

**LABORATÓRIO NACIONAL
DE ENGENHARIA CIVIL**

**ARTIFICIAL ACCELERATED WEATHERING
OF PVC FOR OUTDOOR APPLICATIONS:
THE EVOLUTION OF THE MECHANICAL PROPERTIES**

Budapest, 2 de Julho de 2002

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Comunicação apresentada na 2nd International Conference on Polymer Modification,
Degradation and Stabilisation, MoDeSt 2002, Budapest

ENVELHECIMENTO ARTIFICIAL ACELERADO DE PVC PARA APLICAÇÕES EXTERIORES: EVOLUÇÃO DAS PROPRIEDADES FÍSICAS E MECÂNICAS

RESUMO

Procurou-se com a presente comunicação apresentar os resultados obtidos durante os anos de 2001 e 2002 de um estudo desenvolvido no LNEC, cujo objectivo foi avaliar o efeito sinérgico dos três agentes climáticos de degradação mais importantes (radiação, temperatura e água), na evolução das propriedades de PVC rígido estabilizado com dióxido de titânio, para aplicações exteriores. Para o efeito submeteram-se diversas amostras a envelhecimento natural e artificial, e fez-se a caracterização das suas propriedades físicas e mecânicas utilizando técnicas de análise de avaliação da aparência superficial (cor e brilho), de avaliação das propriedades moleculares por microscopia de infravermelhos (MICROFTIR), e de determinação das propriedades mecânicas em tracção e de avaliação da resistência ao impacto Charpy.

A comunicação foi apresentada oralmente e por poster no painel Ageing, Irradiation, Stabilisation do Congresso MoDeSt 2002. Na circunstância, apresenta-se nesta publicação, o texto da comunicação, o poster e também os slides da comunicação oral apresentada.

O desenvolvimento das formulações, o envelhecimento e a subsequente caracterização por colorimetria, brilho, impacto Charpy e tracção foi realizada no LNEC. A caracterização por microscopia de infravermelhos foi realizada no Laboratoire de Photochimie Moleculaire et Macromoleculaire da Université Blaise-Pascal, Clermont-Ferrand, França.

ARTIFICIAL ACCELERATED WEATHERING OF PVC FOR OUTDOOR APPLICATIONS: EVOLUTION OF THE PHYSICAL AND MECHANICAL PROPERTIES

SUMMARY

The main purpose of this paper is to present the results obtained, during the years 2001 and 2002, from a study developed in *LNEC*. The object of this study was to assess the synergetic effect of three of the most significant deteriorating climatic agents (radiation, temperature and water) on the evolution of the properties of hard PVC stabilised with titanium dioxide, for outdoor applications. For the purpose, several samples were subject to natural and artificial weathering. Moreover, their physical and mechanical properties were characterised by techniques of analysis and assessment of the surface aspect (colour and brightness), of assessment of the molecular properties by infrared microscopy (MICROFTIR), as well as of determination of the tensile mechanical properties and assessment of the Charpy impact resistance.

The paper was both orally presented and by poster at the panel meeting “Ageing, Irradiation, Stabilisation” of the Congress MoDeSt 2002. Therefore, this publication includes the text of the paper, the poster, as well as the slides from the oral communication.

The development of the formulations, the ageing and the subsequent characterisation by colorimetry, brightness, Charpy impact and tension, were done in *LNEC*. The characterisation by infrared microscopy was performed in the *Laboratoire de Photochimie Moleculaire et Macromoleculaire* of the University Blaise-Pascal, Clermont-Ferrand, France.

VIEILLISSEMENT ARTIFICIEL ACCELERE DU PVC POUR DES APPLICATIONS EXTERIEURES: L'EVOLUTION DES PROPRIETES PHYSIQUES ET MECANIQUES

RESUME

L'objectif essentiel de cette communication est de présenter les résultats obtenus, pendant les années 2001 et 2002, avec une étude développée au LNEC, dont l'objet a été d'évaluer l'effet synergique des trois agents climatiques de détérioration les plus importants (la radiation, la température et l'eau) sur l'évolution des propriétés du 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 leurs propriétés physiques et mécaniques ont été caractérisées suivant des techniques d'analyse et d'évaluation de leur apparence superficielle (couleur et brillance), d'évaluation des propriétés moléculaires par microscopie d'infrarouges (MICROFTIR), et de détermination des propriétés mécaniques sous tension et d'évaluation de la résistance à l'impact Charpy.

La communication a été présentée oralement et par poster au panel « *Ageing, Irradiation, Stabilisation* » du Congrès MoDeSt 2002. Ainsi, cette publication comporte le texte de la communication, le poster et aussi les diapositives de la communication orale présentée.

Le développement des formulations, le vieillissement et la caractérisation postérieure par colorimétrie, brillance, impact Charpy et tension ont été effectués au LNEC. La caractérisation par microscopie d'infrarouges a été effectuée au Laboratoire de Photochimie Moléculaire et Macromoléculaire de l'Université Blaise-Pascal, Clermont-Ferrand, France.

ARTIFICIAL ACCELERATED WEATHERING OF PVC FOR OUTDOOR APPLICATIONS: THE EVOLUTION OF THE MECHANICAL PROPERTIES

1. INTRODUCTION

The low cost and the good performance of the poly(vinyl chloride) products have resulted that this polymer is the most utilised in buildings, mainly in exterior applications, like window profiles, cladding structures and siding. However, the ultimate user acceptance of the PVC products for outdoor building applications will therefore depend on their ability to resist to the deterioration of their mechanical and aesthetic properties over long periods of exposure. In order to assure the weatherability of these materials, the PVC resin needs to be compounded and processed properly, using the suitable additives, leading to a complex material, whose behaviour and properties are quite different from the PVC resin by itself. The outdoor degradation of such products is complex and not completely understood for most of the technical formulations, so the study of the photo-degradation of such products still remains a matter of actual interest.

So, in the present work, we had performed the artificial accelerated ageing in xenon light and a natural exposure in Lisbon (hot, Mediterranean climate), using four different types of TiO₂ pigmented PVC formulations, containing various other additives. The samples are designed to outdoor applications and are extruded in form of plates, with 2 mm thickness approximately.

Various evaluation techniques, such as colourimetry, infrared microscopy and mechanical tests, like impact and traction, have been used to evaluate the effects of degradation in the PVC samples, originated by the weathering to light, referred to previously.

2. OBJECTIVE

In this paper, we try to rely the molecular analysis of the oxidative ageing in stabilised PVC to the analysis of their mechanical and aesthetic properties, in function of different conditions of photo-oxidative ageing, such as artificial simulated ageing using xenon sources and natural weathering in Lisbon.

3. SAMPLES: COMPOUNDING AND PROCESSING

In this study, we use 4 different types of TiO₂ pigmented PVC formulations, containing CaCO₃ and various additives, which are designed for outdoor applications. A particular attention was made in the selection of the thermal stabilisers to concern the ecological trends that prevail actually.

The PVC formulations are referred as PVC CZ and PVC S, according the type of thermal stabiliser present in the compositions (respectively Calcium/Zinc or solid tin) The formulations including an additive anti-UV of type benzotriazole (tinuvin P) are marked with a “T” (referred as PVC CZT and PVC ST).

The compounding process of the designed formulations and the extrusion of profiles with 2 mm thickness was made in the Baquelite Liz (Portugal).

4. EXPERIMENTAL METHODS OF ANALYSIS

The analysis of the oxidation at macroscopic scale can be easily performed in the thick plates by means of various evaluation techniques, such as colourimetry, gloss measurements and determination of the mechanical proprieties, like impact and tension strengths. The characterisation of the oxidation products resulting from the ageing process, at microscopic scale, can also be performed in this substract using the infrared micro-spectroscopy (Micro-FTIR).

5. ARTIFICIAL WEATHERING

The artificial simulated weathering were carried out in an Aralab Fitoclima 600 EDTU chamber equipped with a 6000 watt borosilicate glass-filtered xenon arc sources. The program used consists in a continuous radiation, with a relative humidity of 50% and a temperature of the circulating air of 42°C.

The intensity is auto-adjusted to assure a global irradiation of 550 W/m², 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 it was used a calibrated black standard thermometer sensor, which is maintained at 65 ± 3°C. The temperature indicated by the white standard thermometer is 50 ± 3°C.

The test pieces were exposed in a rotational cylindrical sample rack (1 rpm) and were removed periodically to perform all the several test measurements referred previously.

6. NATURAL EXPOSURE

The specimens to perform all measurements are exposed in Mars of 2000 to outdoor weathering at Lisbon (hot, Mediterranean climate), in accordance with ASTM Method D 1435, [1], at an angle of 45°, facing south.

7. RESULTS

7.1. Impact Measurements

To study the influence of surface effects originated by the ageing process, the Charpy tests should be performed using flatwise impact and unnotched or double notched specimens. The unnotched specimens, taken from not weathered extruded profiles, bent and don't break using spans from 40 to 62 mm. Nevertheless, using spans of 40 mm and double -V notched specimens, type ISO179/1fA, was possible to obtain a acceptable percentage of breaks. However, as the thickness of the extruded profiles is lower than the recommend value of ISO standard, the tests are also performed with double specimens, having about 4 mm of thickness. The tests are performed using a Zwick 5102 Testing Machine, using the most suitable hammer (from 0,5 to 4 J), according the method indicated

in International Standard ISO 179:1993, [2]. The notches are provided perpendicular to the direction of blow.

The results obtained from a minimum of 15 specimens from each sample, are submitted to statistical analysis for detection and rejection of outliers, using the methods described in the ASTM standard E 178-94, [7].

The initial values of the impact strength of the 4 PVC formulations studied, are indicated in table 1. This table contains the values determined in both single and double shaped specimens, prepared from extruded profiles.

Table 1: Initial impact strength of the different PVC samples

Formulation	Impact strength (KJ/m ²)	
	Single specimens (2 mm thickness)	Double specimens (4 mm thickness)
PVC CZ	27,1 ± 8,3	15,3 ± 4,8
PVC CZT	20,8 ± 6,8	10,5 ± 3,0
PVC S	23,7 ± 7,6	13,0 ± 3,5
PVC ST	19,8 ± 12,2	10,3 ± 3,3

The formulations not weathered, containing a Ca/Zn stabiliser, gives a % of brakes between 70 to 75% using a span of 40 mm, but the formulations containing the tin stabiliser were more flexible and more difficult to break, giving a % of brakes from 40 to 50% using the same span.. Otherwise, the formulations not containing an UV stabiliser seems to present an initial higher impact strength than the photo-stabilised formulations.

The increase of the thickness of the specimens, resulting from the use of double specimens, leads to the reduction of their flexibility and turns possible to improve the % of brakes of the formulations containing tin for 65%, although increasing the span to 62 mm. However, the double specimens give us a lower value of impact resistance than the single specimens. This can be explained by the difference of spans used in both cases, but can also means that during the impact test of the lower thickness specimens can occurs some other phenomena that are not inherent to the own material characteristics. Indeed, during the impact process we observe a flexion of the single specimens and sometimes they jump from the support, giving us an higher value of the impact resistance than it was to be expected. So, the values obtained with the thin specimens can not be representative of the real impact strength of the polymeric material and, in that case, they only might be used to comparative purposes, like to evaluate the evolution of an apparent strength along the weathering. Such phenomenon wasn't seen using the double specimens, which presents a higher thickness than the minimum recommended by the referred ISO standard. Consequently, the values obtained with the thick specimens can be more representative of the true impact strength of these PVC materials. The evolution of the impact strength during 12 500 hours of artificial weathering with xenon light¹, using single or double specimens, is represented in figures 1 and 2, respectively. The same scale of abscissa axis was maintained to simplify a comparative analysis.

¹ : 12 000 h of xenon light corresponds to 10 years or 15 years of natural weathering at a severe climate (type Arizona) and at a moderate climate (type Florida), respectively, [5, 6].

