

**LABORATÓRIO NACIONAL  
DE ENGENHARIA CIVIL**

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**ARTIFICIAL SIMULATED AND NATURAL WEATHERING  
OF PVC FOR OUTDOOR APPLICATIONS:  
THE INFLUENCE OF THE WATER IN THE EVOLUTION  
OF THE PVC PROPERTIES**

Lyon, 2 de Setembro de 2004

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# **ENVELHECIMENTO NATURAL E ARTIFICIAL SIMULADO DE PVC ESTABILIZADO PARA APLICAÇÕES EXTERIORES: A INFLUÊNCIA DA ÁGUA NA EVOLUÇÃO DAS PROPRIEDADES DO PVC**

## **RESUMO**

Procurou-se com a presente comunicação apresentar os resultados obtidos durante o ano de 2003 de um estudo desenvolvido no LNEC, cujo objectivo foi avaliar o efeito sinérgico de dois agentes climáticos de degradação (radiação e água), na evolução do mecanismo de envelhecimento de placas extrudidas em PVC rígido estabilizado com dióxido de titânio, para aplicações exteriores. Para o efeito submetem-se diversas amostras a envelhecimento natural e artificial, e fez-se a caracterização do seu estado de degradação utilizando técnicas de análise de colorimetria e de espectroscopia de infravermelhos (FTIR).

Inicialmente estava apenas prevista a apresentação de um poster com o título “Artificial and Natural Weathering of Polyvinylchloride for Outdoor Applications: the Influence of the Radiation and Water in the Evolution of the PVC Properties”. Porém, na sequência de um pedido do secretariado do congresso, o autor apresentou também uma comunicação oral versando o mesmo tema, mas incluindo resultados experimentais obtidos durante o ano 2004, não incluídos no poster. Estes resultados, obtidos mediante técnicas de análise de superfície por microscopia electrónica de varrimento (SEM) e por espectroscopia de fotoelectrões-X (XPS), também não foram incluídos no texto da comunicação enviada ao congresso. Na circunstância, apresenta-se nesta publicação, o texto da comunicação referente ao poster, inicialmente prevista, e também os slides da comunicação oral apresentada, contendo adicionalmente alguns resultados obtidos em 2004.

O desenvolvimento das formulações, o envelhecimento e a subsequente caracterização por colorimetria, por espectroscopia de infravermelhos e por microscopia electrónica de varrimento foi realizada no LNEC. A caracterização por espectroscopia de fotoelectrão X foi realizada no Centro de Química-Física Molecular do Instituto Superior Técnico.

# **ARTIFICIAL SIMULATED AND NATURAL WEATHERING OF PVC FOR OUTDOOR APPLICATIONS : THE INFLUENCE OF WATER ON THE EVOLUTION OF THE PVC PROPERTIES**

## **SUMMARY**

The main purpose of this paper is to present the results obtained, during the year 2003, from a study developed in *LNEC*. The object of this study was to assess the synergetic effect of two deteriorating climatic agents (radiation and water) on the evolution of the properties of extruded plates made of hard PVC stabilised with titanium dioxide, for outdoor applications. For the purpose, several samples were subject to natural and artificial weathering, their deterioration condition having been characterised by means of techniques of analysis of colorimetry and infrared spectroscopy (FTIR).

Initially, only the presentation of a poster titled “Artificial and Natural Weathering of Polyvinyl chloride for Outdoor Applications: the Influence of the Radiation and Water on the Evolution of the PVC Properties” was scheduled. Nevertheless, upon request from the secretariat of the Congress, the author also presented an oral paper on the same subject, but including experimental results obtained during the year 2004, which were not mentioned in the poster. Similarly, these results, which were obtained by means of surface analysis techniques by Scanning Electron Microscopy (SEM) and by X photoelectron spectroscopy (XPS), were not included in the paper submitted to the Congress. Therefore, this publication includes the text of the paper referring to the poster, which was initially predicted, as well as the slides of the oral communication presented. It also contains a few results obtained in 2004.

The development of the formulations, as well as the ageing and the subsequent characterisation by colorimetry, by infrared spectroscopy and by scanning electron microscopy were performed in *LNEC*. The characterisation by X photoelectron spectroscopy was conducted at the Molecular Chemistry-Physics Centre of the *Instituto Superior Técnico* (Higher Technical Institute).

# **VIEILLISSEMENT ARTIFICIEL ACCELERE DU PVC POUR DES APPLICATIONS EXTERIEURES: L'INFLUENCE DE L'EAU SUR L'EVOLUTION DES PROPRIETES DU PVC**

## **RESUME**

L'objectif essentiel de cette communication est de présenter les résultats obtenus, pendant l'année de 2003, avec une étude développée au LNEC, dont l'objet a été d'évaluer l'effet synergique de deux agents climatiques de détérioration (la radiation et l'eau) sur l'évolution du mécanisme de vieillissement des plaques extrudées de PVC rigide stabilisé avec le dioxyde de titane, pour des applications extérieures. Pour l'effet, plusieurs échantillons ont été soumis au vieillissement artificiel et naturel et leur état de détérioration a été caractérisé suivant des techniques d'analyse de colorimétrie et de spectroscopie d'infrarouges (FTIR).

Initialement, seule la présentation d'un poster avec le titre "*Artificial and Natural Weathering of Polyvinylchloride for Outdoor Applications : the Influence of the Radiation and Water on the Evolution of the PVC Properties*" était prévue. Toutefois, sous requête du secrétariat du congrès, l'auteur a présenté aussi une communication orale sur le même sujet, mais comprenant les résultats expérimentaux obtenus pendant l'année de 2004, qui n'étaient pas inclus dans le poster. De même, ces résultats, obtenus moyennant des techniques d'analyse de surface par microscopie électronique de balayage (SEM) et par spectroscopie de photoélectrons-X, n'ont pas été inclus dans le texte de la communication soumise au congrès. Ainsi, on présente dans cette publication, le texte de la communication relative au poster, qui était initialement prévue, ainsi que les diapositives de la communication orale présentée, comportant aussi quelques résultats obtenus en 2004.

Le développement des formulations, le vieillissement et la caractérisation postérieure par colorimétrie, par spectroscopie d'infrarouges et par microscopie électronique de balayage ont été effectués au LNEC. La caractérisation par spectroscopie de photoélectron X a été effectuée au Centre de Chimie-Physique Moléculaire de l'Instituto Superior Técnico (Institut Supérieur Technique).



# ARTIFICIAL SIMULATED AND NATURAL WEATHERING OF PVC FOR OUTDOOR APPLICATIONS: THE INFLUENCE OF THE WATER IN THE EVOLUTION OF THE PVC PROPERTIES

## 1. INTRODUCTION

The artificial accelerated methods are universally used and accepted in the prediction of polymer lifetimes. However, in order to evaluate the durability of polymeric materials, it is necessary to reproduce the natural weathering phenomena as much as possible. To attain this target, it is fundamental to understand the role of the atmospheric agents in the photo-degradation of such products. The importance of radiation and temperature in the degradation of polymers is universally recognised. However, there is a trend to underestimate other environmental agents, such as the humidity and rain, which play an important part in the evolution of degradation in certain compounded polymers.

The objective of this paper is to show the fundamental role of water in the mechanism of degradation of the TiO<sub>2</sub> pigmented PVC formulations.

## 2. PART EXPERIMENTAL

In this study, we use 4 different types of TiO<sub>2</sub> pigmented PVC formulations, containing CaCO<sub>3</sub>, two types of thermal stabilisers (based on calcium/zinc or dibutyltin-maleate) and various additives. The samples are designed for outdoor applications and are tested in the form of calendered films.

