

**LABORATÓRIO NACIONAL
DE ENGENHARIA CIVIL, I. P.**

**STUDY OF THE INFLUENCE OF THE
AGEING CONDITIONS IN THE DURABILITY
OF PVC FORMULATIONS USED IN
OUTDOOR APPLICATIONS**

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ESTUDO DA INFLUÊNCIA DAS CONDIÇÕES DE ENVELHECIMENTO NA DURABILIDADE DO PVC ESTABILIZADO PARA APLICAÇÕES EXTERIORES

RESUMO

Procurou-se com a presente comunicação apresentar os resultados de um estudo para avaliar a durabilidade de filmes calandrados e placas extrudidas em PVC rígido, para aplicações exteriores, submetidas a diferentes condições de envelhecimento, utilizando técnicas de análise molecular por espectroscopia de infravermelhos por transformada de Fourier (FTIR), de análise das propriedades macroscópicas, nomeadamente da aparência superficial por colorimetria e das características mecânicas por tracção. O desenvolvimento das formulações, o envelhecimento e a subsequente caracterização foi realizada no LNEC.

Assim, após uma breve introdução, a presente comunicação expõe a parte experimental do estudo, no que se refere à composição das amostras e aos métodos experimentais de degradação e de caracterização. Seguidamente apresentam-se os resultados do estudo, a sua interpretação e as conclusões finais.

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SUMMARY

The main purpose of this paper is to present the results of a study intended to assess the durability of stabilized PVC-U for outdoor applications, in form of calendered films and extruded plates. The samples were subject to different ageing conditions and their degradation state were evaluated, using techniques of molecular analysis, namely Fourier transformed infrared spectroscopy (FTIR), as well techniques for evaluation of macroscopic properties, as colorimetry and tensiles tests. The development of formulations, the ageing and the subsequent characterisation were done in LNEC.

Therefore, after a brief introduction, this paper presents the experimental part of the study, as regards the composition of samples and the experimental methods of deterioration and characterisation. Subsequently, the results of the study, their interpretation and the final conclusions are also presented.

ÉTUDE DE L'INFLUENCE DES CONDITIONS DE VIEILLISSEMENT SUR LA DURABILITÉ DU PVC STABILISÉ POUR DES APPLICATIONS EXTERIEURES.

RÉSUMÉ

L'objectif essentiel de cette communication est de présenter les résultats d'une étude visant à évaluer la durabilité du PVC rigide stabilisé pour des applications extérieures, sous la forme de films calandrés et plaques extrudées. Les samples ont été soumises à de différentes conditions de vieillissement et son étatt de dégradation a été caractérisé, en utilisant des techniques d'analyse moleculaire, nommément la spectroscopie d'infrarouge para transformé de Fourier (FTIR), bien comme d'évaluation des propriétés macroscopiques, nommément la colorimétrie et la traction. Le développement des formulations, le vieillissement et la caractérisation postérieure ont été effectués au LNEC.

Ainsi, après une brève introduction, cette communication présente la partie expérimentale de l'étude, en ce qui concerne la composition des échantillons et les méthodes expérimentales de détérioration et de caractérisation. Par suite, on présente les résultats de l'étude, leur interprétation et les conclusions finales.

STUDY OF THE INFLUENCE OF THE AGEING CONDITIONS IN THE DURABILITY OF PVC FORMULATIONS USED IN OUTDOOR APPLICATIONS

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1. INTRODUCTION

Poly(vinyl chloride) has his largest market in construction, mainly in exterior applications, where weatherability is a primary design factor.

Some artificial accelerated methods are currently used in the prediction of polymer lifetimes, but this subject is controversial.

On that account, we developed a research study concerning the weathering of stabilized PVC. The objectives of this work are the comparison of different artificial accelerated weathering methods and a natural exposure, considering the role of the atmospheric agents and the influence of the additives.

To attain this goal, the photo-oxidative weathering of various polyvinyl chloride formulations was performed using several commercial apparatus and a natural exposure in Lisbon.

The weathering action was evaluated by infrared spectrometry and tensile tests.

The experimental results enabled to make a comparison between the different photo-oxidation conditions used and, consequently, it was also possible to develop statistical correlations and to calculate the acceleration factors.

A statistical distribution analysis of the experimental data was made. A longevity function for each formulation and weathering condition (artificial and natural) was developed, which allows to lifetime prediction through the definition of a critical value of the properties considered relevant for the application of the target materials.

