Test Method

Comparison of different photo-oxidation conditions of poly(vinyl chloride) for outdoor applications

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Abstract

Four different PVC formulations, designed for outdoor applications, in the form of calendared films, were submitted to artificial accelerated ageing under different radiation sources, with and without water spray, and also to natural exposure. The influence of the different photo-oxidation conditions was evaluated by means of surface analysis using X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy. The photo-oxidation of PVC is well monitored by FTIR measurements by following the formation of oxidation products of the carbonyl type, which are due to radical attack on the double bonds in the molecular structure of PVC, and enhanced by radiation and temperature. Results show that relative rates of PVC degradation reactions are different under different photo-oxidative conditions. XPS results show that, in technical PVC formulations, the fraction of chloride ions trapped in the inorganic filler is a better parameter to measure the PVC degradation (measured by the yellowing index variation) than the total remaining (or lost) chlorine in the surface. When the ageing method includes water jets, the top superficial layers made from the inorganic filler and the organic products from the PVC degradation are removed and leave behind a much more homogeneous layer which is more resistant to ageing than the “as processed” one that contains defects introduced by the calendaring process. XPS also makes clear that zinc–calcium additive is a better thermal stabilizer than dibutyltin-maleate, and the presence of tinuvin P retards the PVC degradation. The best simulation of the natural weathering of such PVC materials under laboratory conditions needs to consider, besides the light, the intervention of water jets and/or humidity as well as the existence of light and dark periods.

1. Introduction

The ultimate user acceptance of poly(vinyl chloride) (PVC) products for outdoor building applications will depend on their ability to resist deterioration of their mechanical and aesthetic properties over long periods of exposure, which is only achievable by means of a careful compounding, always demarked by the nowadays environmental demands and quality requests.

The outdoor degradation of such compounds and the resulting final products is complex and not completely understood for most of the technical formulations. Therefore, the study of the photo-degradation of such products still remains a matter of interest.

Many degradation studies of PVC have been performed to test the best additives to minimize damage to the polymer under outdoor conditions. Those studies are usually performed using pristine PVC with a single or a mixture of thermal stabilizers, such as tin maleates [1–3], organic stabilizers [4–6] or calcium–zinc soaps together with organic co-stabilizers [7–9]. However, since industrial PVC products generally have an inorganic filler, studies in the
presence of that filler are also required and in this work its importance will be shown. Also, the most used analytical techniques are infrared spectroscopy and colourimetry, to assess the amount of formed (and destroyed) carbonyl groups and double bonds. The rate of dechlorination is usually measured by conductimetric titrations and by thermogravimetry [10]. This means that, usually, quantitative studies are much more concerned with the amount of chlorine leaving the surface than with the amount and the quality of the remaining chlorine. Other techniques used for degradation studies include Thermostimulated Depolarization Currents [11] and also mechanical tests [3,12]. In this work, by using X-ray photoelectron spectroscopy (XPS), a powerful surface specific technique for elemental analysis, the surface chemical composition of low thickness stabilized PVC calendered samples, after several ageing treatments, is fully studied and correlated to yellowing index variations. Complementary FTIR measurements during weathering of PVC films gave information about the PVC degradation reaction and respective stoichiometry.

In a previous work [13], we found that an initial period of xenon irradiation, without water spray, produces an unexpected phenomenon that minimizes the degradation and the effects of erosion, and avoids additive migration during subsequent artificial ageing with radiation and water. More recently [14], it was shown by means of XPS analysis, complemented by other techniques, that long irradiation periods induce a generalized degradation of the surface of PVC extruded plates, namely, loss of chlorine, and double bond and cross-link formation. Double bonds and cross-links induce shrinking of the surface material and consequent formation of a generalized network of micro-cracks all over the surface. This crack network enables its mechanical destruction by water jets or rain, uncovering a surface which is much more homogeneous and, hence, much more resistant to the ulterior action of radiation. When that previous long period (the minimum duration of this period is not yet well determined) of xenon irradiation is absent, or shortened, the mechanical degradation of the surface is mostly concentrated around defects (not generalized to the entire surface) and the erosion by the water is rather localized.

