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The influence of weathering conditions on the properties of poly(vinyl chloride) for outdoor applications. An analytical study using surface analysis techniques

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Abstract

In the present work, four different PVC formulations, designed for outdoor applications, were submitted to artificial accelerated ageing under xenon light, without and with spray of water, and to natural exposure. The influence of the combined action of water and radiation was evaluated by means of surface analysis using XPS, SEM and colourimetry, permitting comparison of the results obtained under different exposure conditions. Results show that a long preliminary period of irradiation (~2000 h) before the exposure to water increases the resistance of PVC surfaces to weather conditions. The role of that initial irradiation period is to create an erodable layer made of shrunk "PVC" that had lost most of its chlorine atoms and, thence, creating a network of cracks. That layer loses easily adhesion to deeper layers due to erosive action of water spray. The more perfect uncovered surface is better at resisting the effect of radiation.

Keywords: Poly(vinyl chloride); Titanium dioxide pigments; Weathering; XPS; SEM; Colourimetry

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1. Introduction

The low cost and good performance of poly(vinyl chloride) products make this polymer very suitable for components of buildings, mainly in outdoor applications, such as window profiles, cladding and siding. The outdoor degradation of such products is complex and not completely understood for most of the technical formulations. Therefore, the study of the photo-degradation of such products under weather conditions still remains a matter of interest [1].

In previous works [2,3], it was shown by means of techniques of colourimetry and infrared spectroscopy, that there are high increases of conjugated double bonds and carbonyl formation during accelerated artificial ageing with continuous xenon irradiation. It was found that cyclic spraying of water during artificial ageing changes the stoichiometry of the degradation reactions in TiO_2 pigmented PVC formulations, inducing only a low increase

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in the conjugated double bonds and a medium increase in the carbonyl concentration. It was also found that the PVC samples studied did not show yellowing during 5 years of natural exposure, and there was only a very low increase in the carbonyl concentration. More recently, we found that an initial period of xenon irradiation [4], without spray of water, produces an unknown phenomenon that minimizes the degradation and the effects of erosion, and avoids additive migration, during subsequent artificial ageing with radiation and water. Indeed, samples irradiated with xenon light for 7000 h, using cyclic water spray only in the last 4350 h (AR/ARW samples), show a low constant concentration of unsaturation and carbonyl groups in the last 4300 h of irradiation [4]. Moreover, these samples show a better white appearance and less signs of weathering than samples weathered simultaneously in the same chamber, for 4350 h, using xenon light and cyclic spray of water (ARW samples), as can be seen in Fig. 1. These unexpected results stimulated the present work and the recourse to surface analysis techniques.

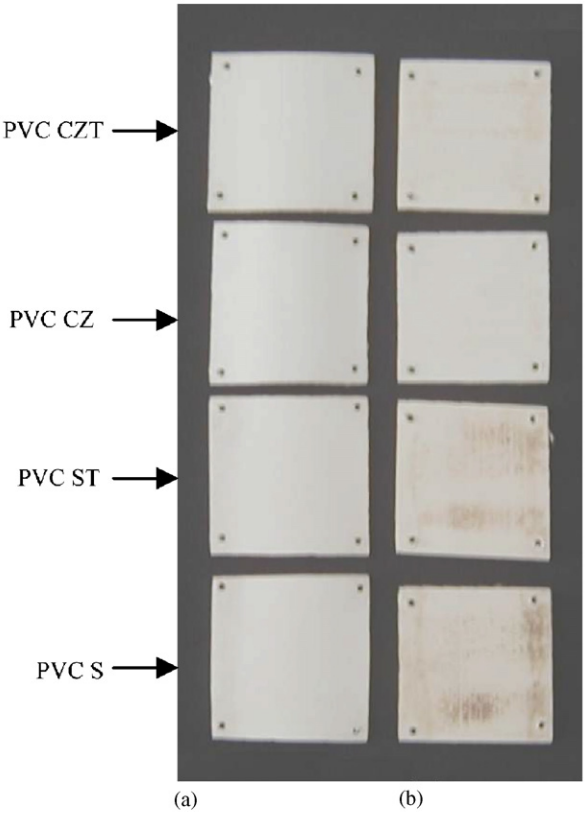

Fig. 1. Extruded plates of four TiO2 PVC composite formulations: (a) samples AR/ARW, irradiated with xenon light for 7000 h, using cyclic spray of water only in the last 4350 h; (b) samples ARW, irradiated with xenon light for 4350 h, using cyclic spray of water. For the definition of formulations, see the Experimental part.

In the present work, we have used X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and colourimetry to evaluate the influence of different photo-oxidation conditions on the surface degradation of stabilized PVC extruded samples.

XPS is a well-established technique that is very useful for surface characterization [5]. However, its application to insulating samples and particularly to halogenated polymers raises two major problems. One is the charge accumulation at the surface which has, as the major consequence, the need of using a neutralizing flood gun and/or finding a reference for correcting the charge shifts [5]. The other one is that the X-ray induces polymer degradation which, in halogenated polymers, is usually measured as a decrease in the halogen/carbon ratio as the irradiation time increases [6]. Nevertheless, charging effects in XPS have been used to good advantage by several authors [7,8]. Also, the degradation by X-ray can be used advantageously in the analysis of a polymer [9] and it will be used in this paper.