2. EXPERIMENTAL

In this study, we use 4 different types of TiO₂ pigmented PVC formulations, designed for outdoor applications, containing CaCO₃, two types of thermal stabilisers (based on calcium/zinc or dibutyltin-maleate) and various additives.

The specimens are submitted to artificial and natural weathering. The artificial simulated weathering was carried out in several laboratory chambers, commercially available, equipped with different artificial irradiation sources, like ATLAS Weatherometer Ci 65, ARALAB Fitoclima 600 EDTU, SEPAP 12/24, SOLAR BOX 3000 E and QUV PANEL UVB313. To evaluate the influence of certain parameters, different exposure conditions are used in same apparatus. The ageing parameters were the irradiation source, alternation of light/dark period, type of filters, relative humidity of the circulating air and cyclic water spray. 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.

The different photo-oxidative conditions are presented in table 1.

Table 1: Set of photo-oxidative conditions

Photo-oxidative condition	Irradiation Source	Cyclic spray of water and relative humidity of air	Dark Period	Time of weathering
ATLAS 1	Continuous 6500 watt borosilicate filtered xenon arc	No; Hr ≈ 10%	No	4755 h
ATLAS 2		18 min each 2 hours		3350 h
ATLAS 3		No; Hr ≈ 10%		2660 h
ATLAS 4		18 min each 2 hours only in last 3550 h (after ATLAS 3)		6010 h
ARALAB 1	Continuous 6000 watt borosilicate-quartz filtered xenon arc	No; Hr ≈ 60%		1400 h
ARALAB 2	Continuous 6000 watt borosilicate filtered xenon arc	No; Hr ≈ 10%		5360 h
SOLAR BOX	2500-Watt borosilicate glass filtered xenon arc	No; Hr ≈ 10%		4750 h
QUV 313	313 nm low-pressure mercury vapour	No	4 h each 12 h with condensation	910 h
SEPAP	Medium-pressure mercury vapour	No; Hr ≈ 10%	No	820 h
LISBON	Sun	Natural rain and dew	Yes (night)	7 years

The quality of the water used in water sprays was controlled by means of a water purity meter. The intensity of xenon radiation was 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 in the xenon arc chambers, a calibrated black standard thermometer sensor was used, which was maintained at $65 \pm 5^\circ\text{C}$. The maximum temperature measured in the exposed surface was 53°C . In the case of ARALAB and ATLAS chambers, 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.

The degradation level induced by photo-oxidative ageing is evaluated by means of infrared spectroscopy and tensile tests.

All specimens were removed periodically to perform the several analysis described above and repositioned after to proceed the ageing.

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 $1600\text{-}1900\text{ cm}^{-1}$ 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 in different commercial apparatus, over different experimental conditions, the spectra of differences of one selected representative formulation, stabilised with calcium/zinc, are represented in the figures 1 to 5. The different spectra are represented at some scale to simplify a comparative analysis.

