

# AGEING OF PVC FOR OUTDOOR APPLICATIONS: ROLE OF WATER AND INORGANIC FILLERS

L.E. Pimentel Real<sup>1</sup>, A.M. Ferraria<sup>2</sup>, A.M. Botelho do Rego<sup>2</sup>

<sup>1</sup>Laboratório Nacional de Engenharia Civil, Departamento de Materiais, Núcleo de Materiais Orgânicos, Av. do Brasil, 1700-066 Lisboa, Portugal

<sup>2</sup>Centro de Química-Física Molecular (CQFM) and IN, IST, Technical University of Lisbon, Complexo Interdisciplinar I., Av. Rovisco Pais, 1049-001 Lisboa, Portugal

## Abstract

In most of polymer ageing studies conducted at laboratory, there is a trend to underestimate some of the parameters involved in natural exposure, leading to poor simulation results and low reliability of the real world phenomena. Moreover, the nature of polymer and its formulation should be taken into account due to possible synergies and antagonisms between environment and polymer additives. Among the underestimated parameters, we can stress the role of ambient humidity and inorganic fillers. These additives are usually considered to be inert regarding the degradation induced by radiation.

In this work, four different PVC formulations, designed for outdoor applications, in the form of calendered films were submitted to artificial accelerated ageing under different radiation sources, without and with spray of water, and to natural exposure. The influence of the different photo-oxidation conditions was evaluated by means of X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (FTIRS).

The photo-oxidation of PVC can be studied by FTIR measurements following the formation of oxidation products of carbonyl type, due to radical attack to the double bonds in the molecular structure of PVC, enhanced by radiation and temperature. Results have shown 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 ion trapped in the inorganic filler is a better parameter to measure the PVC degradation (measured by the yellowing index variation) than the amount of total remaining (or lost) chlorine in the surface. When the ageing method includes water jets, the top superficial layer made from the inorganic filler and the organic products from the PVC degradation is removed and leaves behind a much more homogeneous layer which is more resistant towards ageing than the "as processed" one that contains defects introduced by the calendering process. XPS also makes clear that zinc-calcium additive is a better thermal stabilizer than the dibutyltin-maleate and the presence of the tinuvin P retards the PVC degradation. The best

simulation of the natural weathering of such PVC materials in 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 suitability of poly(vinyl chloride) (PVC) products for outdoor building applications will depend on their ability to resist the deterioration of their mechanical and aesthetic properties over long periods of exposure.

As natural exposure are long term tests, it is important to simulate natural weathering in laboratory, by means of artificial accelerated ageing methods. However, it is difficult to reproduce the climatic parameters, due to their variability with geographical location and their permanent changes along time, even for the same geographic site. Moreover, it is known that the success of this task is also dependent on the polymer to be considered, as well as on the additives present in its composition, and on the property to be measured for evaluation of the polymer degradation. The multiple effects of all parameters enhance the difficulty of conducting a reliable simulation. So, for each polymer and formulation, it is important to check the reliability of the results from artificial ageing, by comparison with reference data from natural exposure.

In the previous conference, results based on FTIRS and tensile tests, concerning the influence of the ageing conditions in the durability of stabilized PVC, designed for outdoor applications were presented. The comparison between the properties of different formulations, submitted to artificial accelerated weathering and natural exposure, was than strongly supported by kinetics and statistical analysis and had taken into account the role of the degradation agents and the influence of the additives present in the formulations, as well as the relationship between the properties at macroscopic and molecular levels.

The main objective of the present paper is to summarize the most relevant conclusions recently obtained with the same PVC formulations above referred, submitted to several photo-oxidation conditions, but now using, mainly, X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (FTIRS).

## **2. Previous Findings**

It was shown in some previous works [1, 2], by means of techniques of colourimetry and infrared spectroscopy (FTIRS), that there are high increases of

conjugated double bond and carbonyl formation during time of accelerated artificial ageing with continuous xenon irradiation. However, we found that the same PVC formulations did not show yellowing during eight years of natural exposure, and there was only a very low increase in the carbonyl concentration.

SEM images of PVC extruded plates, allowed to reveal the significant differences between the state of the surface of samples submitted to different photo-oxidative conditions [2, 3]. It was also evident that the texture of the surface of the sample submitted to a previous period of xenon irradiation, without spray of water, has less signs of degradation induced by weathering than any other surface. This phenomenon is due to a more uniform distribution of defects on specimen surface, which minimizes the internal degradation and the effects of erosion, and avoids the additive migration, during posterior artificial ageing with radiation and water.