The main objective of this paper is to study the influence of the weathering conditions on the degradation level of stabilized PVC products for outdoor applications. The role of PVC formulation and of light and water were studied using artificial weathering with xenon irradiation. Results were compared with degradation induced by natural weathering in Lisbon, Portugal.

2. Experimental

2.1. *Samples: compounding and processing*

In this study, we used 4 different types of PVC formulations, which are designed for outdoor applications, containing calcium carbonate ($CaCO_3$), titanium dioxide (TiO_2) 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). Formulations including additionally a benzotriazole type anti-UV additive (tinuvin P) are marked with a "T" (referred to as PVC CZT and PVC ST).

The compounding of the designed formulations and subsequent extrusion was done at the Baquelite Liz company (Portugal). The extruded plates were around 1.5 mm thick.

Five extruded plates of each formulation were studied: non aged (U), 4900 h of continuous xenon irradiation without spray of water (AR), 7000 h of continuous xenon irradiation with spray of water only for the last 4350 h (AR/ARW), 4350 h of continuous xenon irradiation with spray of water (ARW), and submitted to natural exposition for 5 years (N). We also carried out several XPS determinations on the virgin PVC (PVC) and on some compounds (C).

2.2. *Experimental methods of analysis*

Samples were analysed by XPS under ultra high vacuum (UHV)—a pressure in the range of 10^{-7} Pa—using a XSAM800 (KRATOS) X-ray spectrometer operated in the fixed analyser transmission (FAT) mode, with a pass energy of 20 eV and the non-monochromatic AlKα X-radiation ($h\upsilon = 1486.7$ eV) with a power of 130 W (10 mA and 13 kV). They were analysed at room temperature at a take-off angle relative to the surface of 90°. The roughness of surfaces was too high for performing angle-resolved analysis. Spectra were collected with a step of 0.1 eV, using a Sun SPARC Station 4 with Vision software (Kratos). The curve fitting for component peaks was carried out with a non-linear least-squares algorithm using products of Gaussian and Lorentzian profiles. Sensitivity factors used were 0.25 for C 1s, 0.73 for Cl 2p, 0.66 for O 1s. These factors were provided by Kratos in the Vision software library and checked with several calibrating salts [10]. No charge compensation was used. Charge shifts were corrected using as reference the aliphatic carbon, C 1 s, with a binding energy BE = 285 eV as explained in the next section.

Samples were analysed by SEM using a JEOL JSM 6400, operating with an accelerating potential of 15 kV. The samples were previously coated with carbon, to assure their conductivity, using a Vacuum Evaporator JEOL-JEE-4x.

Samples were also analysed by colourimetry. The colourimetric determinations were done in the reflectance mode on the exposed side of the sample, observing always the same area, using a spectrophotometer HITACHI U3300 equipped with an integrating sphere. The specular component of the reflected light was included in the measurements.

The measured yellowness index is based on CIE standard illuminant D65 and CIE 1931 2° standard observer viewing.

2.3. *Artificial weathering*

The artificially simulated weathering was carried out in two different chambers: an Aralab Fitoclima 600 EDTU and an Atlas Weatherometer Ci 65, respectively, equipped with 6000 and 6500-W borosilicate glass-filtered xenon arc sources. The sample AR was artificially aged in the Aralab chamber for 4900 h (~970 MJ/m^2 of irradiation in the range 290–400 nm) of continuous irradiation, using circulating air with a relative humidity of (60 ± 5)%. The samples AR/ARW and ARW were artificially aged in a continuous irradiation program performed in the Atlas chamber. The program was subdivided into two periods with different exposure conditions: a first period of 2650 h (~525 MJ/m^2) of irradiation without spray of water and a second one of 4350 h (~852 MJ/m^2) with cycles of spray of water for 18 min every 2 h, using circulating air with a relative humidity of (10 ± 5)%. Although both chambers are equipped with water filters, an aquanizer and a deionizer cartridge, 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 both chambers was self-adjusted to assure a global irradiation of 550 W/m^2 in the wavelength range from 290 to 800 nm. The intensity of the radiation sources was frequently checked with both calibrated 340 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. 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 for by rotation of the cylindrical sample rack.

2.4. *Natural exposure*

The specimens to be tested were exposed for 5 years from March 2000 to March 2005 (~1450 MJ/m^2 of UV irradiation) to outdoor weathering in Lisbon, Portugal (severe climate [11]), in accordance with ISO 877:1994, Method A, [12], at an angle of 45°, facing South and were removed periodically to perform the several analyses described above.

3. Results

3.1. Scanning electron microscopy

The SEM produces images by scanning the surface of a specimen with an electron beam. Low energy secondary electrons produce a signal that is strongly influenced by topography. The backscattered electron signal is also sensitive to local topography, but it mainly enables the differentiation between different phases. Fig. 2A) contains the SEM images, resulting from backscattered electrons, of samples of PVCS not weathered and at the end of weathering performed under four different exposure conditions. Similar SEM images resulting from secondary electrons are presented in Fig. 2B).