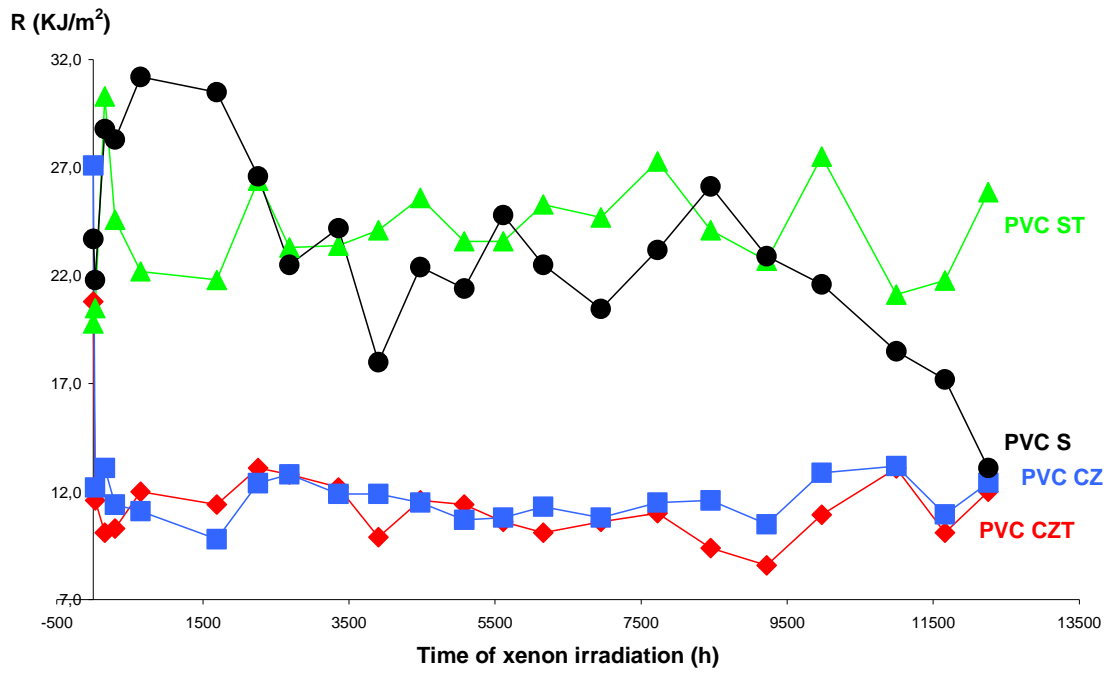


Figure 1: evolution of the Charpy impact strength of single specimens during 12500 hours of artificial weathering with xenon light

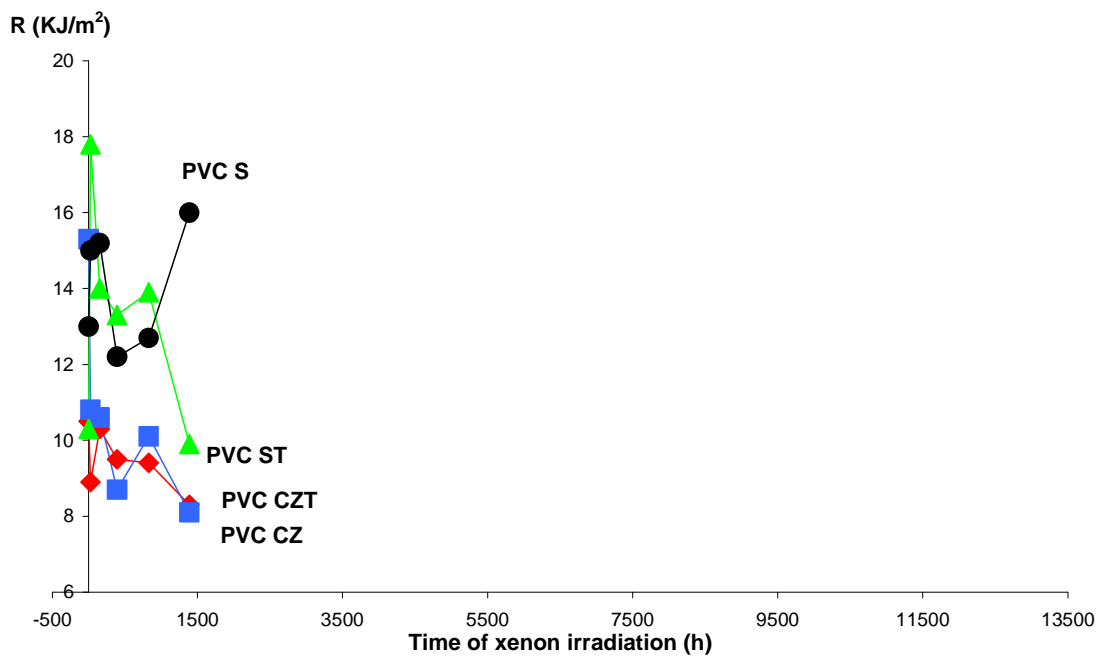


Figure 2: evolution of the Charpy impact strength of double specimens during 1400 hours of artificial weathering with xenon light

The evolution of the impact strength during 1 year of natural exposure is presented in the figures 3 and 4.

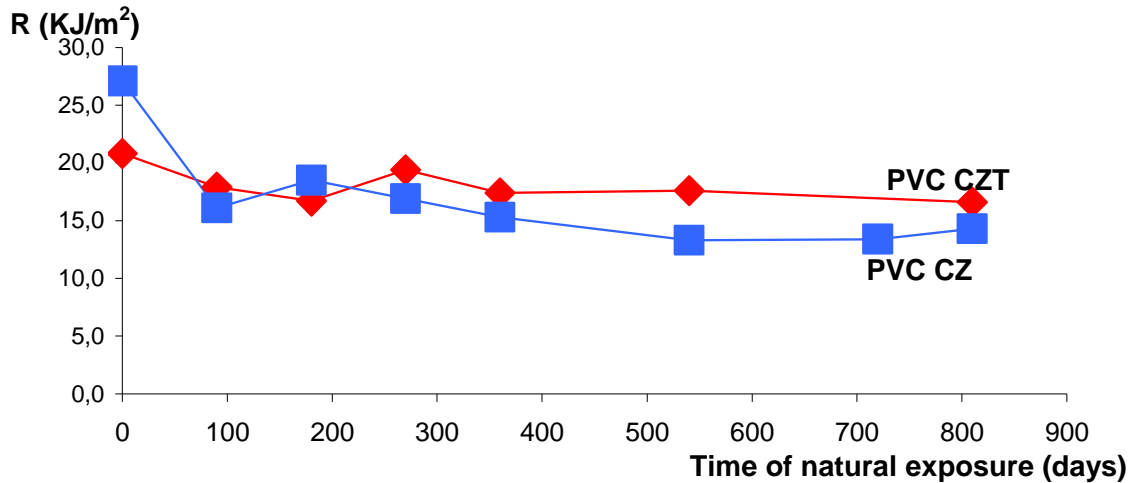


Figure 3: evolution of the Charpy impact strength of single specimens, extracted from PVC extruded profiles stabilised with Calcium/zinc, during 27 months of exposure at Lisbon

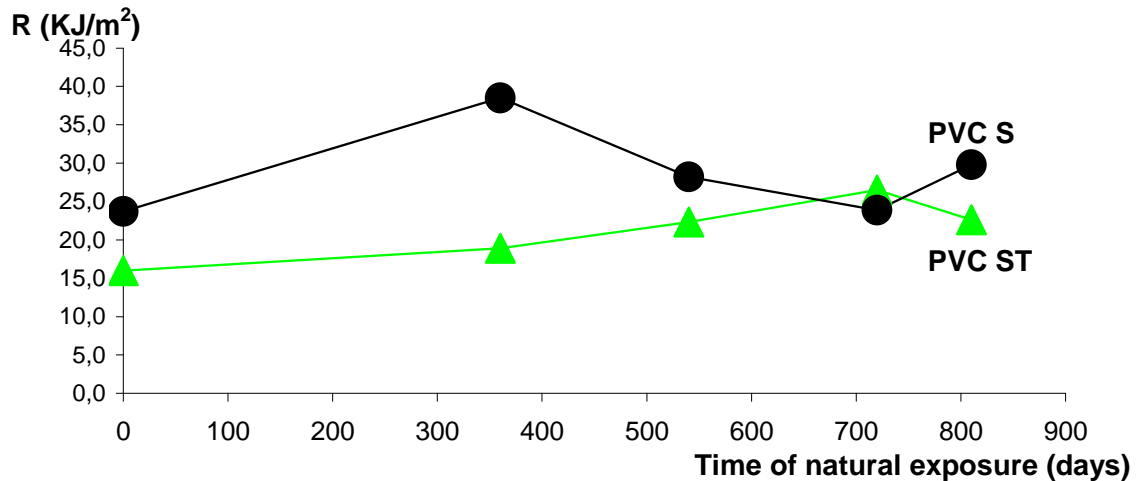


Figure 4: evolution of the Charpy impact strength of single specimens, extracted from PVC extruded profiles stabilised with tin, during 1 year of natural weathering at Lisbon

The results of Charpy impact strength obtained from artificial ageing, represented on figure 1, show us an interesting fact: the formulations stabilised with calcium/zinc had a decrease of the impact strength in the first 25 hours of irradiation and the formulations containing the tin stabiliser had an increase of the same propriety in the first 150 hours. After these periods of time, all formulations retrieve their initial level of strength, which was maintained until 12500 hours of irradiation, with the exception of the PVC S, that seems to begin a continuous decrease of the impact

properties after 10 000 hours of irradiation.

The referred unusual initial behaviour is also observed with the thick specimens (fig. 2) and in simple specimens exposed at Lisbon, confirming that observed slightly initial improvement of the impact strength is exclusive of the compounds stabilised with tin.

These observations lead to the conclusion that the most important modification at the level of the impact strength of the studied PVC formulations occurs in the beginning of the artificial weathering. However, observing the results of the global ageing process, we conclude that, with exception of PVC S, the photo-oxidation didn't induce a significant change in the impact strength of the studied PVC based formulations. So, in the present case, this mechanical propriety wasn't good to evaluate the evolution of the weathering process in these thin polymeric materials. However, it is possible than formulations including an impact modifier, which can migrate or suffer degradation during the photo-oxidation process, could show a different behaviour and, in that case, the Charpy method would be a suitable technique to evaluate the effects of the photo-oxidative ageing.

Concerning the natural exposure, represented in figures 3 and 4, we think that the results are premature and still not conclusive, although they seems to follow the trends of the beginning of the artificial ageing referred before.

7.2 Tension Measurements

The stress and the strain strengths at failure of specimens type 1BA, prepared from thick plates, are performed at LNEC by means of an Universal Testing Machine INSTRON 4483, according the method indicated in International standard ISO 527:1993, [3].

The same statistical methods for detection and rejection of outliers referred before, [7], were applied at a minimum of 15 specimens from each sample.

The initial values of the tensile proprieties of the PVC extruded profiles, containing 4 different formulations, are indicated in table 2. The proprieties presented in these table are the modulus of elasticity (E), the stress at yield (σ_c), the strain at yield (ϵ_c), the stress at break (σ_r) and the strain at break (ϵ_r). The tests are performed at 2 mm/min, in the case of PVC CZ and PVC CZT, and at 5 mm/min, in the case of PVC S and PVC ST. The strains are measured without extensometer, because it was frequent the occurrence of many breaks out of the specimen marks.

Table 2: Initial tensile proprieties of the different PVC samples

Parameter	PVC CZ	PVC CZT	PVC S	PVC ST
E (Mpa)	1512 ± 199	1530 ± 125	1465 ± 143	1431 ± 116
σ_c (Mpa)	52,9 ± 1,3	52,7 ± 1,0	53,2 ± 0,9	51,7 ± 2,3
ϵ_c (%)	6,2 ± 0,8	6,5 ± 1,2	6,2 ± 0,5	6,8 ± 0,4
σ_r (Mpa)	37,7 ± 2,7	38,8 ± 1,3	40,2 ± 3,7	41,5 ± 4,6
ϵ_r (%)	23,9 ± 15,2	34,2 ± 13,9	114,5 ± 59,1	150,6 ± 55,3

As we can conclude from the analysis of table 2, the main difference between the original tensile proprieties of the several PVC formulations studied, occurs at the level of break proprieties. The formulations stabilised with tin present a higher strain at break than the formulations containing a Ca/Zn based thermal stabiliser.