The main objective of this paper is to pursue the study of the influence of the weathering conditions on the degradation level of stabilized PVC products for outdoor applications [14], trying to go deeper in the understanding of the mechanism of both the degradation and the stabilization of the surface of different polymer formulations, processed by calendering. Finally, the ability of several different artificial weathering apparatus, using different photo-oxidative conditions, to simulate natural weathering is evaluated.

2. Experimental

2.1. Samples: compounding and processing

In this study, we used four different PVC formulations, designed for outdoor applications, containing calcium carbonate (CaCO₃), titanium dioxide (TiO₂) and other additives. Particular care was taken to select thermal stabilizers with acceptable ecotoxicological characteristics.

The PVC formulations are referred to as PVC CZ and PVC S, according to the type of thermal stabilizer present (respectively, based on calcium–zinc or dibutyltin–maleate). The formulations including additionally a benzotriazole type anti-UV additive (tinuvin P) are marked with a “T” (referred to as PVC CZT or PVC ST).

The compounding of the formulations was done at the Baquelite Liz Company (Portugal). The subsequent calendering was done at the Adreta Plásticos Company (Portugal). The calendered films were around 120 μm thick.

Five calendered films of each formulation were studied, each one submitted to a different photo-oxidation condition (see Sections 2.3 and 2.4). For control purposes, a non-aged sample (U) of each formulation was also studied by XPS, as well as the unexposed face of some of the naturally weathered samples (Un).

2.2. Experimental methods of analysis

An X-ray photoelectron spectrometer (XPS) XSAM800 (KRATOS) operated in the fixed analyser transmission (FAT) with a power of 120 W (10 mA and 12 kV) was used. All the other experimental conditions were as described elsewhere [14].

The colourimetric determinations were done as in Ref. [14] but in transmission mode, instead of reflection.

The FTIR determinations were performed in transmission mode, observing always the same area, using a spectrophotometer Nicolet Magna-IR 550 Series II, using 32 scans in the range 400–4000 cm⁻¹.

2.3. Artificial weathering

The artificially simulated weathering was carried out in four different chambers: an Aralab Fitoclima 600 EDTU equipped with 6000-W borosilicate glass-filtered xenon arc source (cut-off at 290 nm), an Atlas Weatherometer Ci 65, equipped with 6500-W borosilicate glass-filtered xenon arc source (cut-off at 290 nm), a Solar Box 3000 E, equipped with 2500-W borosilicate glass-filtered xenon arc source (cut-off at 280 nm), a Q-Panel QUV, equipped with four low-pressure Hg fluorescent lamps, with a maximum of emission at 313 nm (type 1). The samples AR were artificially aged in the Aralab chamber, for 5360 h of continuous irradiation, using circulating air with a relative humidity of (60 ± 5)%.

The samples AT were artificially aged in a continuous irradiation program performed in the Atlas chamber, for 3350 h of continuous irradiation with cycles of water spray for 18 min each 2 h, using circulating air with a relative humidity of (10 ± 5)%. The samples SB were artificially aged in a continuous irradiation program performed in the Solar Box chamber, for 4750 h of continuous irradiation without cycles of water spray, using circulating air with a relative humidity of (60 ± 5)%. The samples QUV were artificially aged in the Q-Panel QUV chamber, for 228 cycles of 8 h, each one comprising 4 h of continuous irradiation and 4 h in dark conditions, using circulating air with a relative humidity of (60 ± 5)% during the light period and (50 ± 5) during the dark period. Although all chambers...
are equipped with water filters, the quality of the water fluxing through the specimen and rack sprays was also controlled by means of a water purity meter. The intensity of radiation in all xenon chambers was self-adjusted to assure a global irradiation of 550 W/m², in the wavelength range from 290 to 800 nm. The intensity of the xenon radiation sources was frequently checked with calibrated 340 nm and 295–400 nm radiometers. To assure the correct temperature of the circulating air, a calibrated black standard thermometer sensor was used, which was maintained at 65 ± 5 °C during the irradiation periods. The maximum temperature measured on the exposed surface of the test piece was 53 °C.