SEM observations of unweathered extruded sample U revealed some localized defects resulting from processing, but the surface presents no significant discontinuities or flaws, whereas the exposed side of weathered samples revealed considerable change in texture and surface finish, relative to the unweathered sample.

After Xenon irradiation, the surface of sample AR becomes discontinuous, covered with a crack network, irregular and randomly branched. This sample presents more and deeper cracks than sample AR/RW submitted to an initial period of xenon irradiation. Moreover, the absence of visible cracks in the SEM image of the AR/RW sample, obtained with low energy secondary electrons (Fig. 2Bc), suggests that network cracked area of this sample, observed using the backscattered electrons mode (Fig. 2Ac), should correspond much more to boundaries between different phases formed as the result of accumulation of segregated additives, rather than surface cracks.

The sample ARW submitted to cycles of water from the beginning presents cracked areas and evidence of fast erosion originated by water, such as holes and channels, which are regions of lower density.

The sample N, exposed outdoors, presents some surface defects and signs of the erosion originated by rain, but the surface is more continuous and less degraded than in sample ARW.

SEM images obtained with secondary electrons reveal the significant differences between the state of the surface of sample AR/RW and the surfaces of other weathered samples. It is evident that the texture of the surface of the sample AR/RW, submitted to a previous period of xenon irradiation, has less signs of degradation induced by weathering than any other surface.

3.2. X-ray photoelectron spectroscopy

X-ray irradiation is known to induce degradation on halogenated surfaces [6,9]. This disadvantageous fact can be overcome and even give valuable information about the surface if a systematic study

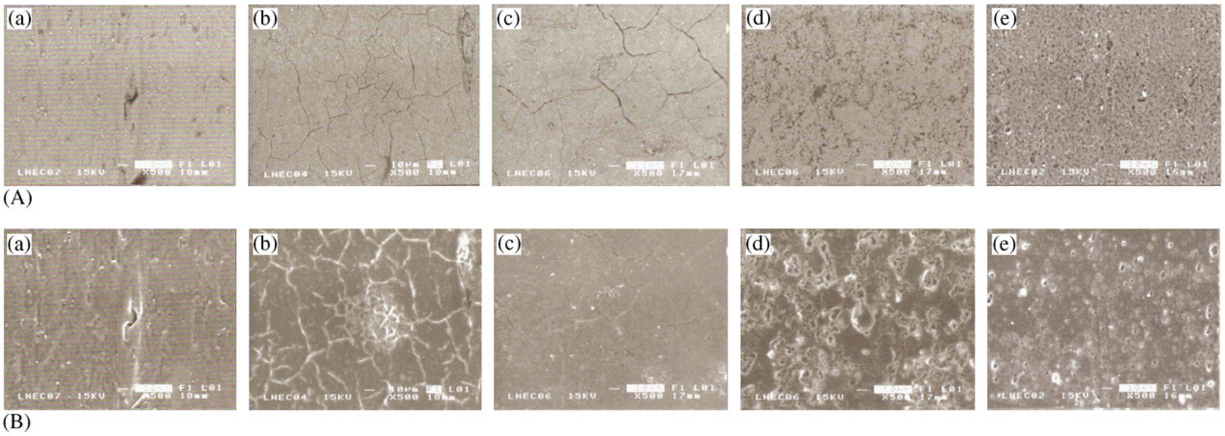

Fig. 2. SEM images of a PVC S (× 500): (A) backscattered electrons; (B) secondary electrons; (a) sample U, after processing, not weathered; (b) sample AR, irradiated with xenon light for 4900 h; (c) sample AR/RW, irradiated with xenon light during 7000 h, using cyclic spray of water only in the last 4350 h; (d) sample ARW, irradiated with xenon light for 4350 h, using cyclic spray of water; (e) sample N, submitted to natural exposure for 5 years.

of the degradation is performed. Carbon and chlorine XPS signals were then continuously measured 33–36 times for periods from 7700 to 8200 s. Another problem related with the use of XPS in the study of halogenated polymers is the choice of a reference for charging correction [5,9]. However, since the surface of the samples studied here revealed very poorly chlorinated surfaces (Cl/C$<$0,15 for all the samples), due to surface degradation during processing, the C 1s peak assignable to aliphatic component (BE = 285 eV) [13] was taken as reference. The carbon peak was fitted with 3 components at 285, 286.7$\pm$0.2 and 288.8$\pm$0.2 eV. The last one is assigned to carbonate [14]. The component at 286.7 eV is usually assigned to carbon bound to chlorine [15]. The chlorine peak was fitted with two components, each of them being a spin–orbit doublet. The Cl $2p_{3/2}$ components of each doublet were located at 198.3$\pm$0.2 and 200.2$\pm$0.2 eV, the first one being assigned to chloride ion and the second one to Cl bound to carbon [16].