The specimens are submitted to artificial and natural weathering. The artificial simulated weathering was carried out in an Atlas Weatherometer Ci 65 chamber equipped with a 6500 watt borosilicate glass-filtered xenon arc source. The program of artificial ageing, consisting in continuous irradiation, was subdivided in two periods with different exposure conditions: a first period of 2660 h of irradiation without spray of water and a last one of 3550 h with cycles of spray of water for 18 minutes each two hours. The quality of the water was controlled by means of a water purity meter. The intensity of radiation was auto-adjusted to assure a global irradiation of 550 W/m<sup>2</sup>, in the wavelength interval from 290 to 800 nm. The intensity of the radiation source was frequently verified with both calibrated 340 nm and 295-400 nm radiometers. To assure the correct temperature of the circulating air, with a relative humidity of 30 ± 10%, a calibrated black standard thermometer sensor was used, which was maintained at 65 ± 5°C. The maximum temperature measured in the exposed surface was 53°C. The test pieces were placed in a similar position relative to the radiation source and any differences in the distribution of the weathering parameters were compensated by rotation of the cylindrical sample rack.

Some specimens have been exposed from March 2000 to outdoor weathering in Lisbon (severe climate, according to [1]), in accordance with ASTM Method D 1435 [2], at an angle of 45°, facing south, and were removed periodically to perform the several analysis described above.

The influence of the water in the photo-oxidative ageing is evaluated by means of molecular analysis, using infrared spectroscopy, and in terms of evolution of the aesthetic properties, using scanning UV-VIS spectroscopy and colourimetry.

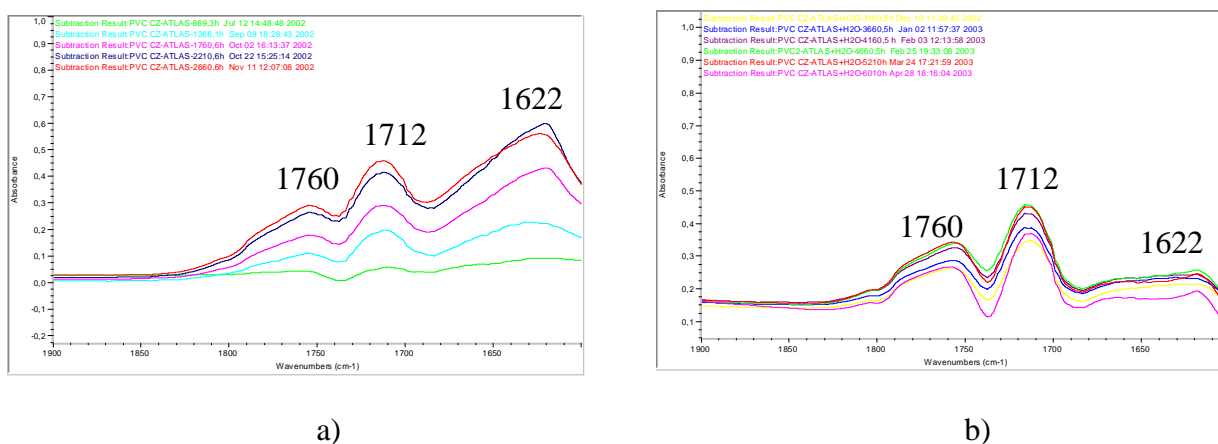
## 3. RESULTS

### 3.1 Infrared Measurements

The oxidation of PVC followed by infrared spectroscopy can normally be detected by the

absorption of oxidation products containing carbonyl groups, in the 1600-1900  $\text{cm}^{-1}$  area. The changes result as well from the consumption of stabilisers as from the increase of carbonyl groups due to the oxidation. So, the periodic measurement of the optical density variation, carried out by subtracting spectra of the same samples, along the ageing process, makes it possible to quantify the oxidation resulting from this process.

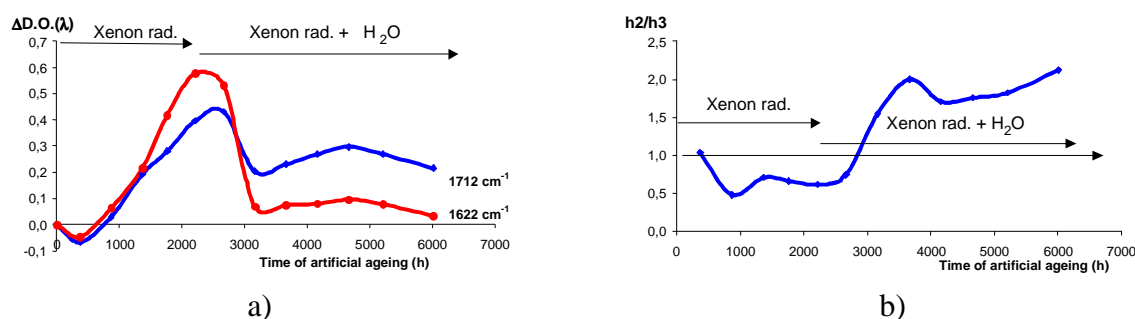
To illustrate the evolution of the bands in the carbonyl range, during each irradiation period in conditions of artificial ageing, the spectra of differences of a PVC CZ film are represented in the figure 1. The programme started with 2660 hours of continuous irradiation without spray of water (figure 1a). The last 3350 hours of irradiation (figure 1b) was combined with cyclic spray of water (18 minutes each two hours). The different spectra are represented at some scale to simplify a comparative analysis.



**Figure 1:** FTIR spectra of differences of a PVC CZ film, in the carbonyl domain: a) during the first 2660 h of artificial accelerated ageing with xenon light, without spray of water; b) during 6010 h of artificial accelerated ageing with xenon light, using cyclic spray of water only in the last 3350 h of irradiation

The spectral modifications detected in the case of the PVC CZ film was also observed in the FTIR spectra of the other PVC film formulations studied.

In order to show the changes induced by water in the stoichiometry of the PVC degradation mechanism, figure 2 presents the evolution of the optical densities at 1712  $\text{cm}^{-1}$  and 1622  $\text{cm}^{-1}$  of the PVC CZ formulation, as well as the rate of the magnitudes of these bands during the artificial ageing.

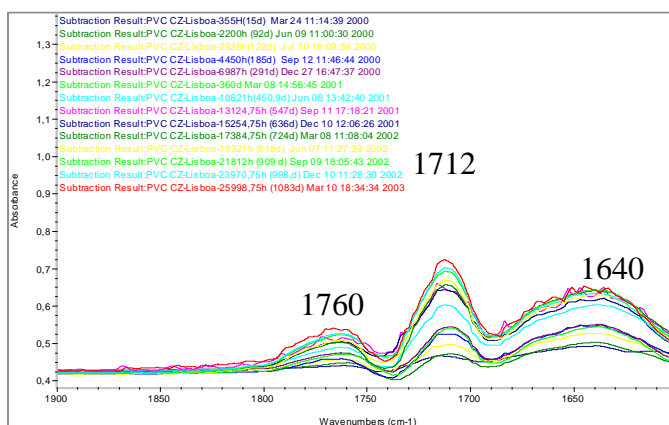


**Figure 2:** Evolution of the PVC CZ FTIR data, during 6010 h of artificial accelerated ageing with xenon light, using cyclic spray of water only in the last 3350 h of irradiation: a) optical density of main carbonyl bands; b) rate of the optical densities at main carbonyl bands