Concerning the evolution of the tensile proprieties of the studied PVC materials during the weathering, there weren't any significant modification of the yield proprieties during the course of photo-oxidation. On the contrary, the decrease of the strain at break induced by the weathering is generalised at all PVC formulations, but it occurs at one more interesting scale with compounds containing the tin thermal stabiliser. The evolution of this parameter, obtained after irradiation with xenon light, is presented in the figures 5 and 6. The correspondent evolution in conditions of natural exposure at Lisbon is presented in figures 7 and 8.

Similarly what had happen with the impact strength, also the most important modification of the strain at break occurred in the first stages of the weathering. However, this phenomenon didn't happen with the PVC CZT submitted to the natural exposure, possibly due to the positive role performed by the Tinuvin P, which retarded the photo-oxidation process. Interesting is also the swinging behaviour of the PVC ST at first year of natural weathering at Lisbon, characteristic that was also observed with other physical proprieties, such as gloss.

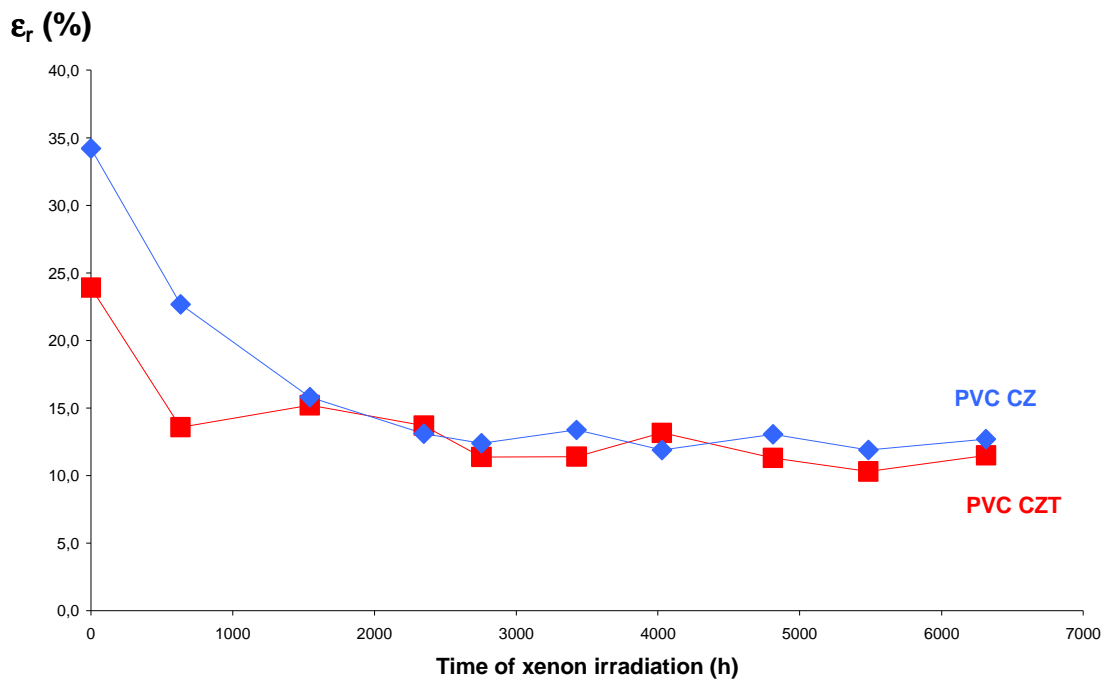


Figure 5: evolution of the strain at break of specimens, extracted from PVC profiles stabilised with calcium/zinc, during 6500 hours of artificial weathering with xenon light

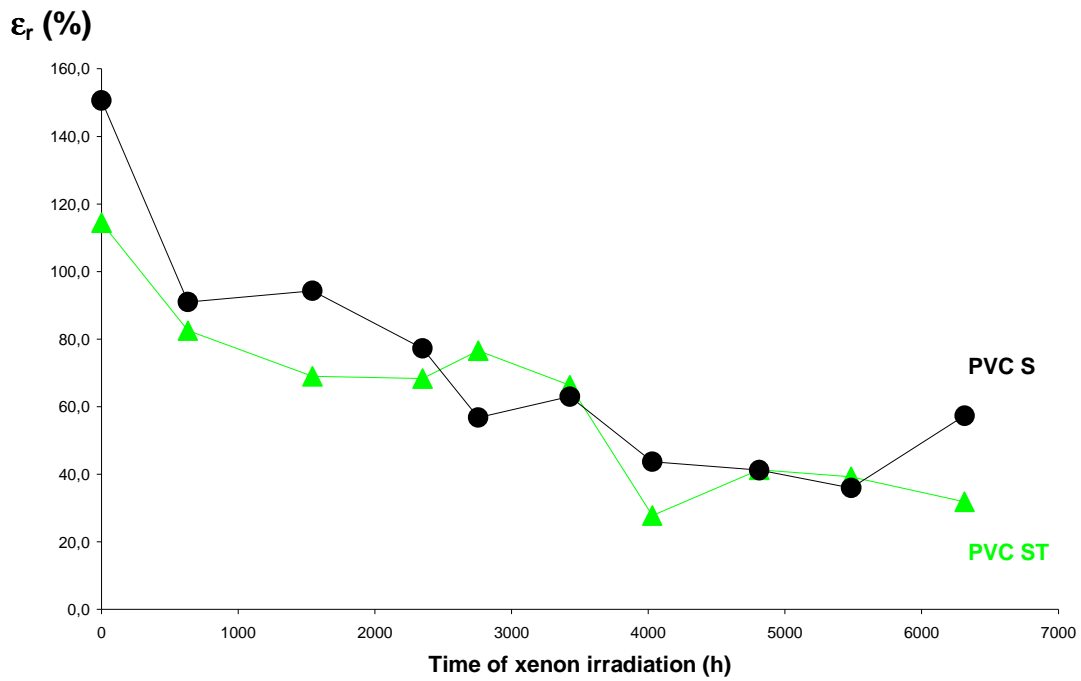


Figure 6: evolution of the strain at break of specimens, extracted from PVC profiles stabilised with tin, during 6500 hours of artificial weathering with xenon light

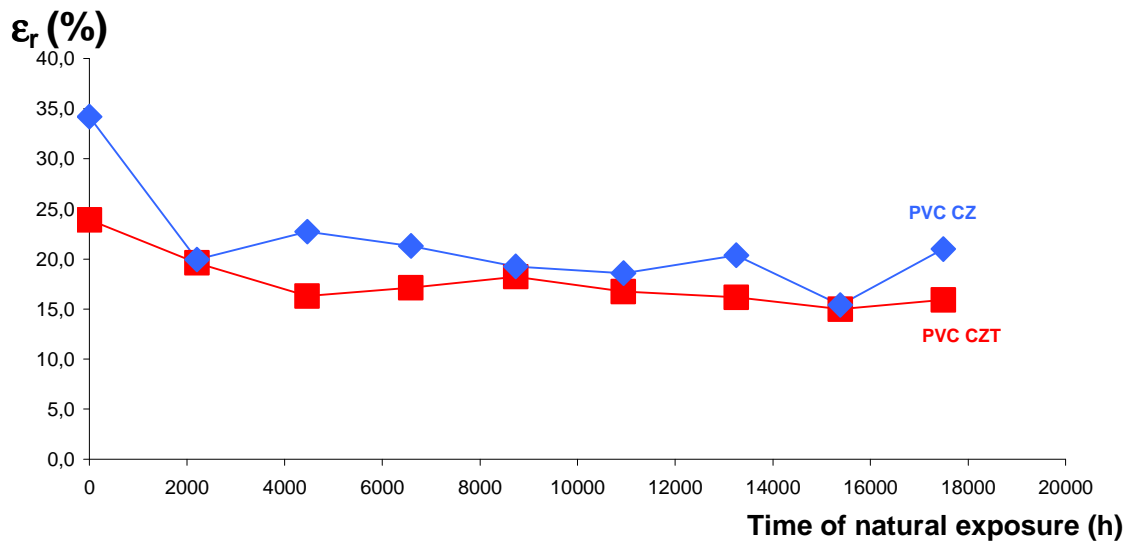


Figure 7: evolution of the strain at break of specimens, extracted from PVC profiles stabilised with calcium/zinc, during 2 years of natural weathering in Lisbon

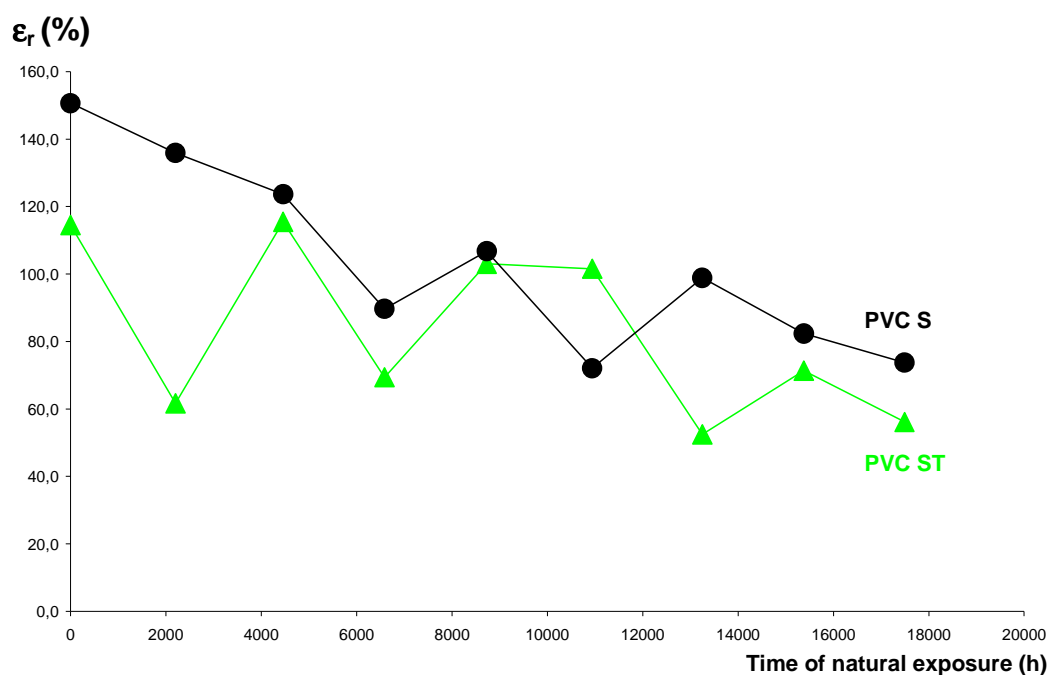


Figure 8: evolution of the strain at break of specimens, extracted from PVC profiles stabilised with tin, during 2 years of natural weathering in Lisbon

7.3 Infrared Microscopic Measurements

The IR microscopy depth profiling is performed using a Nicolet Magna-IR 760 Spectrometer E.S.P. and a microscope Nicolet Nic-Plan IR, by the classical procedure consisting in cross-sectional analysis of slices microtomed from thick plates, [4], using steps of 5 μm and 20 μm for width of spectral window.

The first photo-oxidation profiles detected by this technique was in PVC S at 4478 hours of xenon irradiation, followed by the PVC ST after 5611 hours, but only at 6950 hours in the case of the PVC CZ and, finally, the PVC CZT at 8450 hours.

This means that the formulations stabilised with tin are more susceptible of photo-degradation than the formulations containing a stabiliser based on calcium/zinc, which is also consistent with observations made at level of evolution of the mechanical proprieties during the artificial weathering. Moreover, these results lead to the conclusion that the additive anti-UV perform a positive role in the PVC formulations studied.

To illustrate the phenomenon of photo-oxidation, we present in the figure 9 the group of Micro-FTIR spectra, in the carbonyls region, obtained with a PVC S after 8450 hours of xenon irradiation. The spectra of differences are referenced to the initial values of the sample, not aged. The spectres are corrected from vacuum effects in the first layers, by using the peak at 877,5 cm^{-1} , which not undergo significant changes during the photo-degradation process. The correspondent group of difference spectra is presented in the figure 10. The figure 11 represents the oxidation profile at 1732 cm^{-1} .