Table 1 presents the XPS Cl/C ratio measured for samples freshly introduced into the XPS analysis chamber. These results show that the sample AR/RW, submitted to a previous period of xenon irradiation, presents an initial Cl/C ratio similar to the sample N, exposed to natural environment, and that this ratio is higher than in other weathered samples, which is consistent with a surface richer in PVC, i.e. to a higher concentration of chlorine.

The results obtained from sample C confirm also that the processing is very aggressive to the surface of PVC materials, due to thermo-oxidative degradation, which decreases the concentration of Cl at the outermost surface region. Similar degradation occurred during storage and blending of PVC compounds and during preparation of pressed pellets for XPS analysis. In fact, even the PVC film prepared from PVC pressed pellets presents a Cl/C ratio considerably lower than the expected 0.5, which is the stoichiometric ratio. Unweathered extruded samples present even smaller ratios (~0.02 to ~0.05).

The relation between Cl/C ratios and the yellowing index was also analysed. Both parameters obtained with the samples studied in this work, are presented in Fig. 3.

Since the mechanism of yellowing is due to the breaking of Cl–C bonds and to the subsequent formation of conjugated π bonds, there is an inverse correlation between the yellowing index and the relative amount of chlorine in the medium, as expected. However, during artificial weathering, a small influence of the thermal stabilizer is noticed: for the same Cl/C ratio, less yellowing is observed when the thermal stabilizer based on calcium/zinc is used. The ARW sample is an exception to the rule above, shown in the graphic as encircled points. The Cl/C ratio is kept low and the yellowing index is

Table 1
Cl/C ratio measured by XPS in various samples from different formulations: virgin PVC, formulated compounds, unweathered extruded plates and weathered under different conditions

	Formulation	Cl/C
CZ	PVC	0.23
	AR	0.04
	AR + RW	0.1
	ARW	0.01
	U	0.02
CZT	C	0.03
	N	0.13
	U	0.03
S	AR	0.02
	AR + RW	0.11
	ARW	0.02
	U	0.05
ST	N	0.11
	U	0.05
	C	0.02

Measurements were performed on samples freshly introduced in the chamber.

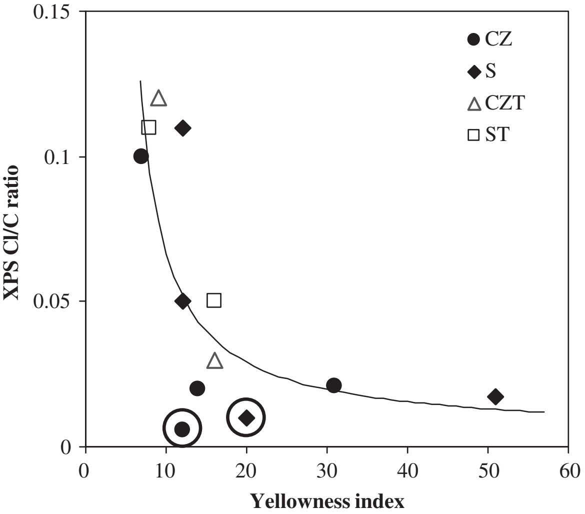

Fig. 3. Correlation between XPS Cl/C ratio and yellowness index. Encircled points concern the ARW sample.

also moderately low. The explanation for this will be given later.

Table 2 presents XPS atomic percentages for oxygen, calcium and tin relative to carbon for PVC S samples. These results show that sample ARW, submitted to cycles of water during xenon irradiation, presents much more oxygen than any other sample, suggesting that this element is inside the holes and channels formed by the erosive action of water in the form of entrapped oxygen or water. The results suggest also that tin thermal stabilizer segregates at the surface as a consequence of the prolonged action of xenon irradiation and it is not washed out by water.

The XPS results also suggest that the irradiation causes the accumulation of Ca^{2+} on the exposed surface, and this additive is then partially washed out by water action, as the calcium concentration is higher in weathered, unwashed samples. Indeed, there is more calcium in sample AR, submitted to continuous xenon irradiation without water, and less calcium in samples continuously irradiated with cycles of water (samples ARW and AR/RW). Finally, the less degraded samples present the lowest concentration of calcium, confirming what was mentioned before.

The high silicon concentration detected by XPS in all specimens was surprising. By means of a sequential analysis, we found that silicon was introduced in the processing and during artificial weathering, probably due to products used in the cleaning of blenders and extruders, and from silica present in water. These findings confirm that XPS can be used as a processing optimization tool, detecting undesirable contamination elements.

The degradation induced by X-ray irradiation is usually evaluated in PVC by means of the rate of decrease of the Cl/C ratio. The follow-up of that degradation may be very instructive about the mechanism of chlorine loss (under the form of HCl or Cl_2), during degradation. To attain this target, we performed some XPS experiments on the same virgin PVC that was used in our PVC formulations. As Fig. 4 shows, the Cl migration rate to the surface is lower than the Cl escape rate to the vacuum, since the net result is a decrease of the Cl amount at the surface.

