidative degradation pathway of urethane bonds and the photolytic degradation pathway for ester bond scission.

Finally, the PU coating was found to be highly resistant against hydrolysis reactions and thermal degradation in the absence of light.

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