The test pieces were placed in a similar position relative to the radiation source and the differences in the distribution of the weathering parameters were compensated by rotation of the cylindrical sample rack (in the case of Atlas and Aralab chambers) or periodic change of position of the lamps (in the case of QUV apparatus). In the case of Solar Box apparatus, the samples were randomly distributed after each periodic FTIR analysis. Photo-oxidation duration was different from method to method. The ageing was stopped when the oxidation level, measured by FTIR was different from method to method. The ageing was the degradation reactions.

2.4. Natural exposure

The specimens referred to here were exposed for 5.5 years from March 2001 to October 2006 to outdoor weathering in Lisbon, Portugal (severe climate [15]), in accordance with ISO 877, Method A [16], at an angle of 45°, facing South.

3. Results

3.1. Colourimetry

The yellowing index variation, $\Delta Y$, is an important parameter represented by a number calculated from spectrophotometric data which describes the change in colour of a test sample from clear or white toward yellow, and is most commonly used to evaluate colour changes in a material caused by real or simulated outdoor exposure.

Table 1 shows the final yellowing index, $Y$, and its variation, $\Delta Y$, for films prepared from all formulations and aged under several conditions.

The colourimetric data confirms that the greatest improvement, from the point of view of resistance to yellowing during weathering conditions, is generally achieved with the addition of tinuvin P to the formulations.

3.2. X-ray photoelectron spectroscopy

3.2.1. Qualitative studies

X-ray photoelectron spectroscopy analyses were performed on all the samples. The regions C 1s, Cl 2p and O 1s were acquired for 90 s each and the acquisition was repeated more than 33 times in order to follow the X-ray induced degradation of each sample. C 1s region presents mainly three peaks: one centred at 285 eV, assignable to aliphatic carbon and taken as reference for charge correction purposes; another one at 286.6 ± 0.2 eV, assignable to carbon bound to chlorine and to oxygen or nitrogen by single bonds; and a third one at 288.9 ± 0.2 eV, assignable mainly to carbon in carbonate ions but also to carbon in carbonyl groups. In Fig. 1, two typical C 1s regions are shown for films with formulation ST (but representative of all the other formulations) submitted to two different weathering conditions which yield surfaces with very different compositions as regards chlorine and calcium contents.

Cl 2p presents, for almost all the samples (the only exceptions are samples weathered in Atlas chamber), two doublets where the separation between the Cl 2p3/2 and Cl 2p1/2 was set to 1.6 eV. The first one is centred at 198.3 ± 0.2 eV, assignable to chloride ions and the second one is centred at 199.9 ± 0.2 eV and is assignable to chlorine bound to carbon. Fig. 2 displays the Cl 2p region for two typical cases: a sample where no Cl– exists (AtlasST) and another one where Cl– is the major form of chlorine (AralabST).

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Formulation</th>
<th>AR</th>
<th>AT</th>
<th>QUV</th>
<th>SB</th>
<th>N</th>
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<td>3</td>
<td>33</td>
<td>35</td>
<td>–7</td>
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<tr>
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<td>7</td>
<td>8</td>
<td>64</td>
<td>–2</td>
</tr>
<tr>
<td></td>
<td>CZT</td>
<td>40</td>
<td>–4</td>
<td>15</td>
<td>28</td>
<td>2</td>
</tr>
<tr>
<td>$\Delta Y$</td>
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<td>49</td>
<td>113</td>
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<tr>
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<tr>
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<td>56</td>
<td>56</td>
<td>73</td>
<td>51</td>
</tr>
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</table>

Fig. 1. XPS C 1s region for films with ST formulation submitted to two different artificial weathering procedures yielding different chlorine contents.