It was shown by XPS that initial Cl<sup>-</sup>/C ratio, measured at the beginning of X-ray irradiation, agrees well with the yellowing index of weathered samples [4, 5]. Basically, high yellowing indices correspond to low Cl<sup>-</sup>/C ratios and vice-versa, as expected. Correlation of XPS results with yellowing index variation parameter had shown that UV-absorbers greatly improve resistance to light, mainly in natural exposure conditions [3].

The SEM and XPS results also agree well with previous results from FTIRS, and are compatible with the following ageing mechanism [4]:

1. Long irradiation periods induce a generalized degradation of the surface, namely, loss of Cl and consequent double bond and cross-link formation. Double bonds and cross-links induce the 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 it needs a long period of irradiation to occur.
2. The first action of water consists in the formation of oxidation products mainly of carbonyl type (C=O), originated by OH\* radical attack to any unsaturation in the polymer, due to photo-activity of TiO<sub>2</sub> pigments in the presence of water, resulting in whitening of the surface.
3. The subsequent action of water consists essentially on 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 long period is absent or shortened, the mechanical degradation of the surface is still concentrated around defects (not generalized to all surface) and the erosion by 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.

We found also that XPS helps to optimize the formulation before starting the production at an industrial scale, because XPS allows measurement of degradation levels of PVC compounds induced by the various stages of processing (by means of Cl/C, Cl<sup>-</sup> fraction and O/C ratios) [2, 4]. Also the contamination levels at each stage of production or testing can be evaluated and its source detected.

### 3. Experimental

In this study, we used 4 different types of PVC formulations, which are designed for outdoor applications, containing calcium carbonate (CaCO<sub>3</sub>), titanium dioxide (TiO<sub>2</sub>) and other additives, in the form of calendered films around 120 μm thick. The PVC formulations are referred to as PVC CZ and PVC S, according to the type of thermal stabiliser 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).

Other details about compounding and processing, as well as about experimental methods of analysis, can be found elsewhere [4, 5].

The specimens were exposed for 5.5 years from March 2001 to October 2006 to outdoor weathering in Lisbon, Portugal (severe climate [6]), in accordance with ISO 877, Method A [7] at an angle of 45°, facing South.

The artificially simulated weathering was carried out in four different chambers: an Aralab Fitoclima 600 EDTU equipped with 6000-Watt borosilicate glass-filtered xenon arc source (cut-off at 290 nm), an Atlas Weatherometer Ci 65, equipped with 6500-Watt borosilicate glass-filtered xenon arc source (cut-off at 290 nm), a Solar Box 3000 E, equipped with 2500-Watt borosilicate glass-filtered xenon arc source (cut-off at 280 nm), a Q Panel Q-U-V, equipped with four low-pressure Hg fluorescent lamps, with a maximum of emission at 313 nm (type 1). The ageing conditions used for each chamber are indicated in Table 1. Information about irradiation and temperature

control, as well about other details concerning other experimental conditions used, is indicated elsewhere [5].

*Table 1: Set of photo-oxidative conditions*

<b>Photo-oxidative condition</b>	<b>Irradiation Source</b>	<b>Cyclic spray of water and relative humidity of air</b>	<b>Dark Period</b>	<b>Time of weathering</b>
ATLAS (AT)	Continuous 6500 watt borosilicate-quartz filtered xenon arc	18 min each 2 hours; Hr = $60 \pm 5\%$	No	3350 h
ARALAB (AR)	Continuous 6000 watt borosilicate-quartz filtered xenon arc	No; Hr = $60 \pm 5\%$		5360 h
SOLAR BOX (SB)	2500-Watt borosilicate glass filtered xenon arc	No; Hr = $60 \pm 5\%$		4750 h
QUV 313 (QUV)	313 nm low-pressure mercury vapour	No; Hr = $50 \pm 10\%$	4 h each 12 h with condensation	910 h
LISBON (N)	Sun	Natural rain and dew	Yes (night)	5,5 years

In spite of the duration of photo-oxidation to be different from method to method, the ageing was stopped when the oxidation level, measured by FTIR analysis in carbonyl domain, was high enough to make kinetic data analysis and follow the degradation reactions.

#### 4. Results

Figure 1a, shows a plot of yellowing index variation,  $\Delta Y_i$ , as a function of XPS Cl/C global ratio for the four formulations here studied. Since the mechanism of yellowing is due to the breaking of Cl–C bonds and to the subsequent formation of conjugated  $\pi$  bonds, an inverse correlation between the yellowing index variation and the relative amount of chlorine in the medium should be expected. However, the number of exceptions to the inverse rule is rather large.