Table 2
Initial Ca/C, Sn/C and O/C atomic ratios of a PVC S, measured by XPS in the unweathered extruded plate and in samples weathered under different conditions

	U	AR	ARW	AR/ARW	N
O/C	0.15	0.19	0.99	0.28	0.21
Ca/C	0.002	0.013	0.006	0.003	0.003
Sn/C	0.001	0.002	0.003	0.005	0.001

The kinetics of chlorine decrease follows an exponential law of the type $Cl/C = a\exp(-kt)$ and the value of k equals $7.0 \times 10^{-3}\,min^{-1} = 1.1 \times 10^{-4}\,s^{-1}$ within the expected range for pristine PVC [6].

In addition to the total amount of chlorine, it is also interesting to know how the XPS spectra of PVC elements (C 1s and Cl 2p) change during irradiation (Fig. 5).

Initially, we have, in the C 1s region, components due to CO, C–Cl, C–C and CH_2 groups, and only one Cl component (Cl–C), the doublet $2p_{3/2}$ and $2p_{1/2}$. At the end, the C 1s region is enriched in the CH_2 and C–C components, and the one corresponding to the C–Cl bond, as well as the intensity of the chlorine peak, decreased, as should be expected by the known "unzipping" mechanism of PVC degradation.

We also performed similar XPS measurements on the various PVC formulated compounds (C). The results are presented in Figs. 6 and 7.

From Fig. 6, it can be seen that the evolution and whole quantities of Cl/C and C/O ratios are similar in both compounds, but completely different from those obtained from PVC resin: Cl/C ratio increases during X-ray irradiation instead of

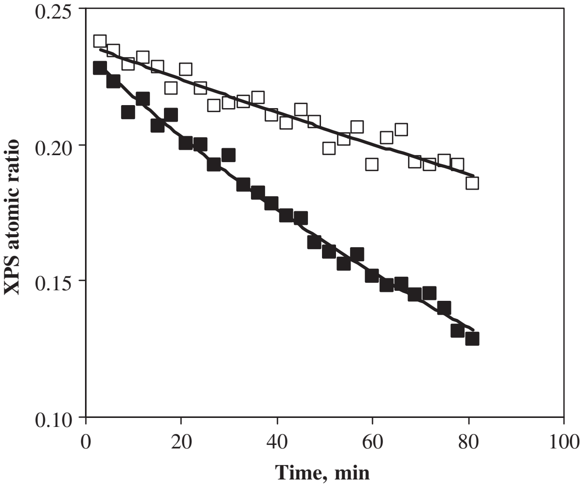

Fig. 4. Evolution of Cl/C (full symbols) and O/C (empty symbols) ratios of a virgin PVC, during XPS irradiation. Fitted lines are $(Cl/C) = 0.23\exp(-0.007t)$ and $O/C = 0.24\exp(-0.0028t)$.

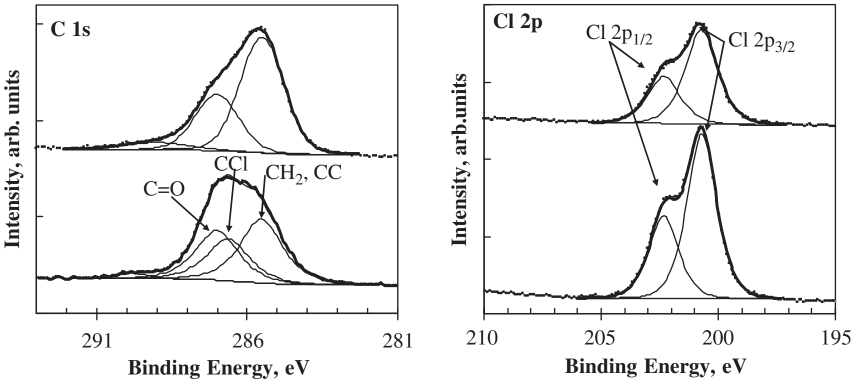

Fig. 5. Initial (bottom) and final (top) bands of a virgin PVC, for C 1s and Cl 2p XPS regions.

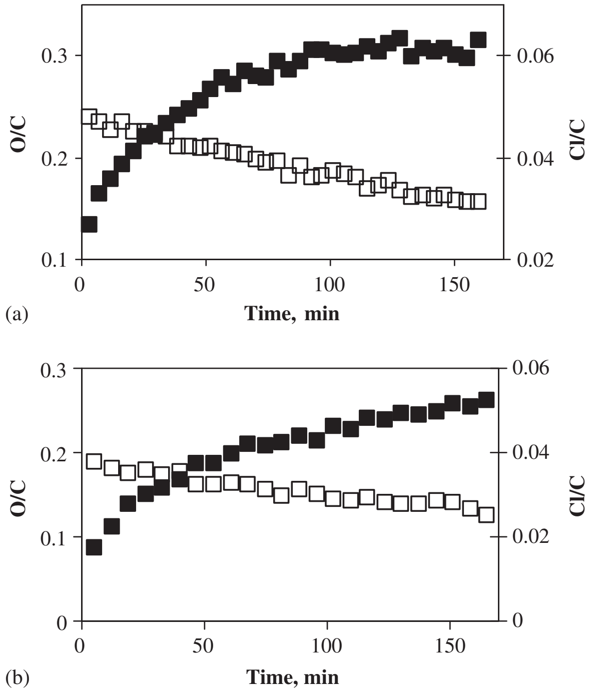

Fig. 6. Evolution of Cl/C (full symbols) and O/C (empty symbols) ratios of two stabilized PVC compounds, during XPS irradiation: (a) PVC CZT; (b) PVC ST.