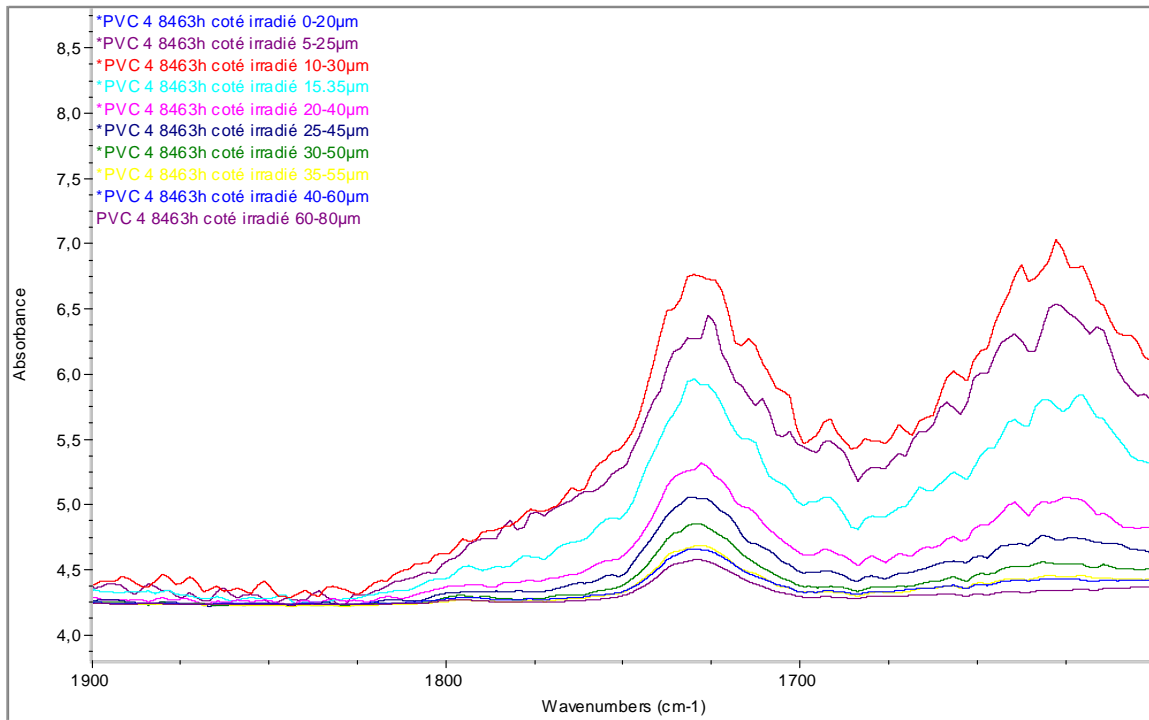


Figure 9: Infrared microscopy spectra, in the carbonyl region, obtained from a sample of a PVC S plate weathered during 8450 hours in xenon light

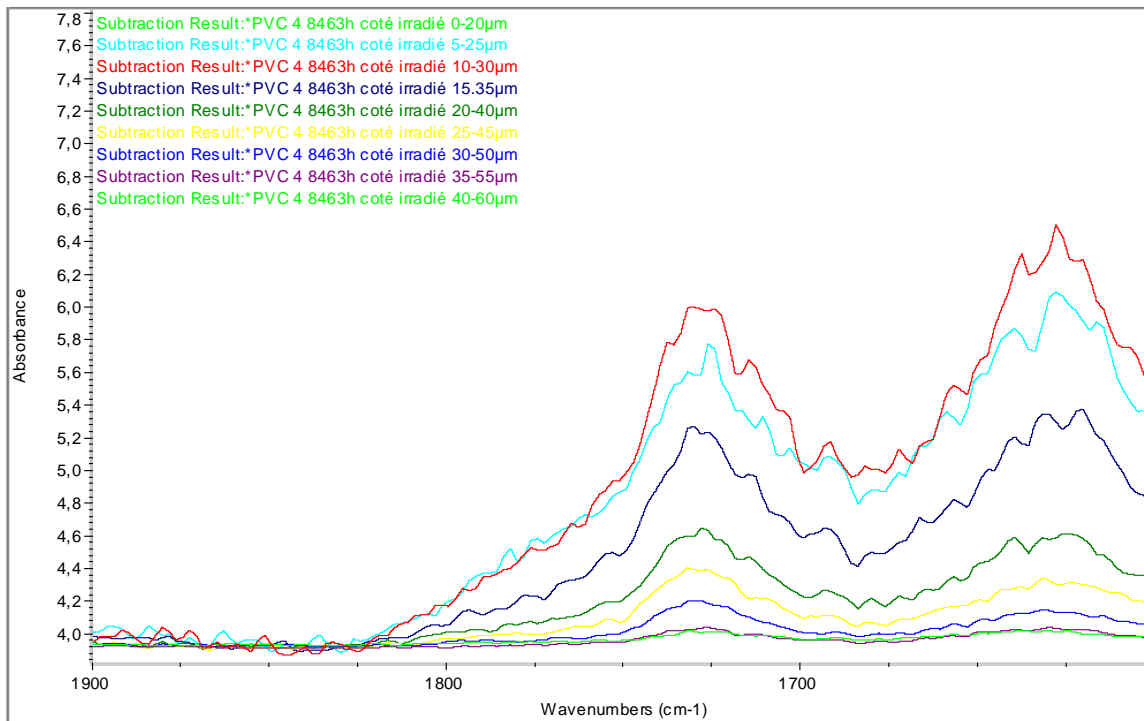


Figure 10: Infrared microscopy spectra of differences, in the carbonyl region, obtained from a sample of a PVC S plate weathered during 8450 hours in xenon light

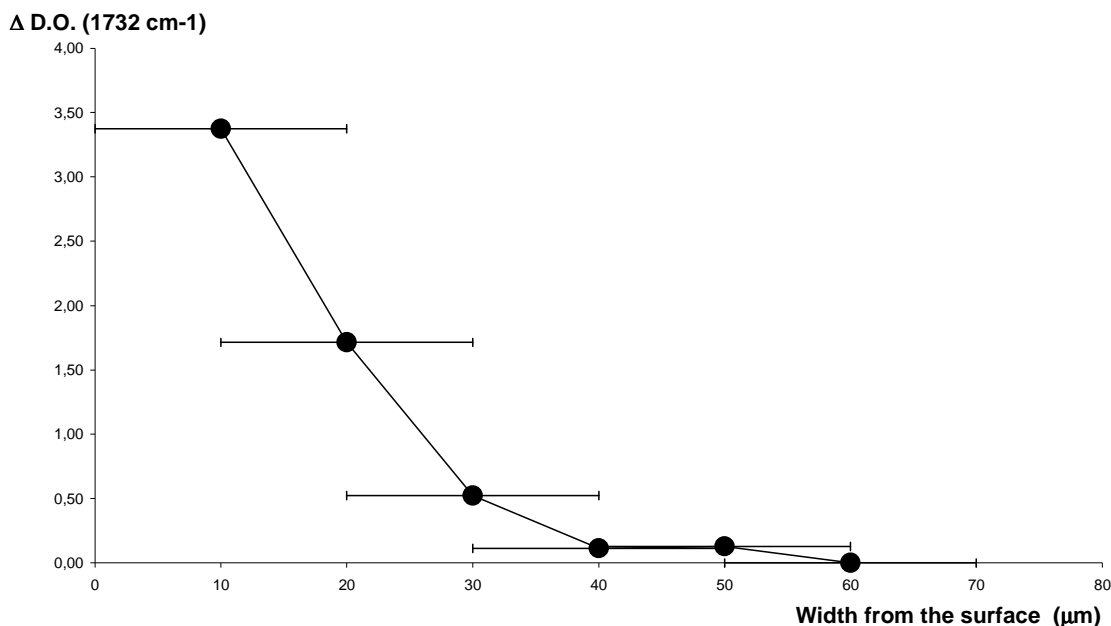


Figure 11: Oxidation profile at 1732 cm⁻¹ of a PVC S plate weathered during 8450 hours in xenon light

7.4 Colourimetric Measurements

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

The samples were prepared from extruded thick plates, with the compositions referred before. The colour difference determined in each period of exposition was calculated in relation to the initial values of the sample, still not aged.

The most correct way to evaluate the evolution of the colour during the weathering process consists on a graphic representation of the yellowness index, which is based on CIE standard illuminant D65 and CIE 1931 2° standard observer viewing.

The yellowness index differences obtained with the samples aged artificially with Xenon light are presented in the figure 12. The figure 13 presents the yellowness index differences of analogous samples submitted to natural exposure in Lisbon during 27 months.

We can extract from the plots of these figures that there was an initial whiteness of the samples, resulting from the photo-oxidation of the conjugated double bonds formed during the processing of the polymer.

This phenomenon can mask the truth magnitude of the colourimetric evolution, during the weathering. However, the yellowing of samples was well observed by means of a modified representation, starting all the curves in a common point of yellowing, after the conclusion of the initial whiteness of samples. This apparent yellowness index, in arbitrary units, is illustrated only for the artificial weathering (figure 14), because the samples naturally exposed are even in the whiteness period.

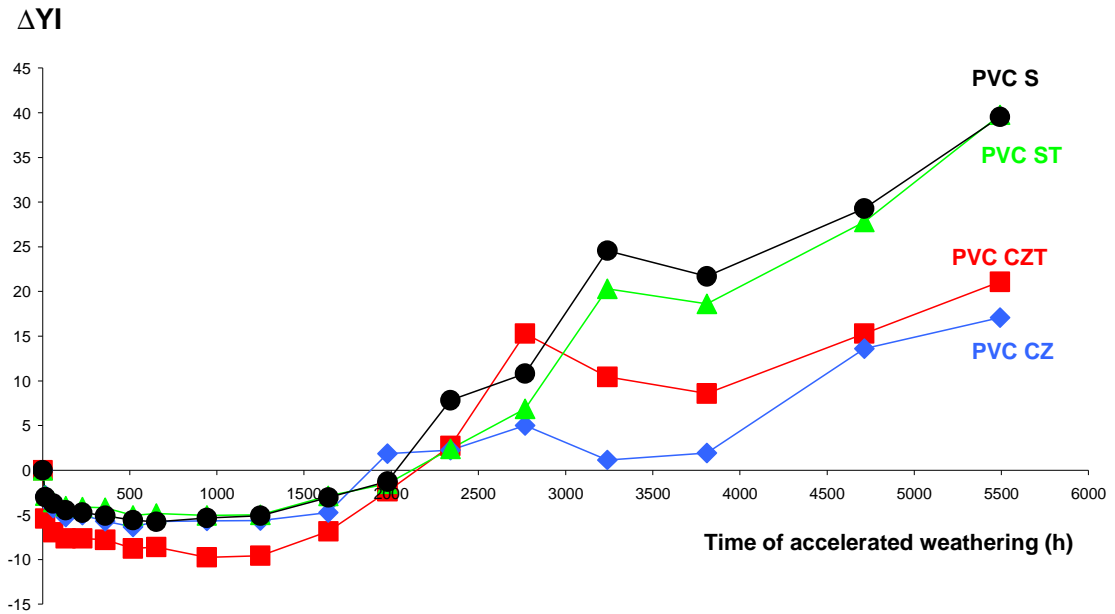


Figure 12: Evolution of the yellowness index difference during 5500 h of artificial weathering in xenon light

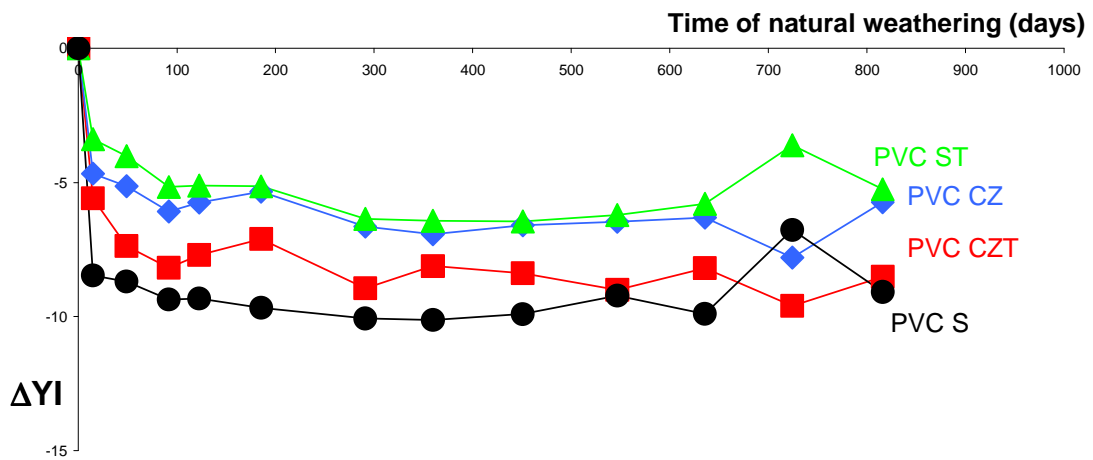


Figure 13: Evolution of the yellowness index difference during 27 months of natural weathering in Lisbon

The colourimetric results obtained leads to the conclusion that it is the formulations containing a calcium/zinc thermal stabiliser that have shown the best behaviour in the accelerated weathering tests using xenon light. We see also that, contrarily which was expected, the UV absorber Tinuvin P didn't play a positive role at level of colour formation during the photo-oxidation.