A better correlation exists with the  $Cl^-/Cl-C$  ratio, as shown in Figure 1 b). In the non washed samples, the large amount of inorganic material there present traps the atoms of chlorine under the form of chloride ions. Thence, the parameter Cl/C alone, without specifying its nature, is not a good parameter to test the degree of degradation of the surface. Inversely, the  $Cl^-$  fraction, correlates well with the yellowing index variation confirming the origin of chloride ions and its trapping at the surface.

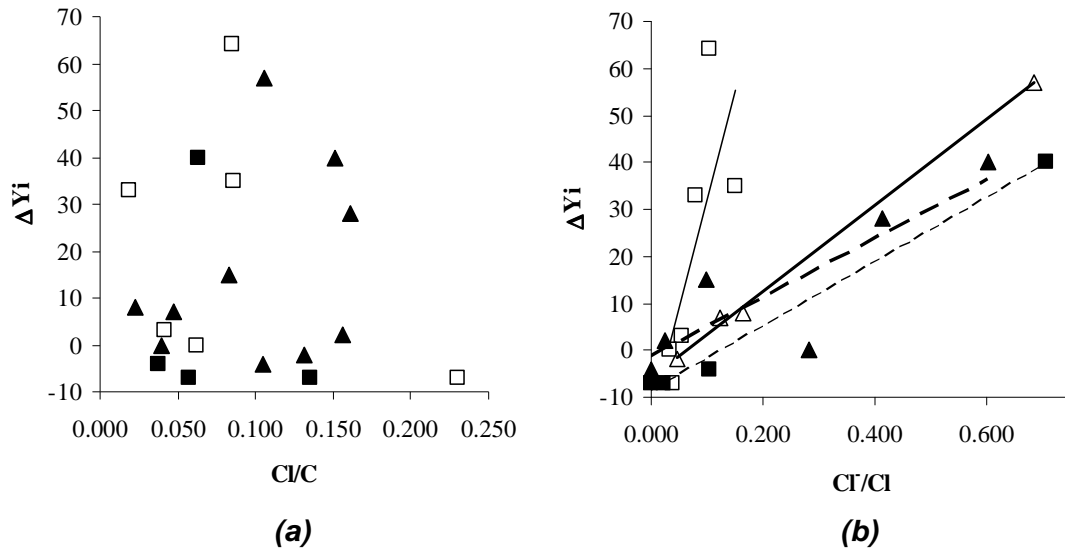


Figure 1 – Yellowing index variation,  $\Delta Y_i$ , for the aged samples as a function of global Cl/C ratio (a) and Cl/Cl ratio (b). Triangles are for CZ samples and squares for S samples. Full symbols are for samples with the tinuvin P (anti-UV) additive.

This observation is once again confirmed by the study of these two parameters as a function of the ageing method used for the samples (Figure 2).