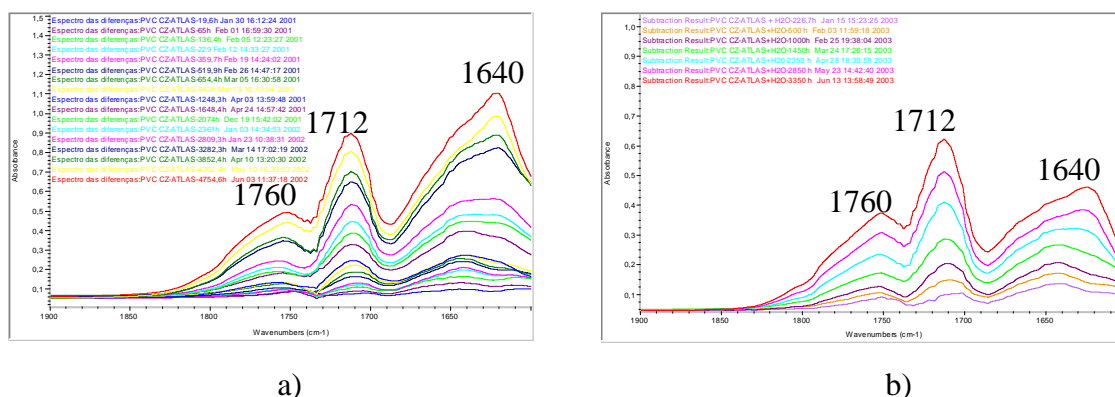
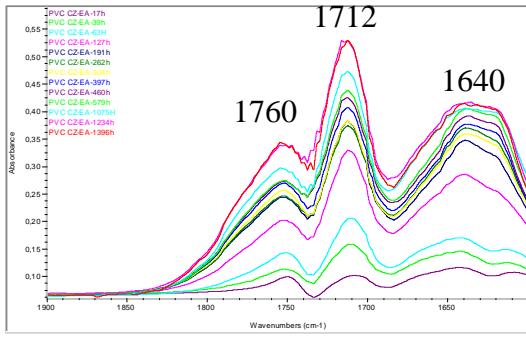
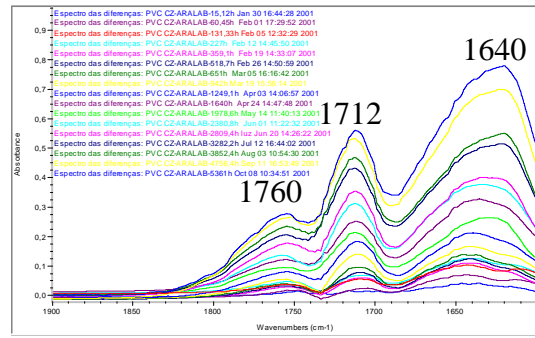


Figure 1- Effect of water in a continuous irradiance program (cut-off at 290 nm): a) ATLAS 1; b) ATLAS 2

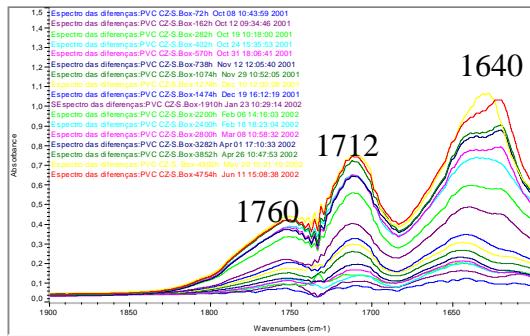


a)

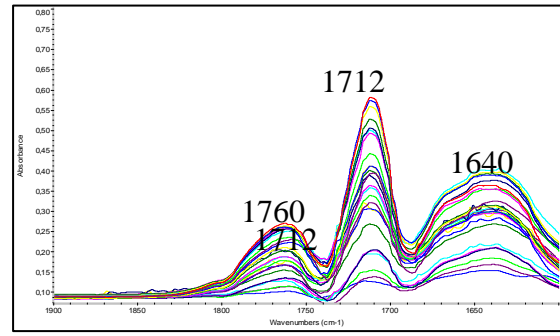


b)

Figure 2 - Effect of the filter in Xenon sources: a) ARALAB 1 (cut-off at 290 nm); b) ARALAB 2 (cut-off lower than 280 nm)

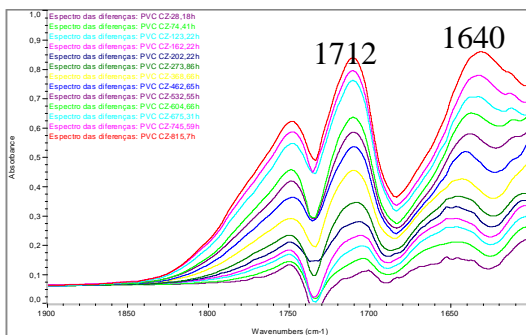


a)

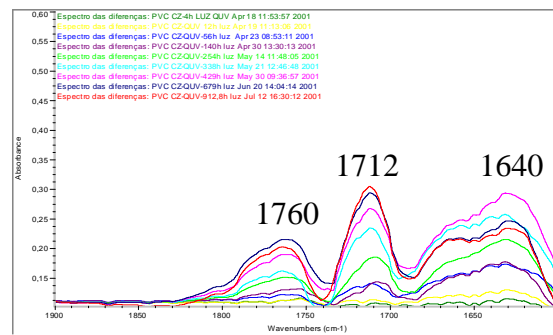


b)

Figure 3 - Effect of artificial simulated and natural light sources: a) SOLAR BOX (cut-off at 280 nm); b) LISBON



a)



b)