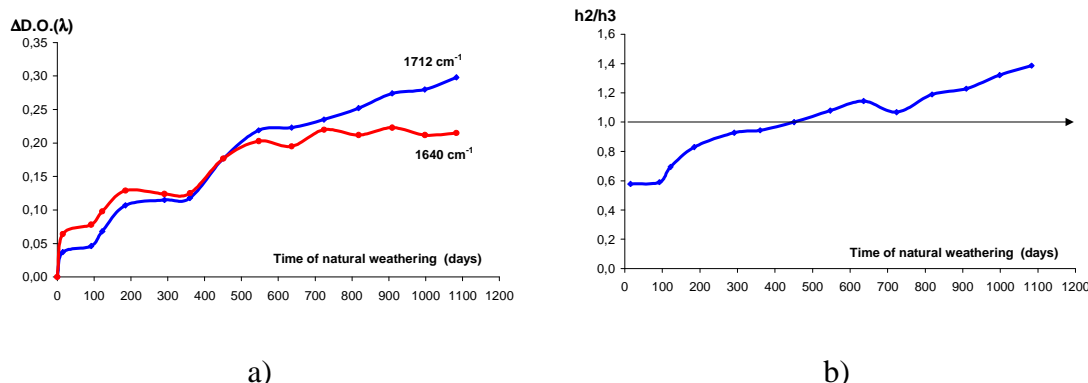


This figure shows that the introduction of water during artificial ageing created large changes in the stoichiometry and concentration of the oxidation products resulting from the reactions of photo-oxidative degradation. These changes are fundamentally expressed by the decrease in the magnitude of the maximum absorption bands in the carbonyl range. A similar decrease in the magnitude of the hydroxyl band, not reported in the present work, was also observed in the spectra of the others formulations studied. Moreover, the drastic decrease of the band near  $1622\text{ cm}^{-1}$ , leads to the inversion of the relation between the magnitude of the two main carbonyl bands, at  $1712\text{ cm}^{-1}$  and  $1622\text{ cm}^{-1}$ , used to evaluate the stoichiometry of the degradation mechanism.

For comparative purposes with natural exposure, figures 3 and 4 contain representations similar to those given above for artificial ageing.



**Figure 3: FTIR spectra of differences of a PVC CZ film, in the carbonyl domain, during 3 years of natural exposure in Lisbon**



**Figure 4: Evolution of FTIR properties of a PVC CZ film, during 3 years of natural exposure in Lisbon: a) optical density of main carbonyl bands; b) rate of the optical densities at main carbonyl bands**

The photo-activity of TiO<sub>2</sub> pigments [3-6] should result in the formation of oxidation products, originated by radical attack to any unsaturation in the polymer, responsible for the yellowing in PVC. The alcohols, ketones, aldehyde and other functional groups resulting from the oxidation process, are sensible structures that lose the adhesion to the polymeric matrix surface by

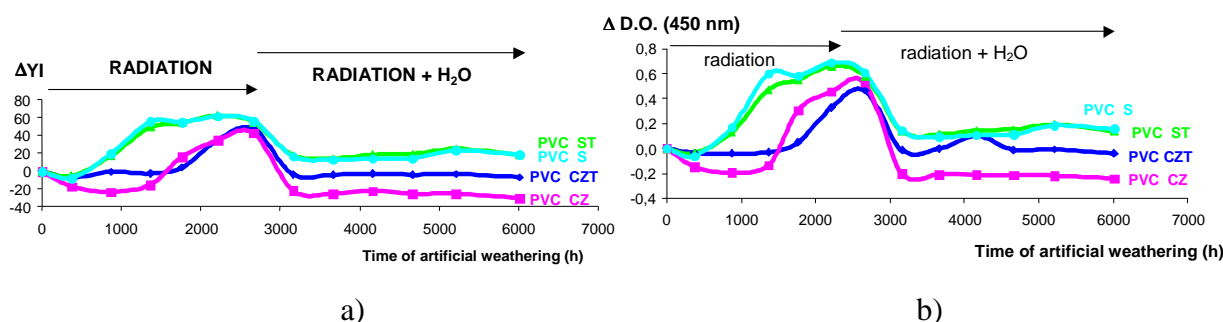
water action. This effect and the fact that no new band in the infrared spectra was detected are consistent with experimental observations during the artificial weathering. This confirms that the decrease in the concentration of the oxidation products formed with the participation of titanium dioxide present in the PVC formulations, after initiation of the cyclic spray of water, results from an erosion phenomenon. The detection of changes in the unsaturation of such materials by means of infrared spectroscopy is not easy, but it can be performed all the more readily by means of UV-VIS spectroscopy and colourimetry.

As can also be seen in the previous figures, concerning infrared data in the carbonyl range, there is a good similarity between artificial ageing with cyclic spray of water and natural weathering.

### 3.2 Colourimetric Measurements

The easiest way to evaluate the evolution of the colour of the PVC during the weathering process consists of a graphic representation of the yellowness index, which is based on CIE standard illuminant D65 and CIE 1931 2° standard observer viewing. The differences should be referred to as the original properties of the samples, still not aged. The evolution of parameter  $b^*$  is an alternative representation of the yellowness index, and both plots are similar. Another interesting representation is the evolution of the optical density at 450 nm, which follows a similar trend as the yellowness index [7, 8].

The referred parameters, obtained with the samples aged artificially with Xenon light are presented in figure 5. Figure 6 presents the evolution of the same parameters measured for analogous samples, during 3 years of natural exposure in Lisbon.

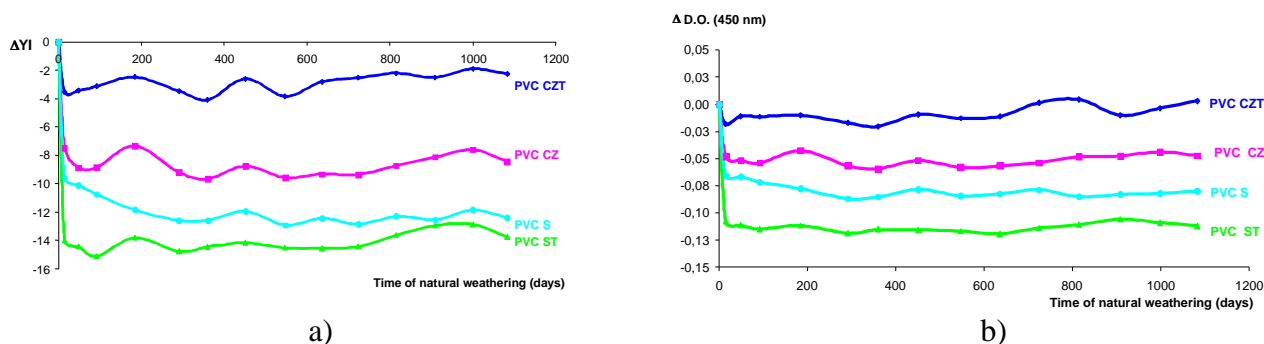


**Figure 5: Evolution of the UV-VIS parameters during 6010 h of artificial simulated ageing with xenon light, using cyclic spray of water in the last 3350 h of irradiation: a) yellowness index difference; b) optical density difference at 450 nm**

As it is expressed, the colourimetric changes that were observed during the initial stages of artificial ageing, without intervention of water, consisted of a brief initial whiteness, followed by a recuperation of the initial appearance and subsequent yellowness. The initial whitening of the samples results from the photo-oxidation of the conjugated double bonds formed during the processing of the polymer. The introduction of cyclic spray of water during the artificial ageing, which occurred after 2660h of xenon irradiation, leads to an important change in the colourimetric properties of the samples, originating chalking and bleaching in all PVC formulations. The whitening effect was maintained during the last 3550 h of irradiation. The reduction of the yellowness in PVC compounds, during irradiation with a different artificial source in humid conditions, was also reported by other author [9].