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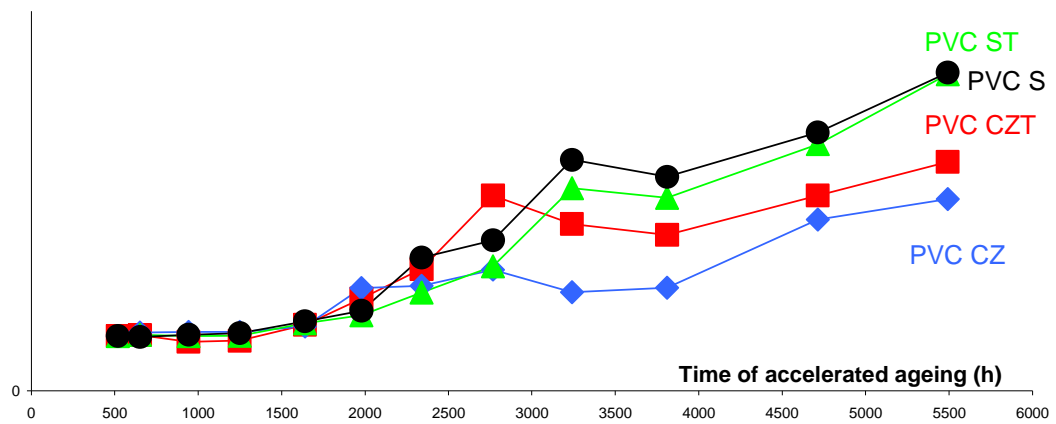


Figure 14: Evolution of the apparent yellowness index (after withness) during 5500 h of artificial weathering in xenon light

7.5 Gloss Measurements

The gloss measurements of the exposed surfaces of the thick plates exposed at LNEC, are made at an angle of 60°, using a gloss-meter Statistical Novo-Gloss.

The gloss results from measurements in samples submitted to artificial and natural weathering are presented in the figures 15 and 16, respectively. The representations are made at same ordinate axis scale to simplify a comparison.

In both types of weathering was observed a swinging variation of the gloss of samples.

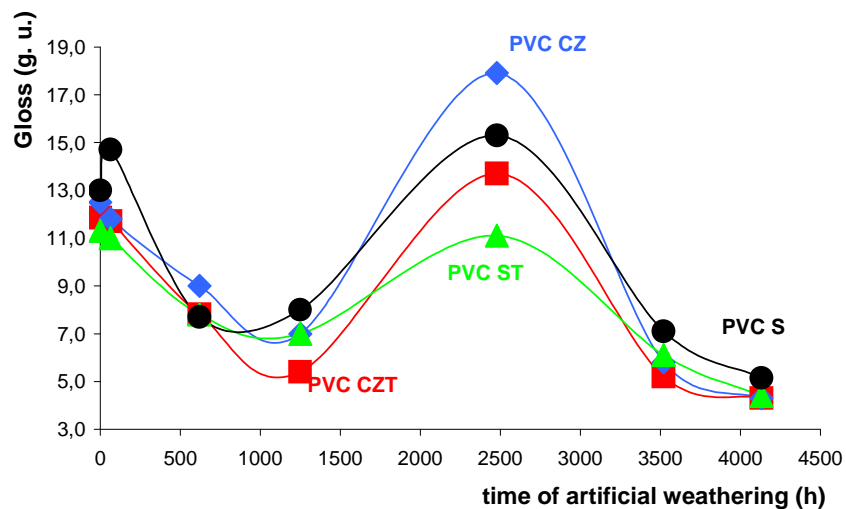


Figure 15: Evolution of the gloss during 4200 h of artificial weathering in xenon light

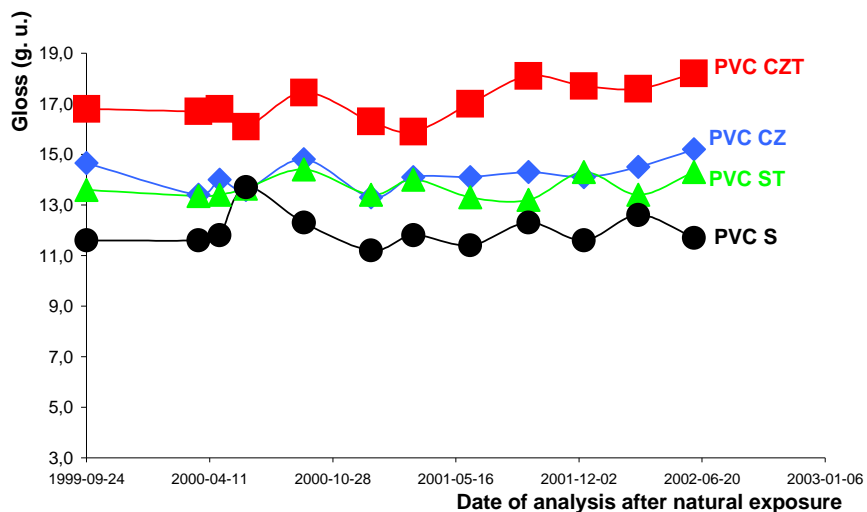


Figure 16: Evolution of the gloss during 27 months of natural weathering at Lisbon

8. CONCLUSIONS

We saw that the most important modification at the level of the mechanical proprieties of the studied PVC formulations, such as the Charpy impact strength and tensile strain at break, occurs in the beginning of the artificial weathering.

However, after some time of irradiation, all formulations retrieve their initial level of impact strength, and with exception of one formulation (PVC S), the photo-oxidation didn't induce a significant change in this mechanical propriety. So, it seems to us that the Charpy impact strength couldn't be a suitable characteristic to evaluate the evolution of the photo-oxidative ageing in thin PVC extruded materials, fundamentally when their formulations not include impact modifiers.

The results obtained show us that the PVC formulations stabilised with tin present a higher strain at break than the formulations containing a Ca/Zn based thermal stabiliser and that propriety had a significant decrease during the weathering of all PVC formulations studied, although at larger scale in the case of those that present initial higher values of strain. So, it seems to us that this mechanical propriety could be very suitable to evaluate the course of the photo-oxidative ageing.

The results obtained from infrared microscopy leads to the conclusion that the formulations stabilised with tin are more susceptible of photo-degradation than the formulations containing a stabiliser based on calcium/zinc, which is also consistent with observations made at level of evolution of the strain at break. Moreover, the results of infrared spectroscopy show us that the tinuvin P performs a positive role decreasing the quantity of oxidation products resulting from the photo-degradation process. However, this technique of analysis had permitted only to detect photo-oxidation profiles, at minimum, after 4478 hours of xenon irradiation, at a point when the strain at break was lower than 50% of its initial value. This fact permits us to conclude that, possibly, the strain at break could be a more sensible characteristic to detect the effects of weathering.

The colourimetric results shown us that there are an initial whiteness of the samples, resulting from the photo-oxidation of the conjugated double bonds formed during the processing of the polymer and that this phenomenon can mask the truth magnitude of the colourimetric evolution, during the weathering. So, this leads to the conclusion that the best way of evaluating the magnitude of the yellowness during the photo-degradation consists in a graphical representation of the apparent

yellowness index, in which the plots are initiated in a common point, after the end of the referred whiteness of samples.

The colourimetric results obtained led also to the conclusion that it is the formulations containing a calcium/zinc thermal stabiliser that have shown the best behaviour in the accelerated weathering tests using xenon light, which agreed with the results obtained by infrared microscopy.

Finally, we concluded that the evolution of the gloss in the weathered surfaces of all PVC profiles studied are similar, which is characterised by a swinging behaviour, which can't be explained by the theory of the multilayer weathering, [8]. Indeed, a cyclic regeneration process of the sample surfaces, resulting from the erosion caused by the water or the wind action, would lead to a partial regeneration of the coloration and of mechanical properties, and loss of gloss. However, this last effect wasn't seen in the present study. Moreover, the accelerated weathering was performed at continuous irradiation and without water aspersion, so the phenomenon of removal of the degraded layer by erosion action will be difficult to occur.

9. REFERENCES

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- [5]: EN 513 (1998): Unplasticized polyvinylchloride (PVC-U) profiles for fabrication of windows and doors – Determination of the resistance to artificial weathering
- [6]: EN 12 608 (1998): Unplasticized polyvinylchloride (PVC-U) profiles for fabrication of windows – Classification, requirements and Test Methods
- [7]: ASTM E 178-94: Standard Practice for Dealing With Outlying Observations
- [8]: Magnus, R. *Kunststoffe*, “Multilayer Weathering of PVC – Practical Consequences for the User”, 81 (12), p. 1113-1117 (1991)

SLIDES



VARIABILITY BETWEEN DIFFERENT ARTIFICIAL ACCELERATED WEATHERING DEVICES IN THE PHOTOOXIDATION OF POLYVINYLCHLORIDE FOR OUTDOOR APPLICATIONS: CORRELATION WITH NATURAL EXPOSURE

Luís E. Pimentel Real



Laboratório Nacional de Engenharia Civil
Lisboa, Portugal

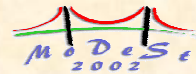
Jean-Luc Gardette



Université Blaise Pascal
Aubière, France



INTRODUCTION



Increase of PVC in outdoor applications.

Advantages:

- Low cost
- Good technological performance
- Good ecological characteristics

Disadvantages:

- Discoloration (or yellowing)

Important characteristic: **Durability**

→ to reduce the effect of the negative aspects

→ compounding

→ complex material, which degradation mechanism is also complex



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MAIN OBJECTIVES



- To determine the **degree of acceleration** and to evaluate the weather simulation capacity of several different artificial accelerated weathering apparatus and different radiation sources.
- To deepen the knowledge about the **degradation and stabilisation mechanisms**.
- To evaluate the **performance** of different **stabilisers**
- To develop a method for estimate the **durability** of PVC based materials.



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SAMPLES



- unstabilised PE Films (reference material)
- PVC formulations for outdoor applications, containing several additives: fillers (CaCO_3), pigment light screens (TiO_2), thermal stabilisers (DBTM, Ca/Zn), ultraviolet light absorbers (benzotriazole type), lubricants and processing aids
- extruded thick plates (1,5 to 2,5 mm)
- calendered films, with thickness between 100 and 150 μm



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WEATHERING METHODS



Artificial simulated weathering with xenon sources

- Aralab Fitoclima 700 EDTU , 6000 watt
- Atlas Weatherometer Ci 65, 6500 watt
- Solar Box 3000e, 2500 watt

Artificial accelerated ageing with medium pressure mercury source

- SEPAP 12/24

Artificial accelerated ageing with fluorescent lamps containing low pressure mercury arc

- QUV PANEL UVB 313 nm

Natural weathering

- Lisbon (hot, mediterranean climate)
Angle of 45° to the horizontal, facing South)



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EXPERIMENTAL METHODS OF ANALYSIS OF THE DEGRADATION PRODUCTS



AGEING → **oxidation** products containing carbonyl, hydroxyl and chromophoric functional groups

→ Infrared spectroscopy (FTIR) and infrared microscopy (Micro-FTIR) in the 1600-1900 cm⁻¹ region of the spectrum (Analysis of the oxidative process at **molecular scale**)

→ UV-Visible spectrometry and determination of the colourimetric proprieties (Analysis of the effects at **macroscopic scale**)

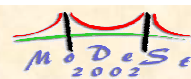
The formation of conjugated double bonds in the polymeric backbone can be simultaneous with the oxidation process. The preponderance of one of these processes is determined by the type of degradation mechanism, which is dependent of the experimental conditions of the photo-oxidation process (radiation wavelength, spectral characteristics of the radiation source and temperature).