Figure 4 - Effect of mercury vapour pressure: a) SEPAP 12/24; b) QUV UVB 313

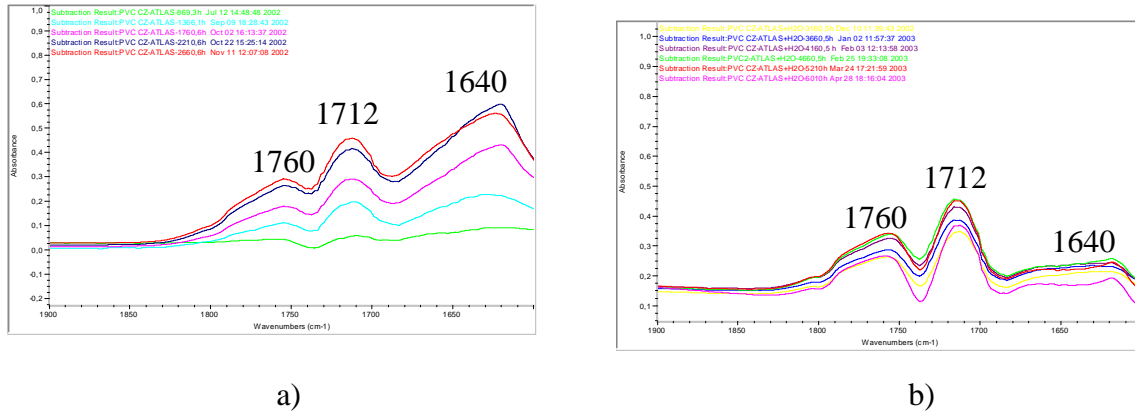


Figure 5 - Effect of initial period of continuous irradiation: a) ATLAS 3 (cut-off at 290 nm); b) ATLAS 4 (cut-off at 290 nm)

Analysing the different spectra, we found that all have peaks at same wavelength (1760, ≈1712 and 1640 nm), concerning to the same degradation products, which means that different photo-oxidative conditions allows to the same PVC degradation reaction. However, the spectral modifications detected between different spectra show also that this reaction has different stoichiometries, resulting from the different photo-oxidative conditions.

In order to illustrate the changes induced by different parameters in the stoichiometry of the PVC degradation mechanism, figure from 6 presents the evolution of the rate of the magnitudes of optical densities at 1712 cm⁻¹ (h₂) and 1640 cm⁻¹ (h₃), during the artificial ageing of the reported PVC formulation at different photo-oxidative conditions.

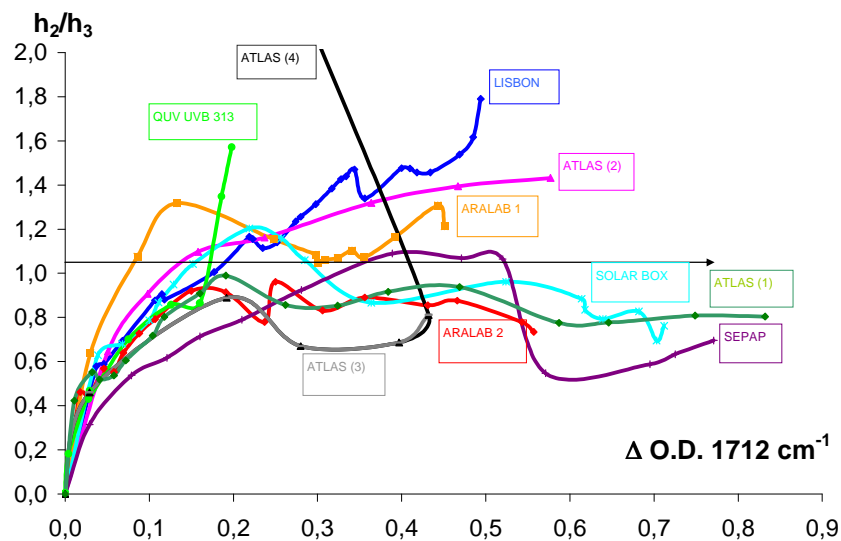


Figure 6: rate of the magnitudes of main carbonyl bands vs. optical density at 1712 cm⁻¹, during the weathering performed under different photo-oxidative conditions

Considering the data represented in previous figure, it is possible to evaluate the degree of correlation between different photo-oxidation systems, based on the FTIR spectra, which is related with the stoichiometry of degradation reaction. To attain this target, a previous statistical evaluation was made using the methods of Pearson and Spearman [3-5]. After selection of the systems presenting a good correlation, a second evaluation is made considering the observation of the evolution of the correlation parameter (h_2/h_3) in relation to the value “1”, when both bands has the same magnitude. This final observation is necessary to detect systems with good correlation, but presenting an inverse evolution of the related bands.