* – Peak assigned to sample holder contamination. Before the charge correction, it is at 285.5 eV.
The XPS oxygen peak is, with a few exceptions, well fitted with a single peak centred at 532.1 ± 0.3 eV, which is mainly assignable to oxygen in carbonate and in carbonyl groups. The only clear exceptions are samples weathered in the Atlas chamber, where a component around 533.15 ± 0.15 eV dominates the spectra. These are also the samples where a large amount of silica is found (see below); this last component is, hence, likely due to the silica oxygen contribution [17]. Fig. 3 shows the oxygen peak for the ST formulation for the same weathering conditions as in Figs. 1 and 2.

At the end of the analysis of the three main elements, another run was performed to analyse other elements present in the surface, such as silicon (Si 2p), calcium (Ca 2p), zinc (Zn 2p), tin (Sn 3d), nitrogen (N 1s) and sodium (Na 1s). Si 2p, Ca 2p, Zn 2p and Sn 3d XPS regions are doublets with energy separations of 0.61, 3.5, 23.1 and 8.7 eV, respectively. Si 2p3/2 is centred at 103.0 ± 0.2 eV. This binding energy is typical of silicon bound to oxygen as in silica. Ca 2p3/2 is at 348.0 ± 0.2 eV and is assigned to calcium carbonate (CaCO3). Zn 2p3/2 is centred at 1022.2 ± 0.2 eV and is present only in some of the CZT PVC samples. On the other hand, tin is present only in S PVC samples. Sn 3d5/2 is centred at 487.3 ± 0.2 eV and is attributed to tin in dibutyltin-maleate. N 1s is centred at 400.3 ± 0.2 eV and reveals just trace amounts. In the samples with the anti-UV additive (ST and CZT), this may be the source. In the samples S and CZ, no explanation was found for the presence of nitrogen. Some of the samples also present residual amounts of sodium.

### 3.2.2. Quantitative studies

In a preceding study performed on plates [14], several parameters were shown to be highly correlated with the degradation state of the surface: XPS Cl/C global ratio measured for samples freshly introduced in the chamber, decay of this same ratio over time, and the fraction of chlorine in the form of chloride ions, Cl−/Cl. In that study, it was verified that, generically, an inverse correlation was obtained between the yellowing index or the yellowing index variation and the Cl/C ratio, even if a few exceptions were also verified. In Fig. 4a, the same plot shows that, for the four formulations studied here, the number of exceptions to the inverse rule is rather large.

A better correlation exists with the Cl−/Cl ratio, as shown in Fig. 4b. Since the mechanism of yellowing is due to the breaking of Cl–C bonds and to the subsequent formation of conjugated π bonds, an inverse correlation between the yellowing index variation and the relative amount of chlorine in the medium should be expected. However, as already shown in the plates study, not all of the chlorine resulting from the degradation mechanism leaves the surface in the form of Cl2 or HCl. In the non-washed samples, the large amount of inorganic material present traps the atoms of chlorine in the form of chloride ions. Hence, the parameter Cl/C alone, without specifying its nature, is not a good one to test the degree of degradation of the surface. Conversely, the Cl− fraction correlates well with the yellowing index variation, confirming the origin of chloride ions and its trapping at the surface. This observation is once again confirmed by the study of these two parameters as a function of the ageing method used for the samples (Fig. 5).

In Fig. 5, it is evident that the Cl− fraction Cl−/Cl correlates better with the ageing method than the Cl/C parameter. It also confirms the conclusion reached through the yellowing index variation analysis: the tinuvin P additive is mainly responsible for resistance to the yellowing phenomenon. In a preceding paper [14], it was suggested that the trapping of chloride ions at the surface, resulting from degradation of Cl–C bonds, was due to the inorganic filler (mainly calcium carbonate) but no evidence for that
fact was presented. The systematic study of these films fully confirmed this hypothesis. In Fig. 6, the XPS atomic ratios of Ca/C for all the formulations, as a function of the ageing method, are presented.