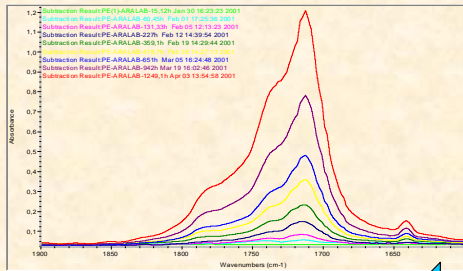
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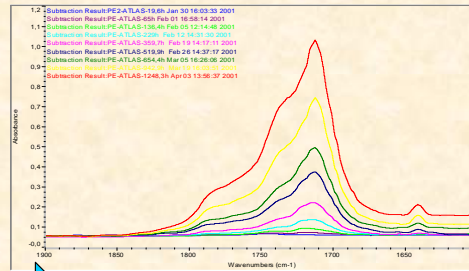
FTIR RESULTS



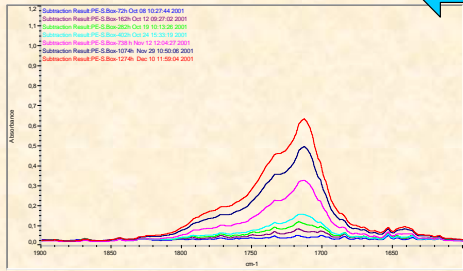
PE - Difference Spectra in the carbonyl region



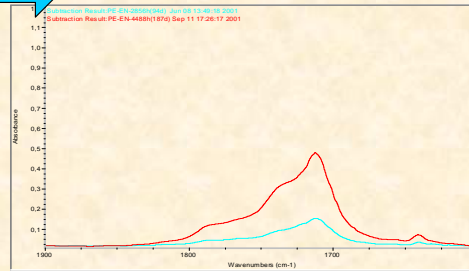
ARALAB: 1249 h



ATLAS: 1248 h



SOLAR BOX: 1274 h



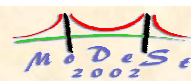
LISBON: 6 months



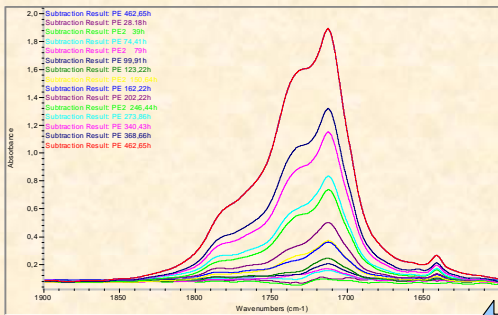
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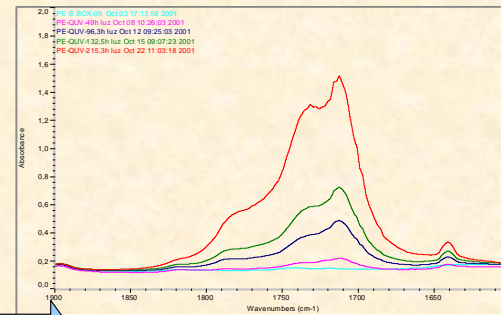
FTIR RESULTS



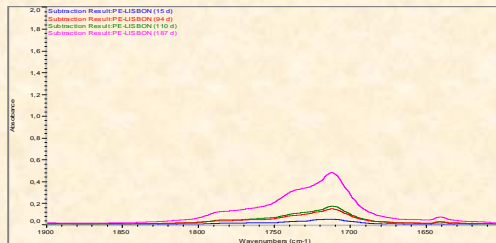
PE - Difference Spectra in the carbonyl region



SEPAP 12/24: 463 h



QUV: 215 h



LISBON: 6 months



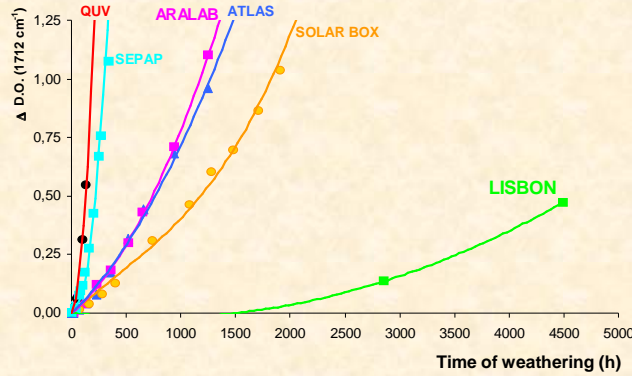
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KINETIC FTIR RESULTS



FTIR Kinetics (PE)



CONDITION	ACCELERATION FACTOR
SEPAP/ LISBON	21,2
QUV/ LISBON	35,9
SOLAR BOX/ LISBON	3,9
ATLAS/ LISBON	6,0
ARALAB/ LISBON	6,2



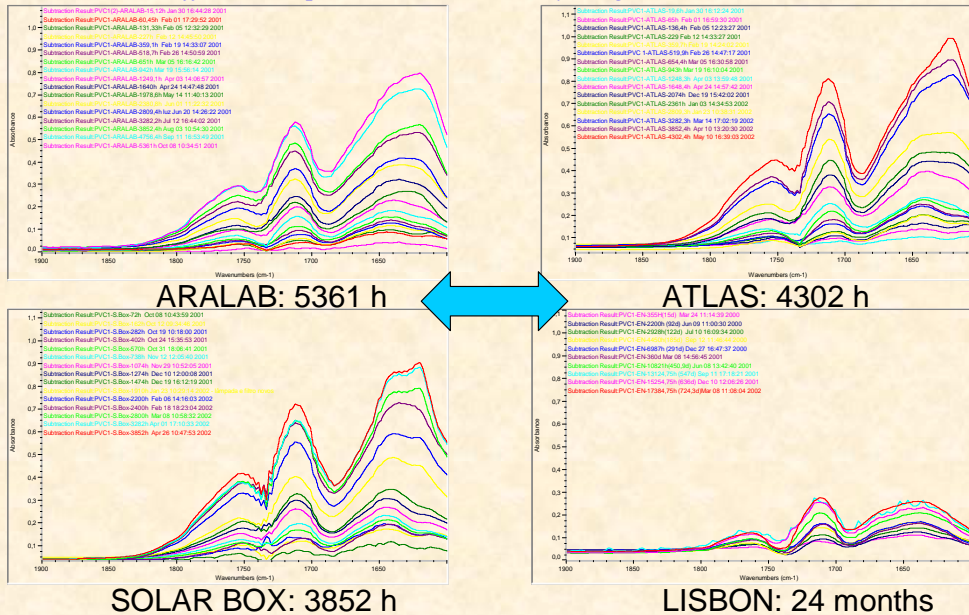
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FTIR RESULTS



PVC CZ - Difference Spectra in the carbonyl region



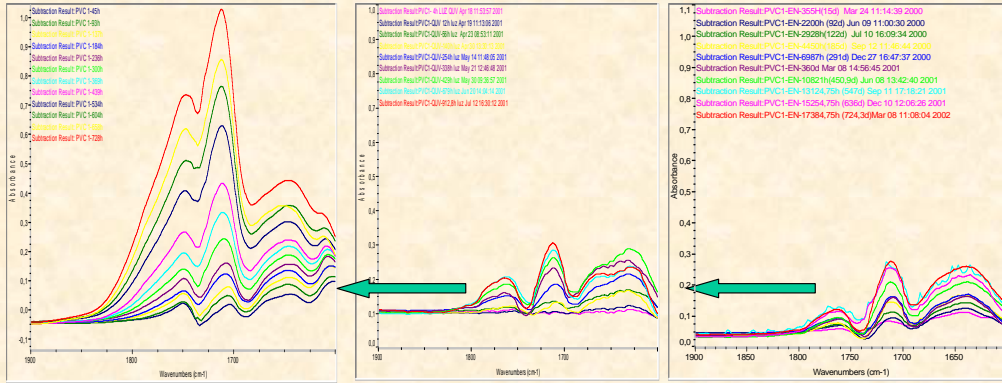
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FTIR RESULTS



PVC CZ - Difference Spectra in the carbonyl region



SEPAP: 727 h ↔ QUV: 913 h ↔ LISBON: 24 months



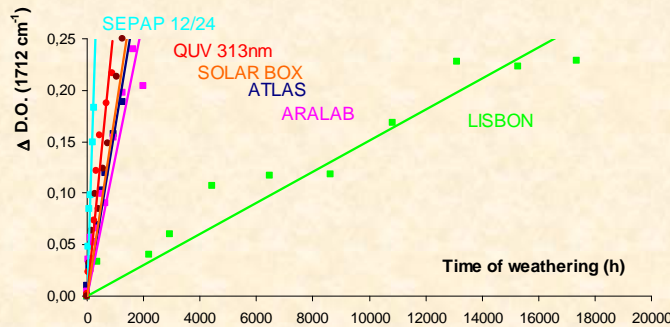
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KINETIC FTIR RESULTS



FTIR Kinetics (PVC CZ)



CONDITION	ACCELERATION FACTOR
SEPAP/LISBOA	80,94
QUV/ LISBOA	17,97
SOLAR BOX/LISBOA	13,12
ATLAS/ LISBOA	10,81
ARALAB/ LISBOA	10,33

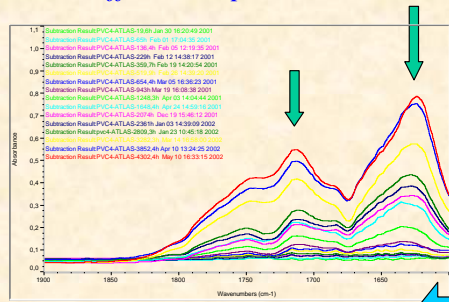


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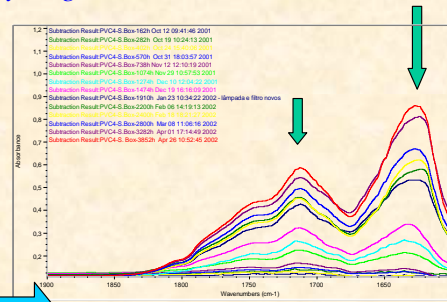


FTIR RESULTS

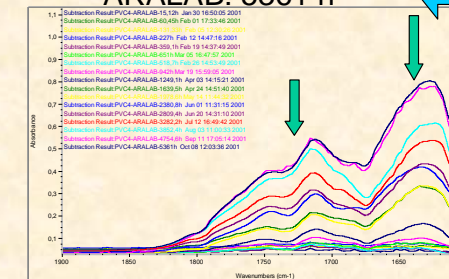
PVC S - Difference Spectra in the carbonyl region



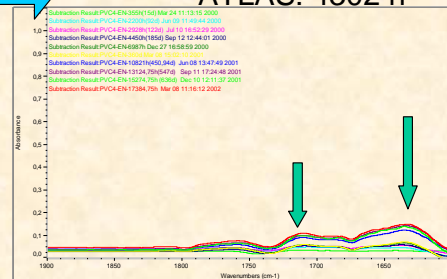
ARALAB: 5361 h



ATLAS: 4302 h



SOLAR BOX: 3852 h



LISBON: 24 months

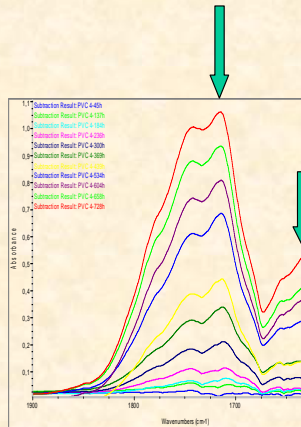


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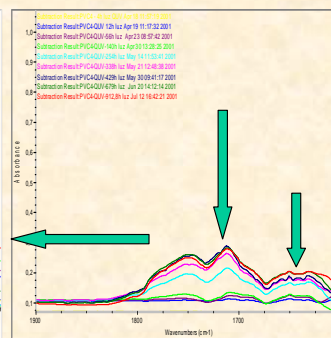