decreasing. This can be explained if chlorine, resulting from the C–Cl bond breaking, has a migration rate to the surface higher than the escape rate to the vacuum. Therefore, some of the chlorine migrating from the interior of the sample remains trapped near the surface. XPS spectra of the Cl 2p region, similar for both compounds, show that the chlorine trapped at the surface is in the form of chloride ions. Fig. 7 displays initial and final spectra for PVC with ST formulation. It presents many differences from spectra of virgin PVC: initially there are two components in the Cl peak (two doublets): Cl^- and Cl–C. At the end of irradiation there is only one doublet: the Cl^- species. Thence, the bound chlorine peak decreases and the chloride ion peak increases.

Concerning the different PVC formulations, after extrusion, but not yet weathered, we performed also similar XPS measurements. Typical results, for two formulations, are presented in Figs. 8 and 9.

From Fig. 8, it can be seen that the evolution of Cl/C ratio is similar in both extruded formulations (Ca/Zn or DBTM stabilized) and also similar to the results obtained from PVC compounds.

However, the spectra are still different from compounds and virgin PVC: There is the same number of components in the Cl peak before and after X-ray irradiation: bound Cl and Cl^-. The bound chlorine peak decreases and the chloride peak increases with irradiation time.

Finally, in the case of weathered samples, we found both kinds of behaviour (Fig. 10).

Taking as an example the tin stabilized samples, the XPS results show that the behaviour of AR/RW and N samples is different from other weathered and unweathered processed samples as regards the Cl/C ratio. In fact, its initial value is much larger than in the other samples, and its evolution during XPS irradiation is also different. For those two kinds of samples the Cl/C ratio decreases following a kinetics of the type $Cl/C = a + b\exp(-kt)$ with $a \approx 0.03$ and $k = 1.4 \times 10^{-4}\,s^{-1}$ for AR/ARW sample and $1.7 \times 10^{-4}\,s^{-1}$ for the N sample. Moreover, the XPS Cl 2p region (not shown) exhibits a main doublet corresponding to Cl–C and a minor doublet corresponding to Cl^-. This means that in these two samples there are two phenomena: chlorine from

C–Cl broken during X-ray irradiation is released from the sample, probably as Cl_2 or HCl, and a part of it, under the form of Cl^-, is trapped at the surface and is responsible for the constant term (a) in the kinetics equation, absent in the pristine PVC. In the other samples, only the phenomenon of transformation of chlorine into chloride trapped at the surface is observed. Natural traps for the chloride ions are the cations belonging to the inorganic charge existing in the compound. In the absence of water spray, the superficial layer made of this inorganic charge together with the polymer made deficient in chlorine during the processing, is thick enough both to decrease dramatically the release of broken Cl and to attenuate the Cl photoelectrons coming from deeper layers. As a consequence, XPS Cl/C ratios are very low and increase with the X-ray irradiation time due to the increase of the Cl^- component corresponding to Cl^- migrating from the interior. The subsequent action of the water (AR/ARW) is to remove most of this layer which is full of cracks and thence has a very low mechanical resistance. In doing so, the uncovered new layer is much freer of defects, its composition is close to the oxidized pristine PVC and, thence, it degrades with X-ray irradiation in a similar way. The difference is that, due to the existence of the inorganic charge, a few chlorine atoms remain trapped at the surface under the form of Cl^- as mentioned above.

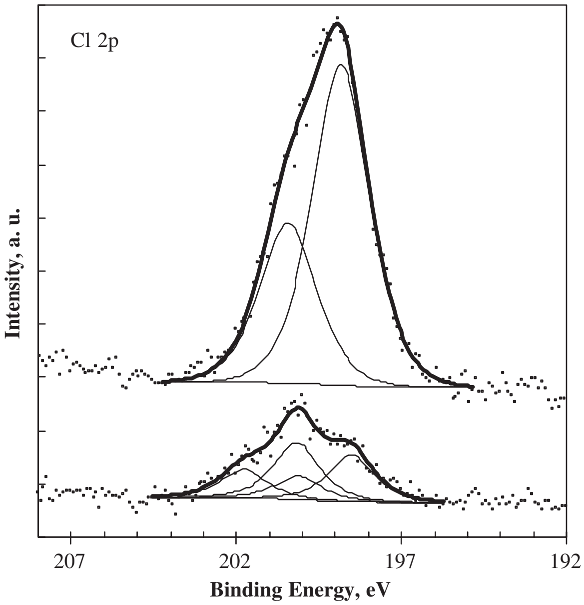

Fig. 7. Initial (bottom) and final (top) Cl 2p bands of stabilized PVC compounds, ST formulation during XPS irradiation.