Comparison of Fig. 5a with Fig. 6 shows that a clear correlation exists between both, giving strength to the suggestion. Concerning differences between ageing methods, the most striking observation concerns samples weathered in Aralab (AR) and Solar Box (SB), i.e. continuously irradiated, which have calcium and chloride ion contents much higher than the unweathered (U) or the unexposed face of the naturally weathered (Nun), showing that the irradiation induces a migration of Ca to the surface. This may be caused by the local increase of temperature, which increases the ion mobility. In samples weathered in the Atlas chamber, two of them present negligible amounts of calcium and chloride ions. This is the only chamber where a water jet exists, strongly suggesting that this water jet is responsible for the washing of calcium. Sample S weathered in the QUV chamber gives an intermediary behaviour. In this chamber, the main difference relative to the Aralab is that there are periods of light and darkness. Therefore, the accumulated energy on the surface during the 4 h irradiation is not enough to promote in sample S calcium diffusion as large as in the samples continuously irradiated (Aralab chamber). In the samples CZ based (CZ and CZT) and S with added tinuvin P, it seems that the irradiation for 4 h does not heat the sample enough for calcium diffusion activation. Therefore, the zinc–calcium additive is a better thermal stabilizer than the dibutyltin-maleate. In the samples weathered under natural conditions, whether because of a balance between the calcium diffusing toward the surface and the rain washing effect or, due to the limited periods of irradiation (less than 12 h in average), the activation energy for calcium migration is not reached, no enrichment in calcium at the surface is observed. The same pattern of diffusion/washing effect is observed in both Zn in CZ formulations and Sn in S formulations.

The detection of Cl\(^-\) as a degradation product gives strength to the hypothesis of an ionic mechanism [18] for polyene propagation involving ion pairs. The ion-pair mechanism is shown in Fig. 7 [reproduced from Ref. [18]].

**Fig. 4.** Yellowing index variation, \( \Delta Y_i \), for the aged samples as a function of global Cl/C ratio (a) and Cl\(^-\)/C ratio (b). Triangles are for CZ samples and squares for S samples. Full symbols are for samples with the tinuvin P (anti-UV) additive.

**Fig. 5.** XPS global Cl\(^-\)/C (a) and Cl/C (b) as a function of the ageing method. The unweathered (U) and the unexposed face of the naturally weathered sample (Nun) were also included for control. Triangles are for CZ samples and squares for S samples. Full symbols are for samples with the tinuvin P (anti-UV) additive.
However, in the presence of an inorganic filler, namely the CaCO₃, besides the HCl formation, Ca₂Cl and CO₂H₂ can be formed. This proves that the dehydrochlorination rate determination using a continuous potentiometric determination of the evolved HCl gas [19] may not tell the whole story about PVC dechlorination if ionic traps are present in the film, as is the case when an inorganic filler is present.

Fig. 8 shows that the sample richer in oxygen is also the most contaminated with silicon and, hence, most of the oxygen is bound to silicon, as already shown in the qualitative study of oxygen. It also shows that the Atlas chamber, the only one equipped with a water jet, is the most pollutant from the point of view of silicon, because in all formulations there is a maximum for the samples aged therein. Hence, silica is placed on the surface by the fluxing water coming, most likely, from the glass water container. From the observation of Fig. 8, we can conclude that the tinuvin P and calcium–zinc additives increase the silica retention at the surface.

The match between Fig. 8a and b fails, especially for samples weathered in Aralab and Solar Box chambers. This is due to the fact that these samples are richer than the others in Ca and, therefore, in CO₃²⁻: in those samples, oxygen is assignable mainly to silica and carbonates.