FTIR RESULTS

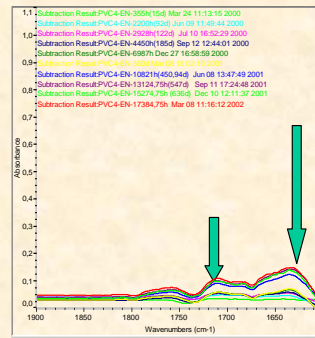
PVC S - Difference Spectra in the carbonyl region



SEPAP: 727 h



QUV: 913 h



LISBON: 24 months

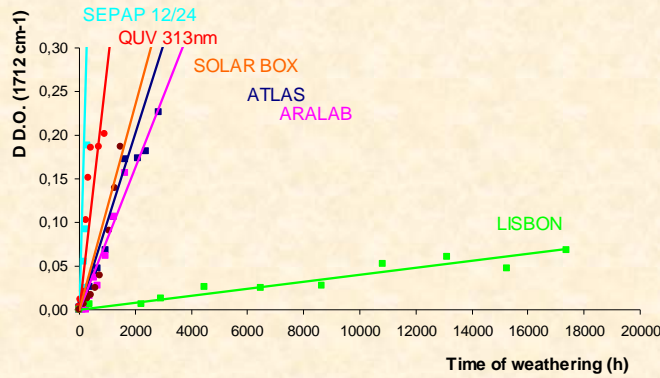
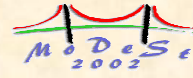


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KINETIC FTIR RESULTS

FTIR Kinetics (PVC S)



CONDITION	ACCELERATION FACTOR
SEPAP/LISBOA	295,87
QUV/ LISBOA	70,39
SOLAR BOX/LISBOA	32,80
ATLAS/ LISBOA	25,46
ARALAB/ LISBOA	20,51

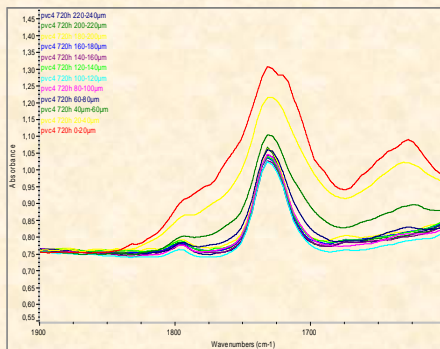


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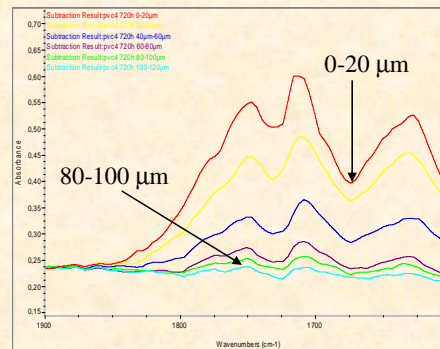


MICRO-FTIR RESULTS

PVC S - Infrared microscopy Spectra in the carbonyl region



(a) Direct spectra



(b) Difference spectra

The results allow to confirm that the photo-oxidative degradation occurs only up to a 80 µm deep from the irradiated surface.



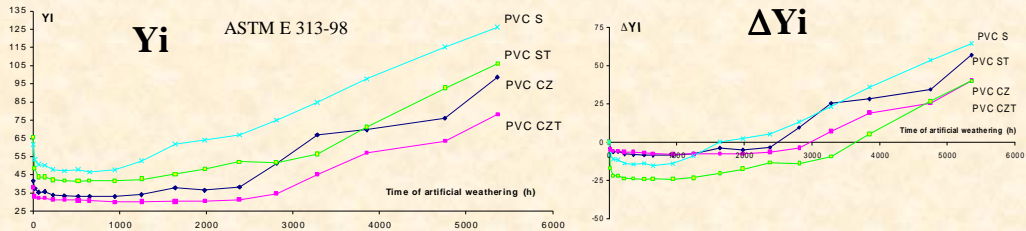
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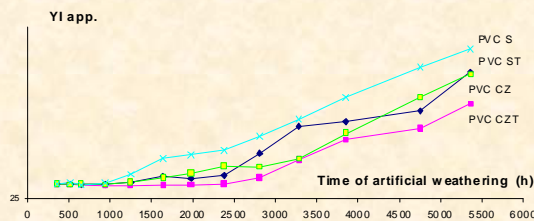
COLOURIMETRIC RESULTS



ARALAB - 5361 h - Yellowness index



Arbitrary units Apparent yellowness index



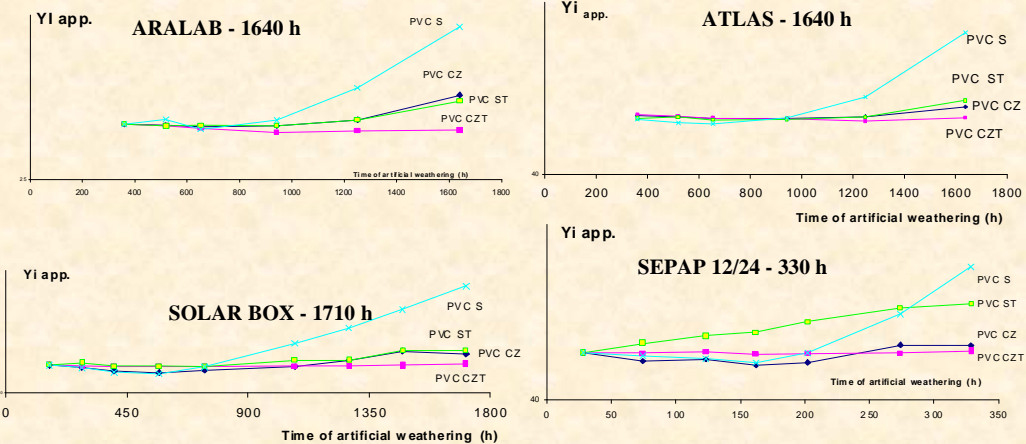
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COLOURIMETRIC RESULTS



apparent Y_i arbitrary units



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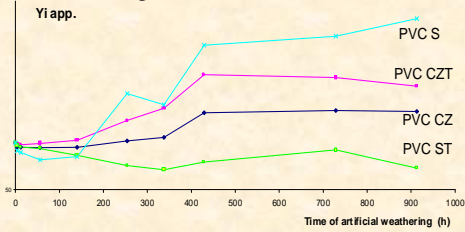


COLOURIMETRIC RESULTS

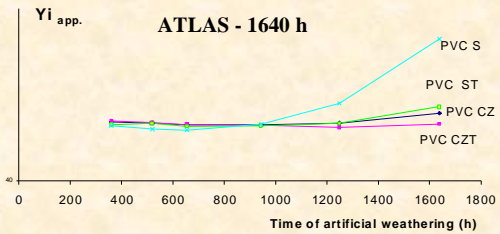


apparent Y_i arbitrary units

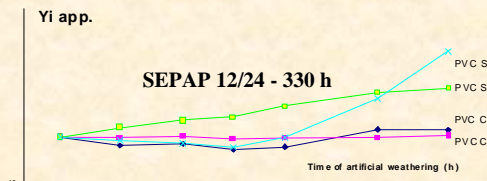
QUV 313 nm - 910 h



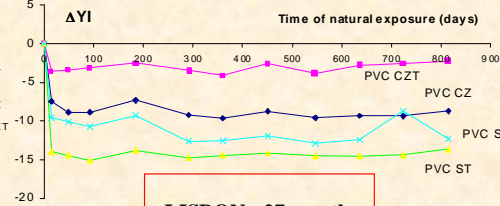
ATLAS - 1640 h



SEPAP 12/24 - 330 h



ΔY_i Time of natural exposure (days)



LISBON - 27 months
NO YELLOWNESS
ONLY WITHESS



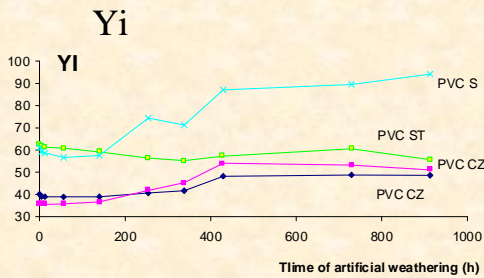
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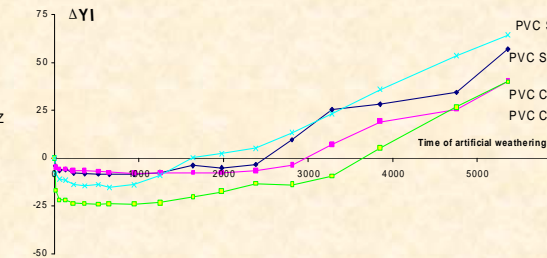
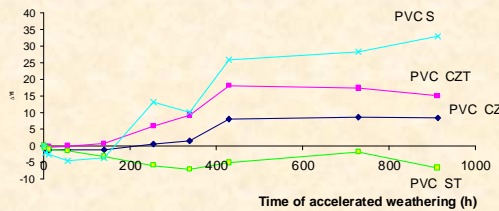
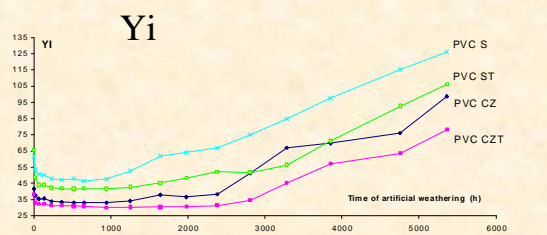
COLOURIMETRIC RESULTS



QUV - 913 h



ARALAB - 5361 h



ΔY_i

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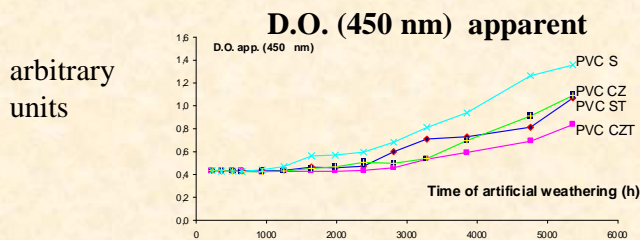
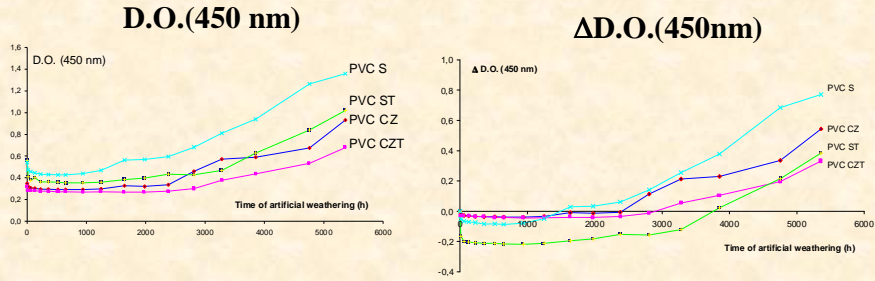
ΔY_i



UV-VIS RESULTS



ARALAB - 5361 h - Absorvance at 450 nm



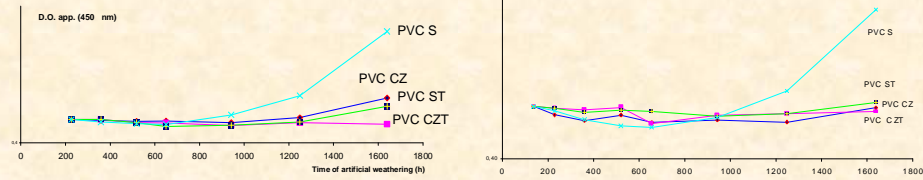
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UV-VIS RESULTS