The same kind of colourimetric evolution was obtained with samples extracted from thick extruded profiles, with the same composition as the films referred above, although with these

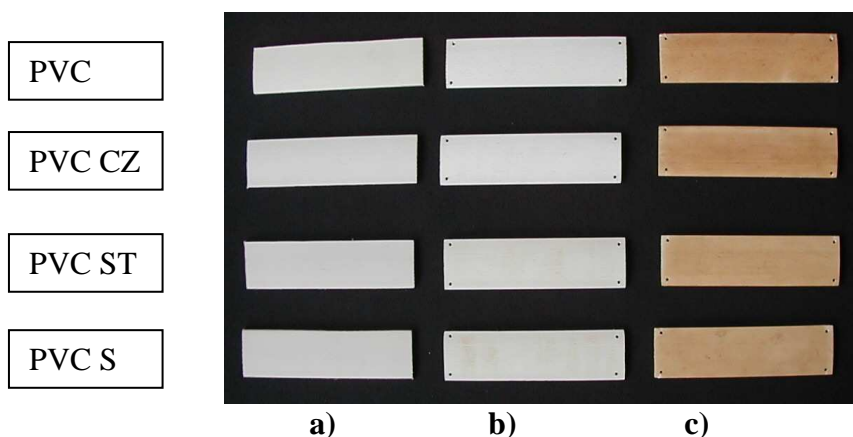
samples the determinations were made in reflection mode.



**Figure 6: Evolution of the UV-VIS parameters over 3 years of natural exposure in Lisbon: a) yellowness index difference; b) optical density difference at 450 nm**

In the samples submitted to natural exposure, similar whitening was also observed. This phenomenon results from the combined action of atmospheric agents in the PVC matrix, certainly with important participation of the rain to enhance the catalytic photo-activity of titanium dioxide pigments, present in such compounds.

To illustrate the differences originated by the intervention of the water in the colourimetric behaviour of the PVC samples studied, figure 7 contains a picture of the various PVC films, submitted to different photo-oxidation conditions. In this figure a control sample, stocked in dark conditions, is included (a), whose colour is still less white than the sample exposed outdoors, because of the whiteness effect that still persists after 3 years of exposure.



**Figure 7: appearance of three PVC samples submitted to different environments: a) control sample; b) sample submitted to 6000 h of artificial ageing with glass filtered xenon light, using cycles of spray of water of 18 minutes each two hours; c) sample after 8000 hours of continuous glass filtered xenon light, without spray of water**

As can be seen in this picture the films of PVC ST and PVC S presented in figure 7 b) contain some staining in the exposed surface, which is very common in products of PVC containing tin stabilisers. In fact, these samples present more yellowing than the samples stabilised with calcium/zinc (figure 5). The films presented in fig. 7 c) presents yellowing on completely exposed surfaces, but they still remain white backwards, which confirms that this phenomenon did not happen beyond the first 100 µm thickness from the exposed surface.

#### 4. CONCLUSIONS

Comparing the colourimetric results and the characteristics of the FTIR spectra of differences, resulting from the photo-oxidative ageing with and without water cycles indicates that the main phenomena that control both processes are quite different.

It is concluded that the whiteness of the samples is a result of a radical attack to any unsaturations in the PVC, responsible for the yellowing. The radicals are formed as a result of the photo-activity of TiO<sub>2</sub> pigments, present in the PVC formulations. The measured decrease in the concentration of the oxidation products formed by this mechanism and the observed whiteness of the PVC samples, during weathering, confirms that these products can be extracted from their polymeric matrix surface by water action.

The results from infrared and ultraviolet-visible spectrometry, showed there is a good similarity between artificial ageing with cyclic spray of water and natural weathering.

This means that a better simulation of the natural weathering of such PVC materials in laboratory conditions has to consider the intervention of water and humidity. Finally it is worthy to notice that rain is beneficial to the maintenance of the white colour of TiO<sub>2</sub> pigmented PVC materials, during outdoors applications.

#### 5. REFERENCES

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***SLIDES***

**ARTIFICIAL AND NATURAL WEATHERING OF  
POLYVINYLCHLORIDE FOR OUTDOOR APPLICATIONS:  
THE INFLUENCE OF THE RADIATION AND WATER IN  
THE EVOLUTION OF THE PVC PROPERTIES**

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**Introduction**

**Increase of PVC in outdoor applications**

✓ **Advantages**

- Low cost
- Good technical performance
- Good ecological characteristics

✓ **Disadvantages**

- Discoloration (yellowing or darkening)

- ➔ To process the polymer
- ➔ To reduce the negative aspects
- ➔ To give special properties
- ➔ To improve the durability

➔ **compounding**



## Objectives



- To evaluate the **simulation capability** of the artificial Xenon radiation sources, carried out with and without cyclic spray of water.
- To confirm the **photo-activity of TiO<sub>2</sub>** pigments
- To show the **influence of the radiation and water** during the photooxidative ageing of TiO<sub>2</sub> stabilised PVC



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## Experimental part: samples

PVC formulations for outdoor applications, containing **CaCO<sub>3</sub>, TiO<sub>2</sub>** - rutile, surface coated, **DBTM or Ca/Zn/ESO**), UV-light absorber (**benzotriazole** type), **lubricants** and a **processing aid**

**Extruded plates (~ 1,5 mm) and calendered films (~ 150 µm)**

- **SAMPLE 1**: not yet aged (reference)
- **SAMPLE 2**: 4900 h of continuous xenon irradiation (60% Hr – humid conditions)
- **SAMPLE 3**: 7010 h of continuous xenon irradiation (5% Hr – dry conditions), using cyclic spray of water in the last 4350 h (18 min in each 2 hours)
- **SAMPLE 4**: 4350 h of continuous xenon irradiation (5% Hr) and cyclic spray of water (18 min in each 2 hours)
- **SAMPLE 5**: 3 years of natural weathering in Lisbon



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## Experimental part: weathering conditions

### Artificial weathering with xenon sources

- Xenon borosilicate filtered continuous irradiation
- Xenon borosilicate filtered continuous irradiation with cyclic spray of water (18 min every 2 hours)



### Natural weathering

LISBON, 45° facing SOUTH



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## Experimental part: methods of characterization

- ➔ Infrared spectroscopy (FTIR) in the 1600-1900  $\text{cm}^{-1}$  region of the spectrum (analysis of the oxidative process at **molecular scale**)
- ➔ X-ray photoelectron spectroscopy (XPS) (surface characterization at **microscopic scale** in depth)
- ➔ Scanning electronic microscopy (SEM) (Surface characterization at **microscopic and macroscopic scale**)
- ➔ Colourimetry (analysis of the effects at **macroscopic scale**)



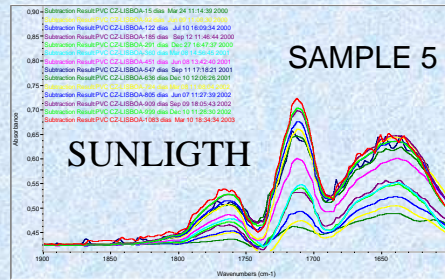
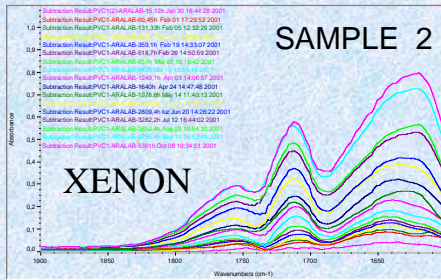
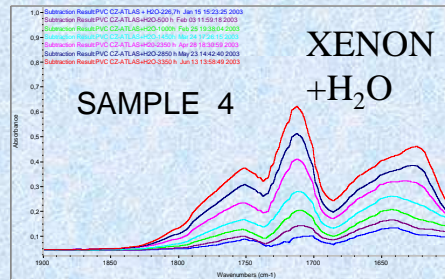
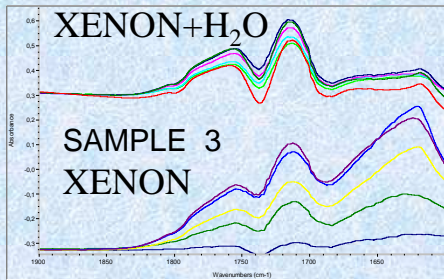
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# FTIR results