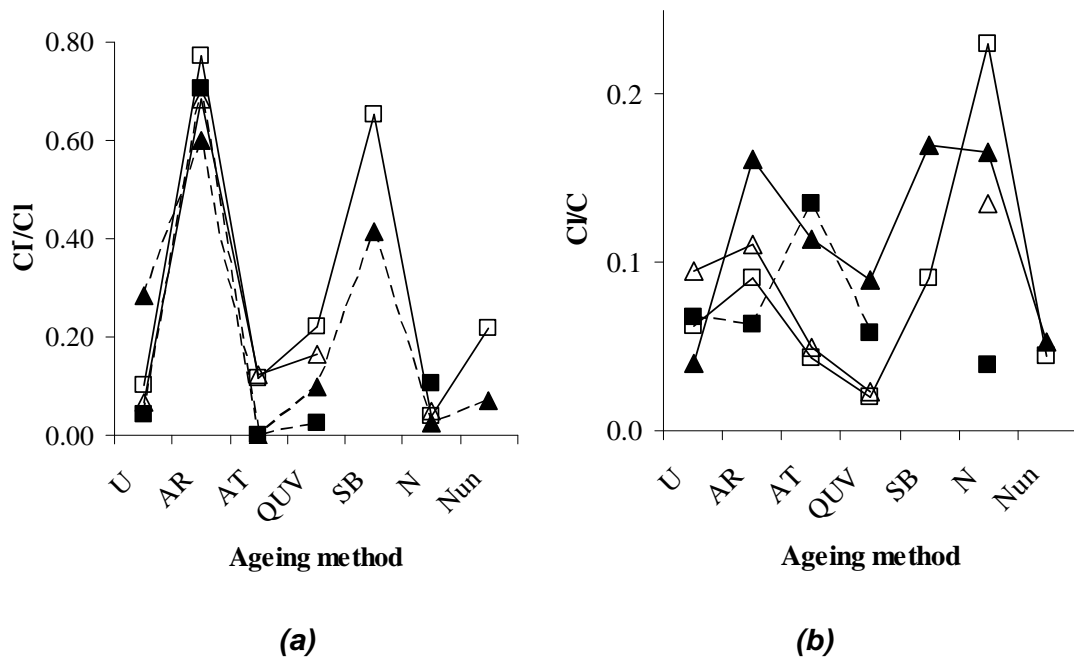


Figure 2 - XPS global Cl/C (a) and Cl/Cl (b) as a function of the ageing method. The unweathered (U) and the unexposed face of the naturally weathered sample (Nun) were also included for control. Triangles are for CZ samples and squares for S samples. Full symbols are for samples with the tinuvin P (anti-UV) additive.

In Figure 2, it is evident that the  $\text{Cl}^-$  fraction  $\text{Cl}^-/\text{Cl}$  correlates better with the ageing method than the  $\text{Cl}/\text{C}$  parameter. And it confirms also the conclusion reached through the yellowing index variation analysis: the tinuvin P additive is the main responsible for the resistance to the yellowing phenomenon. The best candidate for trapping chloride ions at the surface, resulting from degradation of  $\text{Cl}-\text{C}$  bonds is the inorganic filler (mainly calcium carbonate). In Figure 3, the XPS atomic ratios of  $\text{Ca}/\text{C}$  for all the formulations, as a function of the ageing method, are presented.

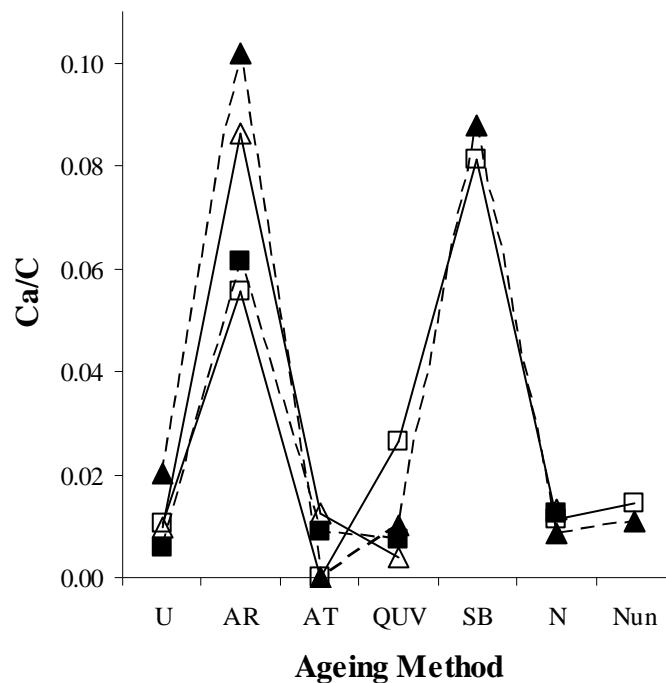


Figure 3 – XPS  $\text{Ca}/\text{C}$  atomic ratios for all the formulations as a function of the ageing method. Triangles are for CZ samples and squares for S samples. Full symbols are for samples with the tinuvin P (anti-UV) additive.

Comparison of Figure 2a) with Figure 3 shows that a clear correlation exists between both, showing that the inorganic filler is, indeed, the trap for the chloride ions. 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. Also the migration of

$\text{Cl}^-$ , by Coulombic interaction, can help that migration. In samples weathered in the Atlas chamber, two of them present negligible amounts of calcium and chloride ion. This is the only chamber where a water jet exists strongly suggesting that this water jet is responsible for the washing of calcium. With an intermediary behaviour, we find sample S weathered in QUV chamber. In this chamber, the main difference relative to the Aralab is that there are alternate periods of light and darkness. Therefore, the accumulated energy on the surface, being irradiated for 4 hours, is not enough to promote, in the sample S, calcium diffusion as large as in the samples continuously irradiated (Aralab chamber). In the samples CZ based (CZ and CZT) and S additivated with tinuvin P, it seems that the irradiation for 4 hours 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 no enrichment in calcium at the surface is observed. This may be due to one of two factors (or to both): i) there is a balance between the calcium diffusing towards the surface and the rain washing effect; ii) due to the limited periods of irradiation (less than 12 h in average), the activation energy for calcium migration is not reached,. The same pattern of diffusion/washing effect is observed for both Zn in CZ formulations and Sn in S formulations.