An interesting case is the one of sample ARW: this sample was irradiated continuously and every 2 h was washed for 18 min. Its difference from the AR/ARW is that there is no initial long period (~2000 h) of irradiation. This difference has a dramatic impact on the yellowness index (see Fig. 1), on the topography (see Fig. 2) and on the Cl/C ratio (see Fig. 10). In fact, this sample presents simultaneously a moderately low yellowness index (behaving almost like the AR/ARW sample), but a very low Cl/C ratio (behaving as the sample AR, which is not washed at all). However, its

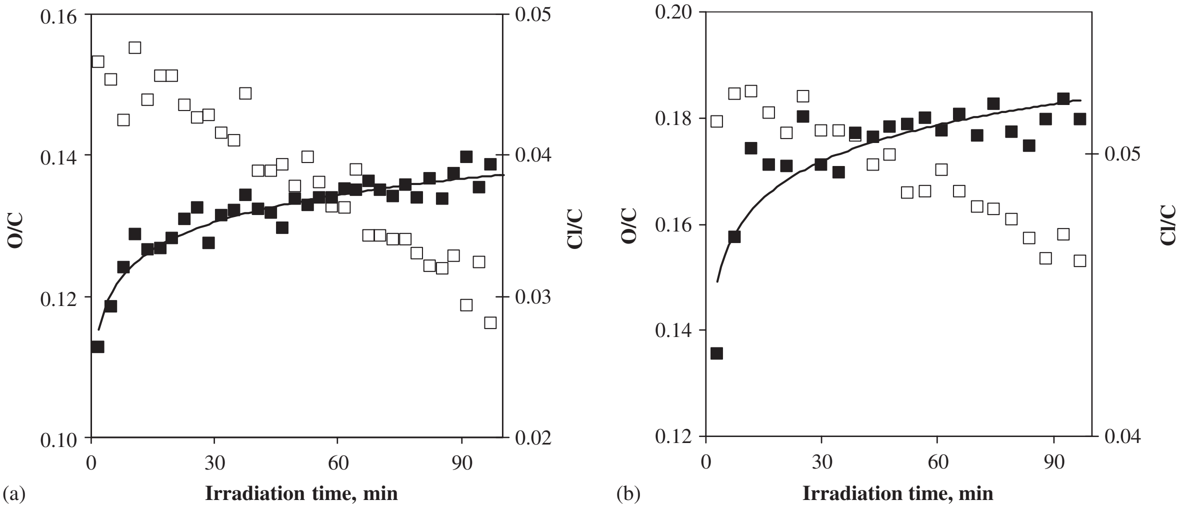

Fig. 8. Evolution of Cl/C (■)and O/C (□) ratios of two stabilized PVC extruded plates, not yet weathered, during XPS irradiation: (a) PVC CZT; (b) PVC S. Lines serve as eye-guides and are logarithmic functions.

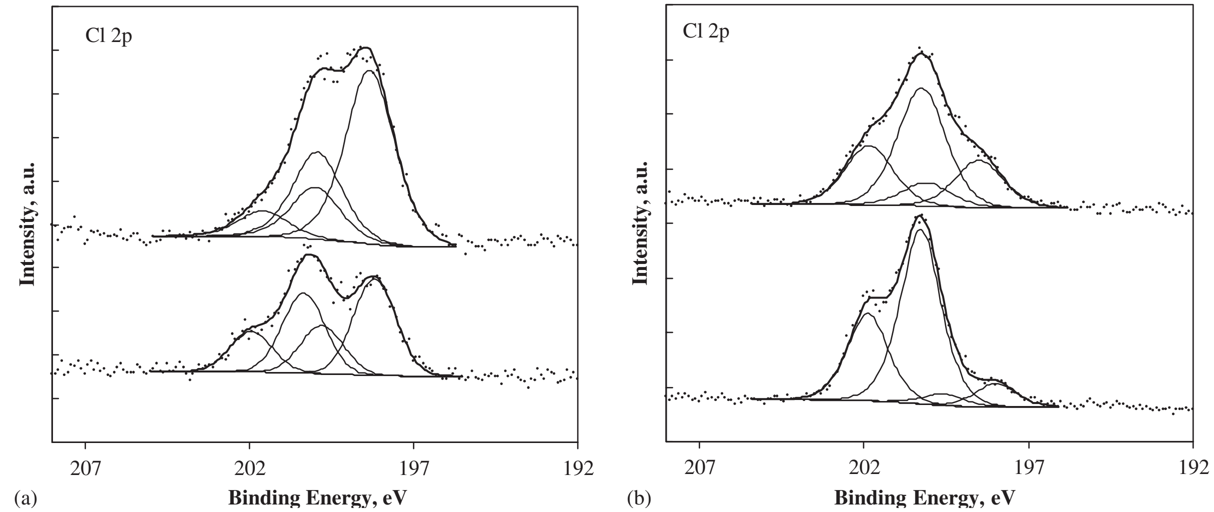

Fig. 9. Initial (bottom) and final (top) XPS Cl 2p region for two stabilized PVC extruded plates, not yet weathered, during XPS irradiation: (a) PVC CZT; (b) PVC S.