## PVC CZ - Difference Spectra in the carbonyl region

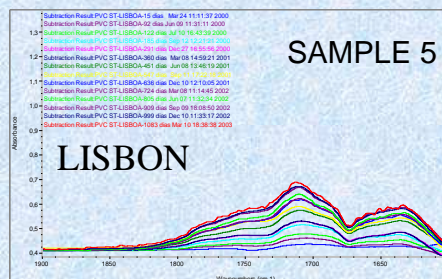
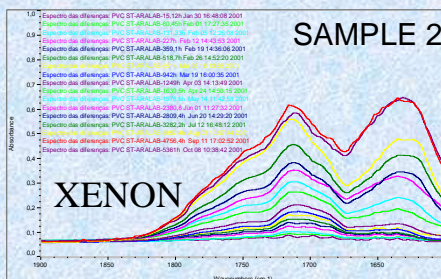
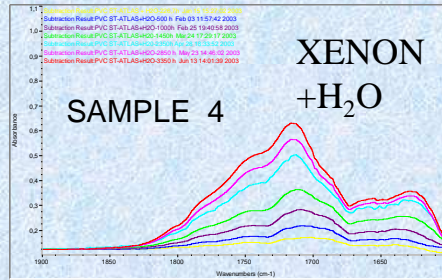
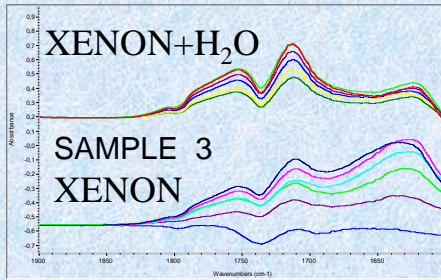


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# FTIR results

## PVC ST - Difference Spectra in the carbonyl region

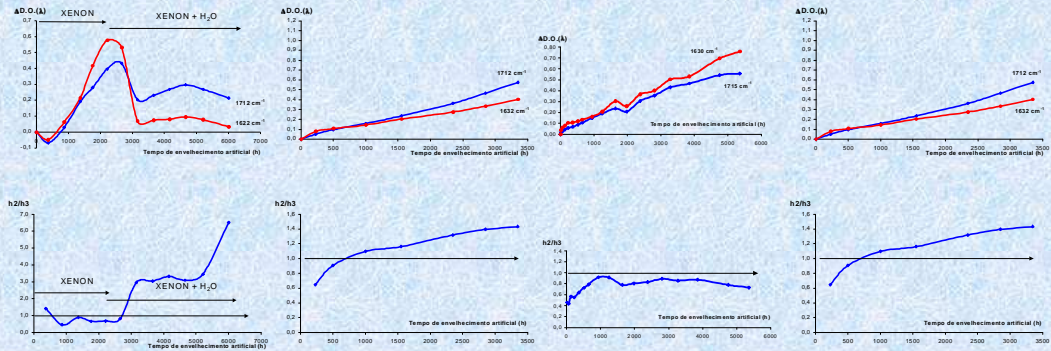


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# FTIR results and correlation

## FTIR Kinetics (PVC CZ) 1712 and 1630 cm<sup>-1</sup>



SAMPLE 3

SAMPLE 4

SAMPLE 2

SAMPLE 5

Excellent correlation



Spearman: 1,000 (n=7, one-tailed probabilities: > 99,95%)

Pearson: 0,982 (n=7, one-tailed probabilities: > 99,95%)

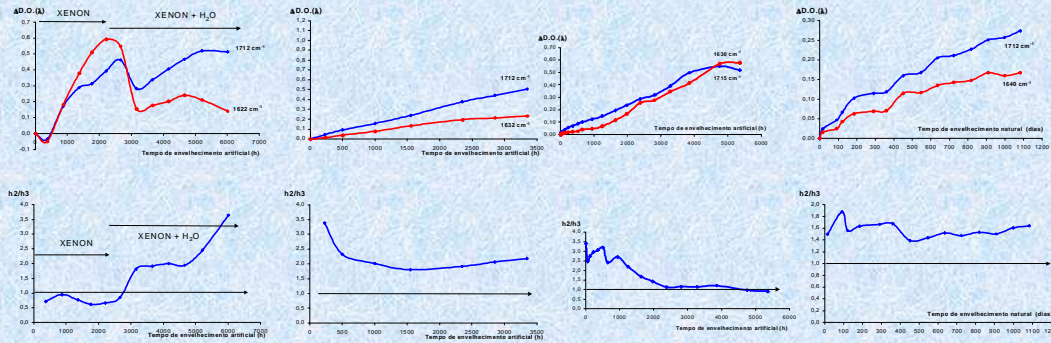


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# FTIR results and correlation

## FTIR Kinetics (PVC ST) 1712 and 1630 cm<sup>-1</sup>



SAMPLE 1

SAMPLE 2

SAMPLE 3

SAMPLE 4

High correlation



Spearman: 1,000 (n=7, one-tailed probabilities: 99,95%)

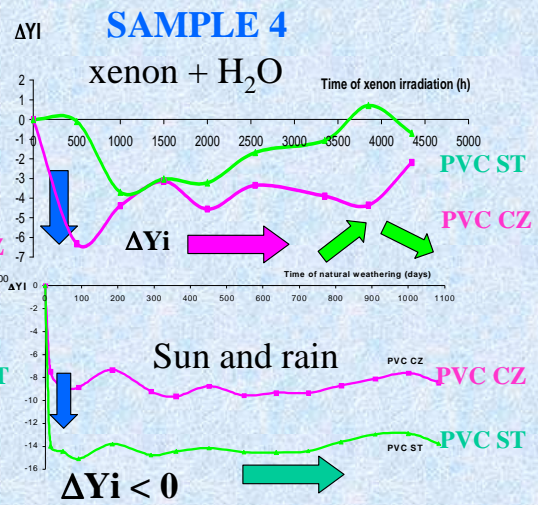
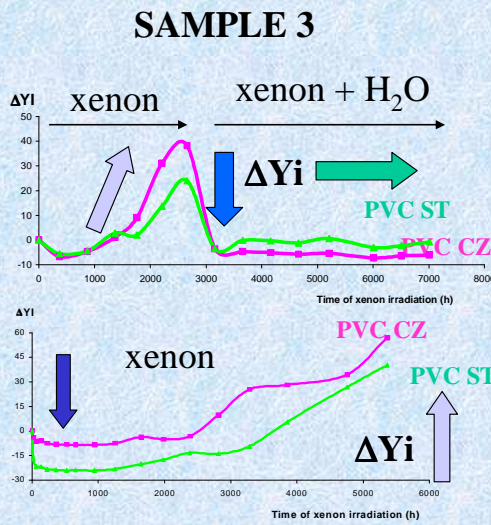
Pearson: 0,696 (n=7, one-tailed probabilities: >95%)