Concerning the comparison of the ageing method from the point of view of their ability to reproduce the natural one, the XPS parameters studied (Cl⁻/Cl and Ca/C) show that the methods that yield the most similar results to the natural ageing are the ones performed in Atlas and QUV chambers. Also, the analysis of the degradation induced by the X-ray used in XPS, measured by both the Cl/C and the Cl⁻/Cl ratios (Fig. 9), shows again that the samples displaying behaviour most similar to the ageing under natural conditions are the ones aged in Atlas and QUV chambers, although none of them has exactly the same behaviour.

An explanation for different trends in the curves was already given elsewhere [14]. Here we will emphasize just the similarities and differences between them. For the Cl/C ratios, the samples which present decreasing behaviour, besides the N sample (both for the exposed and the unexposed faces), are the AT and QUV samples. The unweathered (as processed) sample and the samples SB and AR present very stable Cl/C ratios after a large initial increase in the U sample and very slight increases in the other two samples. Since, as shown above, the ratio Cl⁻/Cl is a better parameter to measure the surface ageing, this ratio is shown in Fig. 9b. It clearly displays that the naturally weathered sample has intermediary behaviour between AT and QUV samples, confirming that both the washing effect of the water and the alternate periods of irradiation and dark play a role in the ageing mechanisms. The best chamber to simulate natural weathering should, therefore, combine these two characteristics. It is also worth commenting on the behaviour of the unexposed face of the naturally weathered sample: relative to the U sample, it has suffered successive heating and cooling since the ambient temperature has a large daily variation in Lisbon. However, the number of photons impinging on the unexposed face is much lower than on the exposed face, and the water which runs off from the other face does not have as severe a mechanical effect on the surface as it has on the exposed face. It displays similar behaviour to the QUV film, illustrating the strong effect of the heating and its frequency on the degradation.

### 3.3. FTIRS

The oxidation of PVC can be followed by FTIRS through the absorbance variation in the range 1600–1900 cm⁻¹ corresponding to the main formed groups: double bonds (between ~1600 and ~1680 cm⁻¹, isolated bonds absorbing at lower frequencies than conjugated bonds) and carbonyl groups (~1650 to ~1800 cm⁻¹). The absorbance variation in this range results from the PVC degradation (dehydrochlorination with the consequent formation of carbonyl groups) but also from the consumption of stabilizers during the ageing process. Therefore, the periodic measurement of the optical density variation, carried out by subtracting spectra of a given sample from the initial one, during the ageing process, is useful to compare the similarity or difference in the ageing effects induced by different methods. In this paper, FTIRS results will be used just to check the ability of the different ageing methods to simulate the natural weathering effects in terms of the above cited double bond and carbonyl formation. In Fig. 10 we compare the evolution of FTIRS spectra in
time for natural ageing (a), with ageing in the QUV chamber (b) and ageing in the Atlas chamber (c), the two artificial methods which by XPS studies were found to better simulate the natural ageing. In Fig. 11 the same evolution is shown for the other two artificial weathering methods: Solar Box (Fig. 11a) and Aralab (Fig. 11b).

All the spectra present three distinct bands, each one having several components. A band from 1600 to \(\sim 1680\) cm\(^{-1}\) where, among others, the isolated (at \(\sim 1630\) cm\(^{-1}\)) and the delocalized (\(\sim 1630\) cm\(^{-1}\)) C=\(\cdot\)C stretch are present. Another one ranging from \(\sim 1680\) to 1730 cm\(^{-1}\) peaking at 1712 cm\(^{-1}\) corresponding to carbonyl groups in an aliphatic neighbourhood. Finally, one from \(\sim 1730\) to \(\sim 1820\) cm\(^{-1}\) where carbonyl groups in the neighbourhood of C–Cl bonds appear. This coincidence of bands in all the weathering conditions means that different photo-oxidative conditions lead to the same PVC degradation reactions. However, the spectral modifications detected between different spectra also show that these reactions have different relative rates, resulting from the different photo-oxidative conditions.