## 5. Conclusions

Four different formulations of technical PVC films submitted to natural and different artificial ageing were studied crossing results from XPS, FTIRS and colourimetry.

Results made clear that UV-absorbers additives greatly improve resistance to light, mainly in natural exposure conditions.

It was also shown that the fraction of chloride ion trapped in the inorganic filler is a better parameter to measure the PVC degradation than the amount of total lost (or remaining) chlorine in the surface. This result shows the relevance of the inorganic filler in the PVC degradation mechanism. In previous studies carried on extruded plates, it was shown that the chlorine remaining on the surface is partly under the form of chloride ions. This means that the chlorine resulting from the degradation mechanism does not entirely leave the surface under the form of  $\text{Cl}_2$  or  $\text{HCl}$ . In the irradiated non washed samples, the large amount of inorganic material there present traps the atoms of chlorine under the form of chloride ions. Therefore, the parameter  $\text{Cl}/\text{C}$  alone,



without specifying its nature, is not a good parameter to test the degree of degradation of the surface. Inversely, the  $\text{Cl}^-$  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 ( $\text{Cl}/\text{C}$  ratio and  $\text{Cl}^-$  fraction) as a function of the ageing method used for the samples.

The irradiation also induces a migration of calcium to the surface (the XPS amount of  $\text{Ca}^{2+}$  is larger than the expected one taking into account the nominal bulk composition), and its washing by water jets present both in the natural weathering (rain) and in the ATLAS chamber. The  $\text{Ca}^{2+}$  migration towards the surface may be induced by the migration of  $\text{Cl}^-$  generated by break of C-Cl bonds.

From the combined results obtained from the battery of techniques employed along this study [3-5], we could conclude that the best weathering conditions to simulate the natural exposure should not be limited to the radiation source choice, but should include also alternate periods of dark and light as well as water jets.

## **6. NEW CHALLENGES**

Our present research efforts in this field are heading towards FTIR spectra peak fitting. As some spectra bands are wide and result from the combination of several peaks, it is important to isolate them and evaluate their evolution during the weathering process. Our knowledge about the PVC degradation mechanism helps to define the most probable type of functional groups that results from photo-oxidation. Evaluating the evolution of intensity of such peaks, during photo-oxidation, and comparing the respective kinetics for each one, it will be possible to conclude about the influence of the different photo-oxidation conditions and to clarify important features, as the role of water and fillers for the degradation mechanism, as well as judge about reliability of the several artificial methods used to simulate the natural exposure. Some of these new findings, not shown here, are included in our oral presentation.

## **7. ACKNOWLEDGEMENTS**

We would like to thank the FCT for a post-doctoral grant (AMF), SFRH/BPD/26239/2006, and to “Fundação Calouste Gulbenkian” for the financial support for attending the EWS 2009 Conference.

## 8. REFERENCES

- [1] Real, L. P; Rocha, A. P.; Gardette, J.-L. Artificial simulated and natural weathering of poly(vinyl chloride) for outdoor applications : the influence of water in the change of properties, *Polymer Degradation and Stability*, **2005**; 88, 257-362
- [2] Real, L.E.P; Botelho do Rego, A.M ; Ferrara, A. M.. The Influence of Weathering Conditions in the Evolution of Molecular Properties of Poly(Vinyl Chloride) for Outdoor Applications. An Analytical Study Using Techniques of Surface Analysis (SEM and XPS). *Oral communication to Conference EUROMAT 2005*, Prague, September **2005**.
- [3] Real, L. P; Rocha, A. P.; Gardette, J.-L. Artificial Accelerated weathering of poly(vinyl chloride) for outdoor applications : the evolution of the mechanical and molecular properties, *Polymer Degradation and Stability*, **2003**; 82, 235-243
- [4] Real, L.E.P; Ferrara, A. M.; Botelho do Rego, A.M. The Influence of Weathering Conditions on the Properties of Poly(Vinyl Chloride) for Outdoor Applications. An Analytical Study Using Surface Analysis Techniques. *Polymer Testing*, **2007**; 26, 77–87.
- [5] Real, L.E.P; Ferrara, A. M.; Botelho do Rego, A.M. “Comparison of different photo-oxidation conditions of poly(vinylchloride) for outdoor applications”, *Polymer Testing*, , **2008**; 27, 743-751
- [6] EN 12608 (**2003**): Unplasticized polyvinylchloride (PVC-U) profiles for fabrication of windows – Classification, requirements and Test Methods.
- [7] ISO 877-2:**2009**: Plastics -- Methods of exposure to solar radiation -- Part 2: Direct weathering and exposure behind window glass.