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## Colourimetric results



SAMPLE 2

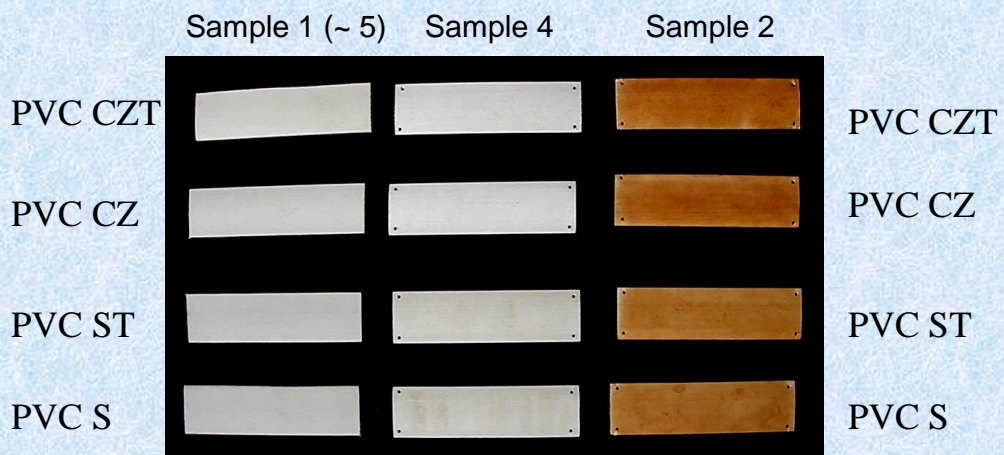
SAMPLE 5



MoDeSt 2004



## Colourimetric results



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## Colourimetric results and correlation

### PVC CZ

SAMPLES 4 AND 5  
Spearman: 0,857 > 0,833  
(n=7, two-tailed  
probabilities: 98%)

SAMPLES 2 AND 5  
no good correlation

### PVC ST

SAMPLES 4 AND 5  
Spearman: 1,000  
(n=7, two-tailed  
probabilities: 99,9%)

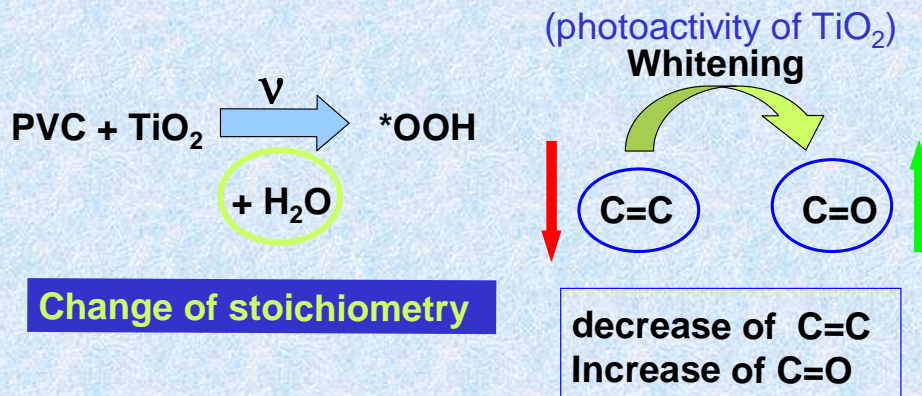
SAMPLE 2 AND 5  
no good correlation



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## Influence of water during weathering



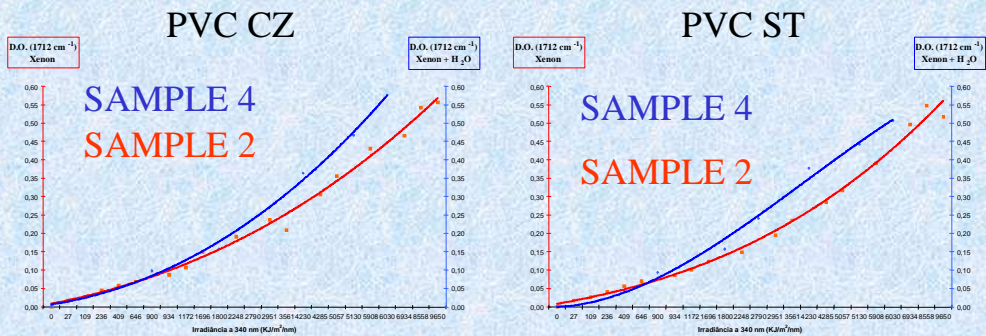
→ ✓ Water contributes to maintain the whitening of  $\text{TiO}_2$  pigmented PVC.



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## Influence of the water during artificial weathering FTIR spectroscopy of films in carbonyl domain



**Confirmation of the photoactivity of TiO<sub>2</sub> in presence of water**



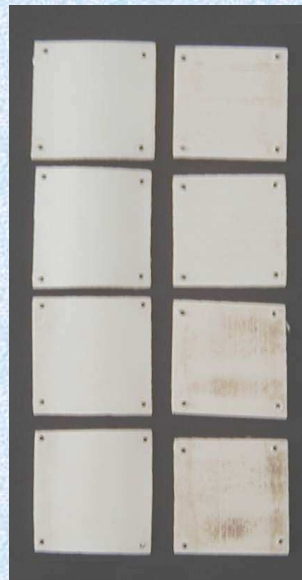
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## New findings

extruded plates

SAMPLE 3  
more  
weathering  
time and  
more  
whitening!



SAMPLE 4  
less  
weathering  
time, but  
more  
yellowing  
and stains!

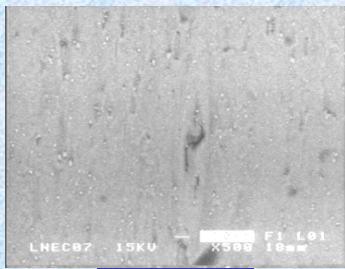
**why?**



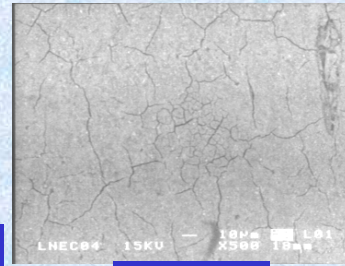
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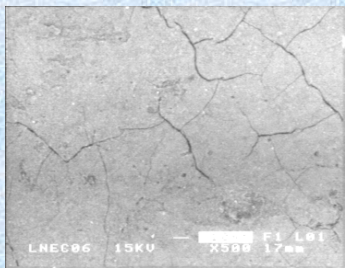
## SEM of extruded PVC S (DBTM stabilised)



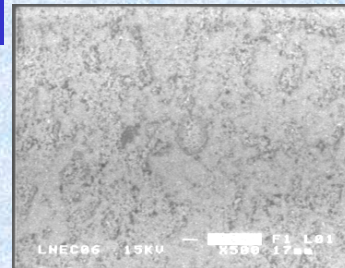
Sample 1



Sample 2



Sample 3



Sample 4

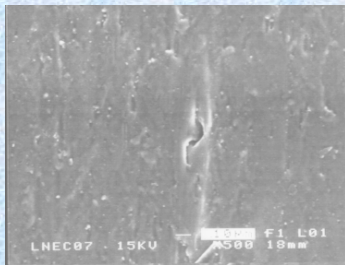
Backscattered  
electrons  
(500x)



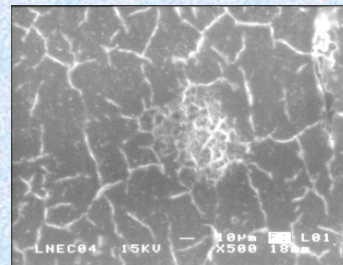
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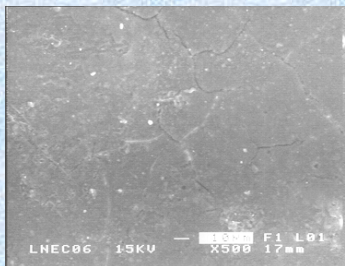
## SEM of extruded PVC S (DBTM stabilised)