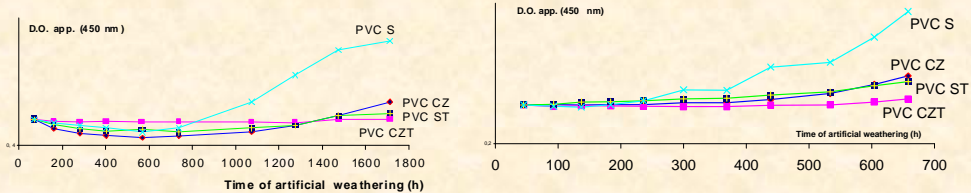


apparent D.O. (450 nm) Arbitrary units



ARALAB - 1640 h

ATLAS - 1640 h



SOLAR BOX - 1710 h

SEPAP 12/24 - 660 h



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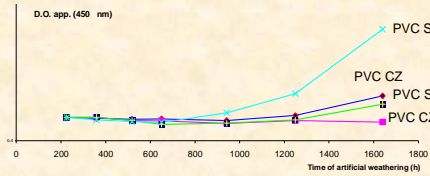


UV-VIS RESULTS

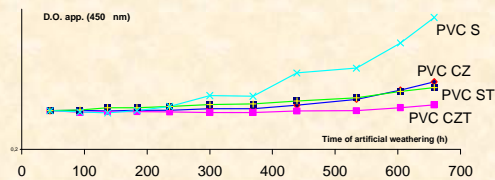


D.O. (450 nm) apparent

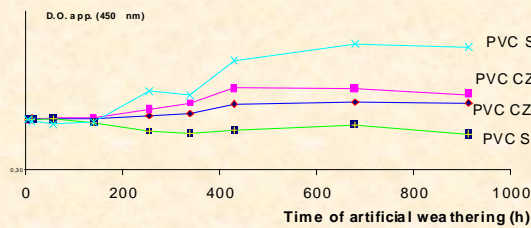
Arbitrary units



ARALAB - 1640 h



SEPAP - 652 h



QUV - 913 h



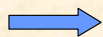
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CONCLUSIONS

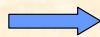


- * FORMATION OF PHOTOOXIDATION PRODUCTS WITH INCREASING ABSORPTION BANDS IN THE CARBONYL REGION



FTIR SPECTROSCOPY/MICROSCOPY

- * FORMATION OF CHROMOPHORIC PRODUCTS DURING THE AGEING PROCESS



UV-VIS SPECTROSCOPY



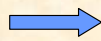
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CONCLUSIONS



- * PE DEGRADATION MECHANISM AND CORRESPONDENT STECHIOMETRY EQUIVALENT UNDER DIFFERENT CONDITIONS OF PHOTOOXIDATION (Hg, Xe, Sun)
- * HIGH REPRESENTIVENESS OF THE ARTIFICIAL ACCELERATED AGEING OF THE PE



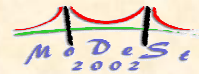
UTILIZATION OF PE IN WEATHERING AS REFERENCE MATERIAL?



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CONCLUSIONS



- * THE STECHIOMETRY OF DEGRADATION MECHANISM IN THE STABILIZED PVC IS HIGHLY DEPENDENT OF THE POLYMER COMPOSITION AND PHOTOOXIDATION CONDITIONS
- * THE MERCURY SOURCES HAVE, IN GENERAL, AN HIGHER AGEING ACCELERATION FACTOR THAN THE XENON SOURCES, BUT AN LOWER LEVEL OF REPRESENTIVENESS (LOWER SIMULATION CAPACITY), PARTICULARLY THE QUV APPARATUS. THIS IS SEEN AT LEVEL OF PHOTO-OXIDATION (CARBONYL FORMATION) AND AT LEVEL OF PHOTOLYSIS (CHROMOPHORE FORMATION)



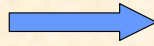
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CONCLUSIONS

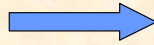


- * THE AGEING ACCELERATION FACTOR IS DEPENDENT OF THE PHOTOOXIDATION CONDITIONS, TYPE AND COMPOSITION OF THE POLYMER



CHECK FROM NATURAL WEATHERING NEEDED (REFERENCE DATA)

- * THE DEGRADATION INDUCED BY THE PHOTOOXIDATION, OCCURS TO A MAXIMAL DEEP OF 80 μm , UNDER THE MINIMAL THICKNESS OF THE FILMS



IT'S VALID TO COMPARE RESULTS FROM DIFFERENT FILMS WITH THICKNESS GREATER THAN 80 μm



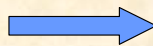
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CONCLUSIONS

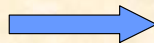


- * THE AGEING PRODUCES THE INITIAL WHITENESS OF THE PVC



OXIDATION OF THE DOUBLE BONDS FORMED DURING THE PROCESSING

- * THE YELLOWNESS IS A CONSEQUENCE OF THE WEATHERING PROCESS



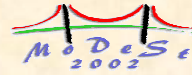
ANALYSIS OF THE EVOLUTION OF THE YELLOWNESS PROCESS AFTER THE INITIAL WHITENESS (apparent yellowness index)



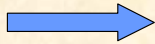
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CONCLUSIONS



- * THE WHITENESS OF THE PVC IS STILL PREDOMINANT AFTER 27 MONTHS OF NATURAL EXPOSURE



IT IS NOT STILL POSSIBLE COMPARE THE EVOLUTION OF THE YELLONESS THAT RESULTS FROM ARTIFICIAL WEATHERING WITH THE EVOLUTION OF COLOUR ORIGINATED BY THE NATURAL EXPOSURE

- * THE FTIR AND COLOURIMETRIC ANALYSIS SHOWS THE POSITIVE ROLE PLAYED BY THE ADDITIVE ANTI-UV IN THE PVC FORMULATIONS
- * THE CALCIUM/ZINC SHOWS A BETTER PERFORMANCE DURING WEATHERING THAN THE SOLID TIN IN PVC STABILIZED FORMULATIONS



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POSTER

1 - OBJECTIVE

- Evolution of the chemical, mechanical and aesthetic properties of stabilised PVC thick plates, designed for outdoor building applications, during natural and artificial weathering.
- Analysis of oxidation at
 - Macroscopic scale: colour, gloss, impact and tension.
 - Microscopic scale: infrared micro-spectroscopy.

2 - SAMPLES AND AGEING METHODS

- Extruded profiles, 2 mm thickness.
- 4 formulations: PVC CZ, PVC CZT, PVC S and PVC ST, differing in thermal stabiliser (Ca/Zn or Sn) and content of anti-UV additive (tinuvin P).
- Natural exposure: Lisbon (hot, Mediterranean climate), 45° facing south, [1].
- Artificial simulated ageing:
 - 6000 watt borosilicate glass-filtered xenon arc source, continuous radiation.
 - Use of calibrated radiometers (340 nm and 295-400 nm).
 - intensity auto-adjusted to a global irradiation of 550 W/m² (290 to 800 nm).
 - temperature of black standard thermometer: 65 ± 3°C.

3 - RESULTS

3.1 Impact Measurements

- Charpy tests: flatwise impact and double -V notched specimens, type ISO179/11A, [2], 40 mm span, notches perpendicular to the direction of blow.
- Minimum of 15 specimens from each sample, submitted to statistical analysis for detection and rejection of outliers, [3].

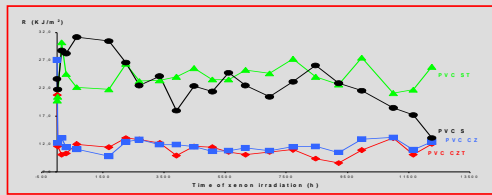


Figure 1: Evolution of the Charpy impact strength of single specimens during 12500 hours of xenon light

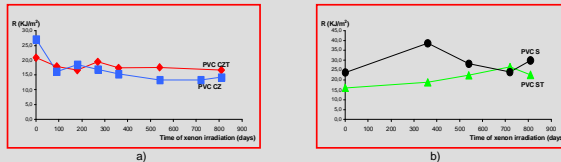


Figure 2: Evolution of the Charpy impact strength during 27 months of exposure at Lisbon, in samples stabilised with a) Calcium/zinc, b) solid tin

3.2 Tension Measurements

- Decrease of the strain at break during weathering of specimens type 1BA, [4].

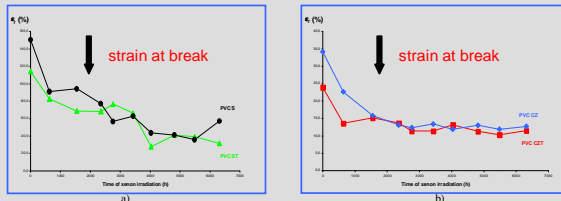


Figure 3: Evolution of the strain at break during 6500 hours of xenon light, in samples stabilised with a) Calcium/zinc, b) solid tin.

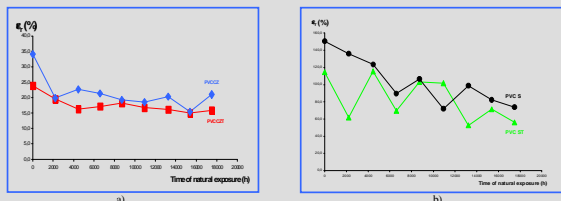


Figure 4: Evolution of the strain at break, during 2 years of natural exposure in Lisbon, in samples stabilised with a) Calcium/zinc, b) solid tin

3.3 Infrared Microscopic Measurements

- IR microscopy depth profiling by the classical procedure of cross-sectional analysis of slices microtomed from thick plates, [5].
- first photo-oxidation profiles (xenon irradiation) at 4478 h (PVC S), 5611 h (PVC ST), 6950 h (PVC CZ) and 8450 h (PVC CZT)

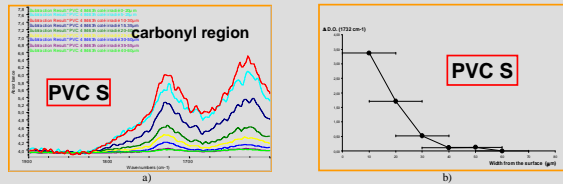


Figure 5: Infrared microscopy results of a sample aged during 8450 hours with xenon light: a) spectra of difference, referenced to not weathered material; b) oxidation profile at 1732 cm⁻¹

3.4 Colourimetric Measurements

- Reflectance 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.

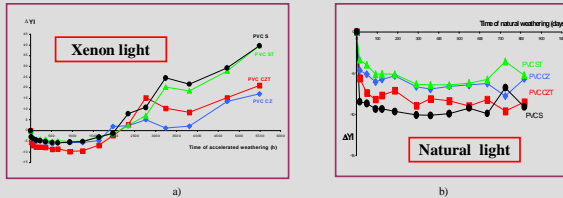


Figure 6: Evolution of the yellowness index differences resulting from: a) 5500 h of artificial weathering; b) 27 months of natural exposure in Lisbon.

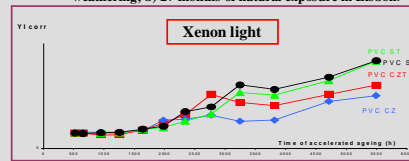


Figure 7: Evolution of the apparent yellowness index, during 5500 h of artificial simulated weathering

3.5 Gloss Measurements at 60°

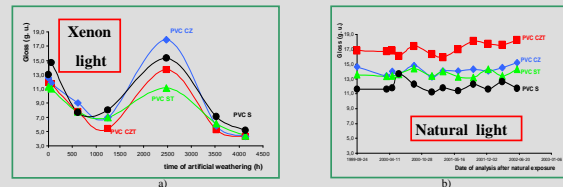


Figure 8: Evolution of the gloss during: a) 4200 h of artificial simulated weathering; b) 27 months of natural exposure in Lisbon.

4. CONCLUSIONS

- Important modification of mechanical properties in the beginning of the artificial weathering.
- Recovery of initial level of impact strength after some time of irradiation without following trends of decreasing.
- More susceptibility of photo-degradation of the tin stabilised PVC.
- Initial whiteness, resulting from the photo-oxidation of the conjugated double bonds formed during the processing of the polymer
- Colourimetric evolution, after whiteness, well represented by an apparent yellowness index.
- No partial regeneration of the coloration or mechanical properties and no loss of gloss. Evolution of gloss not globally explained by the theory of the multilayer weathering, [6].
- Strain at break, probably the most sensible characteristic to evaluate the initial stages of the photo-oxidative ageing in these polymeric materials.

5. REFERENCES

- ASTM D 1435-99: Standard Practice for Outdoor Weathering of Plastics.
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