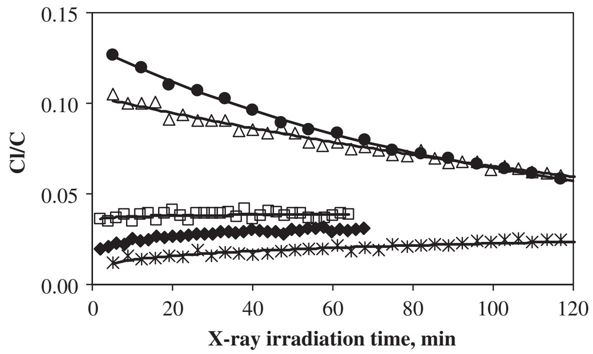

Fig. 10. Evolution of Cl/C ratio of the unweathered extruded PVC S and weathered PVC S samples, during X-ray irradiation. U (◆)$y = 0.018t^{0.13}$; AR/ARW(△) $y = 0.033 + 0.073 \exp(-0.0083t)$; AR (□) $y = 0.036t^{0.019}$; ARW (∗) $y = 0.008t^{0.226}$; N(●) $y = 0.029 + 0.103 \exp(-0.011t)$.

topography is completely different. This is compatible with the following explanation: an irradiation of ~100 min only causes degradation of the points which have already an excess of energy (defect points); no network of cracks is formed. When the water impinges on the surface, only these points are attacked by water which enters the surface and remains entrapped in the small cracks created by the formation of double bonds. The oxygen for these sample presents the highest mean binding energy (>533 eV), confirming the higher content of water in the sample. However, most of the outer layer is not removed. Therefore, the layers not yet degraded are not uncovered and the Cl/C ratio is the same (even smaller, because the entrapped water contributes to attenuate the XPS chlorine signal from the interior) as the one for the processed, unweathered (U) sample. The Cl/C ratio on the sample which is just irradiated is slightly higher than in the U sample, due to the migration of Cl^- ions to the surface during irradiation. In the ARW, this migration must also exist but there is a dilution effect due to the entrapped water. Therefore, an initial period of irradiation long enough to form a thin but complete network of cracks extending over the entire surface is needed so the water can remove it by erosion. The new uncovered surface is much more uniform and the activation energy to break Cl–C bonds increases so much that the surface becomes very stable to the Xenon lamp radiation. The few double bonds $C=C$ resulting from broken Cl–C bond are restored in the form of $C=O$ or C–OH groups and washed out by the water spray. Samples aged under natural conditions (N) behave in a way qualitatively similar to the AR/ARW sample due to the long periods of intense solar irradiation without rain.

The evolution of the Cl/C ratio of PVC plates stabilized with calcium/zinc, during X-ray irradiation, is similar to the one exhibited by PVC plates stabilized with tin maleate.

4. Conclusions

The initial Cl/C ratio, measured by XPS at the beginning of X-ray irradiation, agrees well with the yellowing index of weathered samples, measured in previous works. Basically, high yellowing indices correspond to low Cl/C ratios and vice versa, as expected.

The SEM and XPS results also agree well with previous findings, obtained by FTIR spectroscopy, and are compatible with the following ageing mechanism:

1. Long irradiation periods induce a generalized degradation of the surface, namely, loss of Cl, 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 process is very slow and therefore a period of 2 h (initial irradiation period in ARW sample) is not enough for it to occur.
2. The first action of water consists of the formation of oxidation products, mainly of carbonyl type (C=O), originated by OH* radical attack on any unsaturation in the polymer, due to photo-activity of TiO_2 pigments in the presence of water, resulting in whitening of the surface [3].
3. The subsequent action of water consists essentially of the removal of this low adhesion defect-region overlayer (by erosion), uncovering deeper, more uniform regions of the sample, richer in Cl bound to carbon, having less conjugated double bonds (lower yellowness index). This region, poorer in defects, is not as easily degraded as the initial surface that presents a larger amount of weak points.
4. When that previous long xenon irradiation period is absent or shortened, the mechanical degradation of the surface is still concentrated around defects (not generalized to all of the surface) and the erosion by the water is mostly localized. However, the effect on the double bonds still exists, decreasing the yellowing. Also the Cl/C ratio is kept low since the removal of the entire superficial layer, uncovering rich chlorine regions, does not occur.

Other XPS findings were that the XPS technique might help to improve the polymer processing because it enables an elemental chemical analysis. This allows measurement of degradation levels of PVC compounds induced by the various stages of processing (by means of Cl/C and O/C ratios) and, therefore, to optimize the formulation before starting the production at an industrial scale. Also, the contamination levels can be evaluated. For instance, in this work, we have shown that silicon is introduced during processing and during artificial irradiation, probably by water.

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