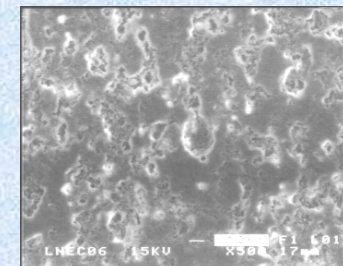
Sample 1



Sample 2



Sample 3



Sample 4

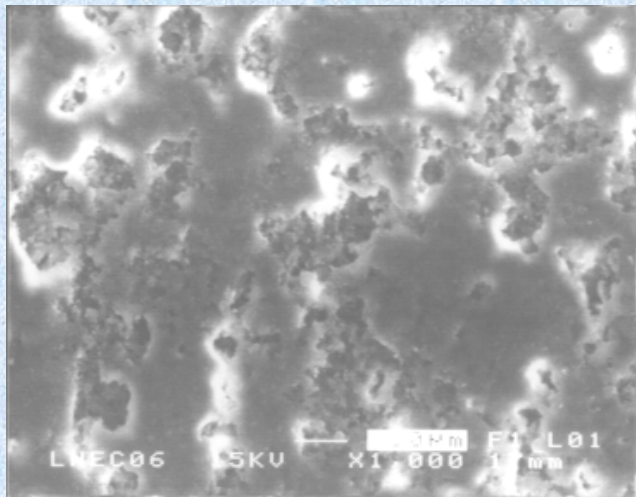
Secondary  
electrons  
(500x)



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## SEM of extruded PVC S (DBTM stabilised)



Secondary electrons  
(500x)

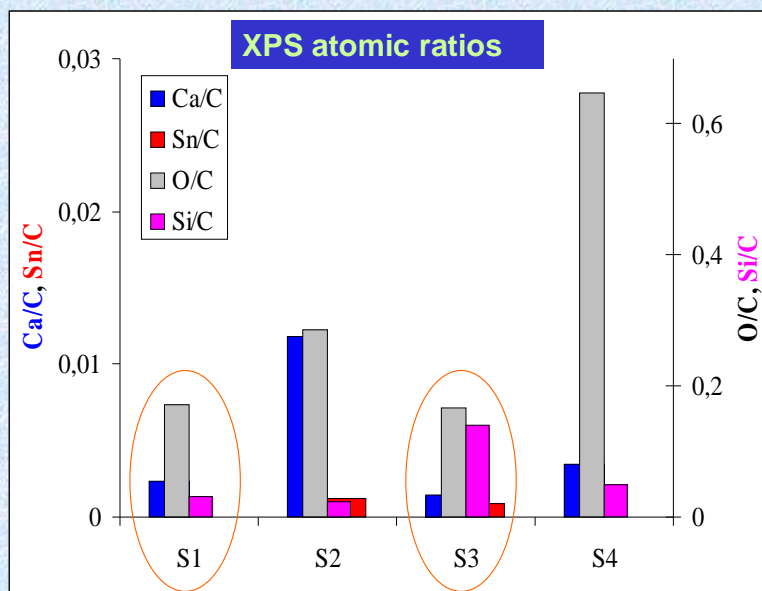
Sample 4



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## XPS of extruded PVC S (DBTM stabilised)

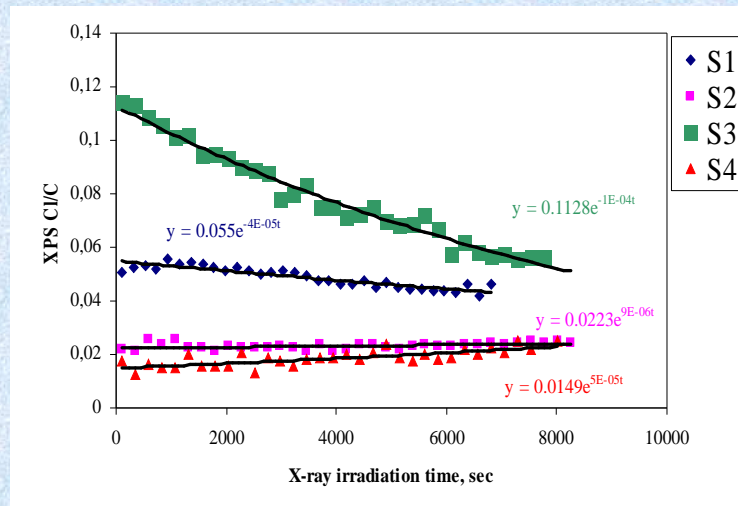


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## XPS of extruded PVC S (DBTM stabilised)

### Cl/C atomic ratios: degradation during X-ray irradiation



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## Conclusions

### colourimetric changes during weathering:

1. **whitening** originated by the photo-oxidation of conjugated double bonds formed during processing.
2. **yellowing** caused by continuous radiation.
3. **New whitening** originated by the formation of oxidation products, resulting from the **photo-activity of  $TiO_2$**  pigments in the presence of water.



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## Conclusions

### Simulation

It was shown that there is an **excellent correlation** between the results obtained from natural weathering and artificial ageing using a xenon source and cyclic spray of water.

### Photoactivity of $\text{TiO}_2$ and erosion

The water introduced in the system leads to the formation of oxidation products ( $\text{C}=\text{O}$ ), resulting from the **photo-activity of  $\text{TiO}_2$**  pigments (whitening and chalking), and wash away the fragments formed (erosion). The eroded surface presents holes and additive aggregates.



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## Conclusions

### Protective layer

1. An initial period of irradiation, in the absence of water, leads to the formation of a **protective layer** in stabilized PVC, assuring the maintenance of its original **white appearance** during outdoor exposure. The degraded surface is removed by the action of rain, but the protective layer minimizes subsequent erosion. XPS shows that Sn may have a crucial role on the formation of that layer.
2. In the absence of environmental conditions propitious to the development of such protective layer, the plastic material will suffer more internal degradation, presenting **yellowing** and **staining**, **stabilizer migration** and suffer subsequent **erosion**.



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***POSTER***



# ARTIFICIAL SIMULATED AND NATURAL WEATHERING OF POLYVINYLCHLORIDE FOR OUTDOOR APPLICATIONS: THE INFLUENCE OF THE RADIATION AND WATER IN THE EVOLUTION OF THE PVC PROPERTIES



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## 1 - OBJECTIVE

- To show the fundamental role of water in the mechanism of degradation of the TiO<sub>2</sub> pigmented PVC formulations, designed for outdoor building applications, based on the evolution of the chemical and aesthetic properties of the specimens, during natural and artificial weathering.
- To show that a previous period of Xenon irradiation, in the absence of rain, induce the formation of a crosslinked layer, near the irradiated surface of the profile, which protect the inner layers from the subsequent erosion effects caused by water and avoid the additive migration.

## 2 - SAMPLES AND AGEING METHODS

- Calendered films (150 μm thickness).
- 4 formulations: PVC CZ, PVC CZT, PVC S and PVC ST, differing in thermal stabiliser (Ca/Zn/ESO or DBTM) and content of the UV absorber (benzotriazol type).
- Natural exposure:
  - Lisbon (severe climate<sup>1</sup>).
  - 45° facing south.
  - Climatic data measured by means of a meteorological station.
- Artificial simulated ageing:
  - 6500 watt borosilicate glass-filtered xenon arc source, continuous radiation, with and without cycles of water (18 min each 2 hours).
  - Use of calibrated radiometers (340 nm and 290-400 nm).
  - intensity auto-adjusted to a global irradiation of (550 ± 50) W/m<sup>2</sup> (290 to 800 nm).
  - relative humidity of (30 ± 10) %.
  - temperature of black standard thermometer: (65 ± 3) °C.