In samples exposed to alternate periods of light and dark (natural and QUV chamber weathering), the ratio (conjugated double bonds/isolated double bond) keeps approximately constant in time, whereas in all the other samples, continually exposed to the radiation, that ratio increases. This confirms the observation made in XPS that the accumulation of energy in these samples is much lower than in the other ones producing, in this case, a lower concentration of excited species.

As regards the ratio carbonyl/double bond concentration, it is highest in samples where a water jet impinges in the surface (natural and Atlas chamber weathering) giving evidence to the role of water in the oxidation of double bonds to carbonyl groups.

For a better understanding of the differences originated by the role of the water in the degradation of the PVC samples, see for instance the Ref. [20], which showed that a strong yellowing of the PVC occurs under xenon irradiation, but that samples become white in the presence of water spray. Both phenomena are related to the competition between double bond and carbonyl formation, each
one leading to opposite effects in the aesthetic properties of PVC.

The whitening phenomenon results from the combined action of atmospheric agents in the PVC matrix, the water enhancing the catalytic photo-activity of titanium dioxide pigments, present in such compounds, which leads to a radical attack on any unsaturated bonds in the PVC responsible for the yellowing.

The observations made by means of FTIR spectra analysis confirm the conclusion reached by means of XPS studies that, to correctly simulate natural weathering, both alternate periods of light and dark and "rain" periods are needed.

Besides these comparisons of FTIR spectra at different photo-oxidation conditions, an analysis of the evolution rate of the magnitudes of optical densities at 1712 and 1640 cm\(^{-1}\), which corresponds to the maximum of the main FTIR bands, during weathering was also made. This analysis allows to conclude that QUV data shows more deviations then Atlas, particularly with change of formulation. Similar inconsistency was found with colourimetric parameters. These findings indicate that the radiation source is also very important in simulation weathering studies and confirms that xenon arc source continues to be the most representative artificial source of the sun's visible spectra.

As a future development, we are planning to perform a thorough peak fitting of several characteristic regions of FTIR spectra as a way to better evaluate the meaning of spectral modifications and to deepen our knowledge about the stoichiometry of the photo-oxidation reactions during weathering.

4. Conclusions

Combined XPS, FTIRS and yellowing index studies were performed on four different formulations of technical PVC films submitted to natural and different artificial ageing.

Correlation of XPS results with yellowing index variation makes clear that UV-absorbers greatly improve resistance to light, mainly in natural exposure conditions.

It also shows that, in technical PVC formulations, the fraction of chloride ions trapped in the inorganic filler is
a better parameter to measure the PVC degradation (from the aesthetical point of view) than the amount of total remaining (or lost) chlorine in the surface. This is a very significant point showing how important the inorganic filler can be in the PVC degradation mechanisms. As already shown in the plates study, not all of the chlorine resulting from the degradation mechanism leaves the surface in the form of Cl₂ or HCl. In the non-washed samples, the large amount of inorganic material present traps the atoms of chlorine in the form of chloride ions. Hence, the parameter Cl/C alone, without specifying its nature, is not a good parameter to test the degree of degradation of the surface. Conversely, the Cl⁻ fraction correlates well with the yellowing index variation, confirming the origin of chloride ions and its trapping at the surface. This observation is once again confirmed by the study of these two parameters (Cl/C ratio and Cl⁻ fraction) as a function of the ageing method used for the samples.

Evidence was also obtained suggesting that the irradiation induces a migration of calcium to the surface, and its washing by water jets present both in the natural weathering (rain) and in the Atlas chamber.

Both FTIRS, through the wavenumber range corresponding to double bonds and carbonyl groups, and XPS allow concluding that the best weathering conditions to simulate the natural one should not be limited to the radiation source, but should include also alternate periods of dark and light as well as water jets.

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