## 3 - RESULTS

### 3.1 Infrared Measurements on PVC films

- Spectra of differences of a PVC film to illustrate the evolution of the bands in the carbonyl range, during each irradiation period in xenon light (figure 1).

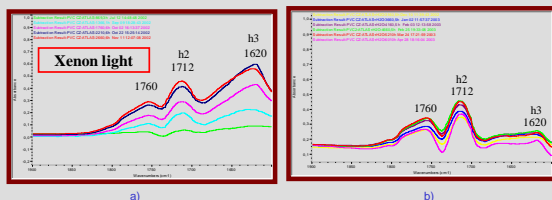


Figure 1: FTIR spectra of differences of a PVC CZ film, in the carbonyl domain, during 6010 hours of artificial accelerated ageing with xenon light; a) during the first 2660 h of irradiation, without spray of water; b) during the last 3350 h of irradiation, using cyclic spray of water.

- Evolution of the optical densities at 1712 cm<sup>-1</sup> and 1620 cm<sup>-1</sup> of the PVC CZ film and rate of the magnitudes of these bands (h2/h3) during the artificial ageing (figure 2). As it is showed (green ellipse), the introduction of water during artificial ageing created large changes in the stoichiometry of photoxidative degradation reactions, which is illustrated by important changes in the concentration of the oxidation products (type C=O) formed during this process.

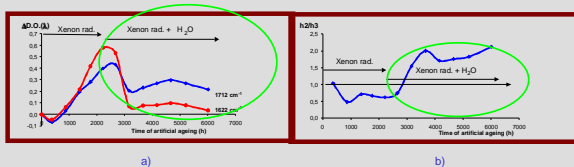


Figure 2: Evolution of the PVC CZ FTIR data, during 6010 h of artificial accelerated ageing with xenon light, using cyclic spray of water only in the last 3350 h of irradiation: a) optical density of main carbonyl bands; b) rate of the optical densities at main carbonyl bands.

- Spectra of differences of a PVC film to illustrate the evolution of the bands in the carbonyl range, during the natural exposure (figure 3 a).
- Evolution of the parameter h2/h3, representing the rate of the magnitudes of the bands at 1712 cm<sup>-1</sup> and 1620 cm<sup>-1</sup> of the PVC CZ film during three years of natural exposure (figure 3 b).

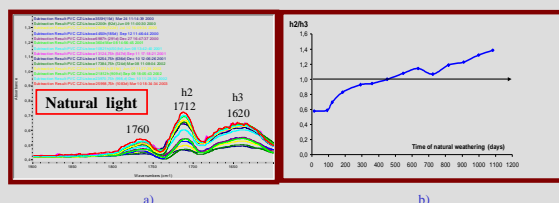


Figure 3: a) FTIR spectra of differences of a PVC CZ film, in the carbonyl domain, during 3 years of natural exposure in Lisbon; b) rate of the optical densities at main carbonyl bands.

### 3.2 Colourimetric Measurements on PVC films

- Transmittance mode, specular component of the reflected light included.
- Evolution of yellowness index, CIE 1931 D65/2°.
- Reference: initial values of the sample, still not aged.
- Evolution of the yellowness index of the PVC films during the artificial ageing (figure 4a). As it is showed (green ellipse), the introduction of water during artificial ageing created large changes in the stoichiometry of photoxidative degradation reactions, which is illustrated by important changes in the concentration of the conjugated unsaturations (chromophores type C=C) responsible by the yellowing of PVC. In natural exposure conditions (figure 4b) there are not yellowing, but only whitening.

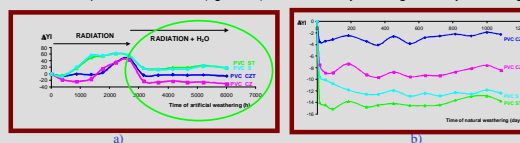


Figure 4: Evolution of the yellowness index difference: a) during 6010 h of artificial simulated ageing with xenon light, using cyclic spray of water in the last 3350 h of irradiation; b) over 3 years of natural exposure in Lisbon.

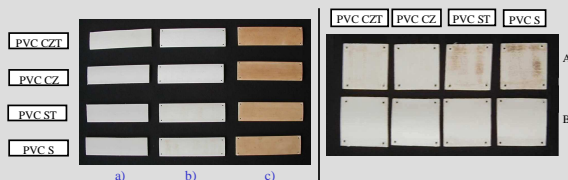


Figure 5: Appearance of three PVC samples submitted to different environments: a) control sample; b) sample submitted to 6000 h of artificial ageing with glass filtered xenon light, using cycles of spray of water of 18 minutes each two hours; c) sample after 6000 hours of continuous glass filtered xenon light, without spray of water.

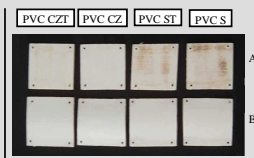


Figure 6: Appearance of two PVC samples submitted to: A) 3350 h of xenon irradiance with water cycles (specimens showing staining); B) 7000 h of xenon irradiance, being the first 2650 h without water cycles and the last 4350 h with water cycles (white protected specimens).

## 4. CONCLUSIONS

- The main phenomena that control the photoxidative ageing with and without water cycles are quite different. Indeed, this climatic agent changes completely the stoichiometry of the photodegradation reaction mechanism.
- The whiteness of the samples is a result of the oxidative attack of the radicals formed as a result of the photo-activity of TiO<sub>2</sub> pigments, in the presence of water, to any unsaturations responsible for the yellowing of the PVC<sup>2</sup>. Consequently, the rain is beneficial to the maintenance of the white colour of TiO<sub>2</sub> pigmented PVC materials, during outdoors applications.
- The decrease in the concentration of the oxidation products formed by this mechanism, measured from the beginning of the rain cycles, in artificial conditions, confirms that these products lose their adhesion to the polymeric matrix surface by water action. The low increase of oxidation products of carbonyl type detected during natural exposure can also be explained from dissolution and erosion effects produced by the rain.
- The results from infrared and ultraviolet-visible spectrometry, showed there is a good similarity between artificial ageing with cyclic spray of water and natural weathering, which means that to simulate the natural weathering of such PVC materials in laboratory conditions, it is important to consider the intervention of water and humidity, under penalty of losing real world representation.
- A previous period of Xenon irradiation (without rain), seems to produce a crosslinked protective layer, near the exposed surface, which protects the more internal layers from the degradation induced by the light, minimizing also the effects of the erosion and the additive migration.
- More susceptibility of staining during artificial photoxidative ageing in the samples stabilised with tin than in the specimens stabilised with Ca/Zn/ESO.

<sup>1</sup>: EN 12 608 (2003): Unplasticized polyvinylchloride (PVC-U) profiles for fabrication of windows – Classification, requirements and Test Methods.

<sup>2</sup>: Voeltz, H. G.; Kaempf, G.; Klaern, A. *Farbe Lack*, 82, p. 805, (1976); Kaempf, G.; Papenroth, W.; Holm, R. J. *Paint Techn.*, 46, p. 56, (1974); Voeltz, H. G.; Kaempf, G.; Flisky, H. G., *Prog. Org. Coat.*, 14, p.1941, (1972); Gesenhues, U., *Double Liaison - Physique, Chimie et Economie des Peintures et Adhesifs*, n° 479-480, pp. 32-41, (1996).