Using this method and considering only the formulation reported here, a good correlation it is found between the artificial accelerated ageing systems ARALAB 2 and ATLAS 1 and between SOLAR BOX and SEPAP 12/24. The more strange behaviour was found in the systems QUV UVB 313 and ATLAS 4, probably due to spray of water after a previous long period of irradiation (in ATLAS) and to dark periods with condensation (in QUV). Considering simulation, good correlations were found between the natural exposure in Lisbon and the artificial ageing performed in ATLAS 2 and ARALAB 1, probably due to the role of water present in the rain, spray and mostly air. However, it is not found a good correlation between two different systems for the set of all formulations. This means that, beside we are considering chemical properties (not physical or mechanical), there is an inherent variability in accelerated weathering tests, not only related with the type of radiation sources, but also with other factors related with interaction between the additives present in the polymer. For example, it can be seen in data of photo-oxidation system ATLAS 4 that certain degradation agents, like water, which effect is usually depreciated, influences the stoichiometry of degradation reaction and also that the previous irradiation story can be drastically important (for instance, compare the figures 1 and 5, as plots of figure 6 concerning ATLAS 1, ATLAS 2 and ATLAS 4).

For a better understanding of the differences originated by the intervention of the water in the behaviour of the PVC samples, see for instance the reference [6], in which has shown that strong yellowing of the PVC occurs under Xénon irradiation, but that in the presence of water spray, occurs the whitening of the samples. Both phenomena are related with the competition between double bond and carbonyl formation, each one allowing opposite effects in the aesthetic properties of PVC.

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

In a more recent research work [7], it was found that long irradiation periods induce a generalized degradation of the surface of PVC extruded plates, namely, loss of Cl, double bond and cross-link formation. Double bonds and cross-links induce the shrinking of the surface material and consequent formation of a generalized network of micro-cracks all over the surface. This crack network enables its mechanical destruction by water jets or rain, discovering a surface which is much more homogeneous and thence much

more resistant to the ulterior action of radiation. When that previous long period of xenon irradiation is absent or shortened, the mechanical degradation of the surface is mostly concentrated around defects (not generalized to all the surface) and the erosion by the water is rather localized.

All interactions between atmospheric agents and additives on stabilised PVC materials difficult the natural exposure simulation. Furthermore, it is also found that the success of simulation depends also of the considered relevant property of the material that is considered for correlation.

3.2 Tensile properties

The stress and the strain strengths at failure of specimens type 1BA [8], were measured at LNEC by means of an Instron 4483 Universal Testing Machine. The results obtained from a minimum of 14 specimens from each sample, were submitted to statistical analysis for detection and rejection of outliers [9].

The tensile strain at break was measured without extensometer, because the occurrence of breaks out of the specimen gauge-length marks was frequent.

The two groups of formulations have different tensile behaviour. The unweathered PVC stabilized with a thermal stabiliser based on calcium/zinc present, in tests conducted at low strain rate (2 mm.s^{-1}), a lower strain at break (≈ 11 to 17%) than the unweathered PVC stabilised with a thermal stabilizer based on or dibutyltin-maleate (DBTM), which presents a strain at break in the range 55 to 80% even conducting the tests at higher strain rate (5 mm.s^{-1}).

Concerning the evolution of the tensile proprieties of the studied PVC materials during the weathering, no significant modification of the elastic modules and yield proprieties was observed 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 a more interesting scale with compounds containing the DBTM thermal stabiliser.

The influence of the artificial ageing in tensile properties of PVC materials weathered during 3 years in Lisbon was published before [10].

The evolution of the relative elongation at break, in conditions of natural exposure at Lisbon during 7 years, is given in Figs. 11 and 12. As can be seen from the analysis of these figures, the most important modifications of the strain at break occurred during first 1460 days (4 years) of the natural weathering. In the last 3 years the value of the elongation at break exhibited an oscillatory behaviour, but after 7 years of natural exposure is nearly the same it was after 4 years. This seasonal behaviour of the formulations, during natural weathering, is also an interesting feature to report.

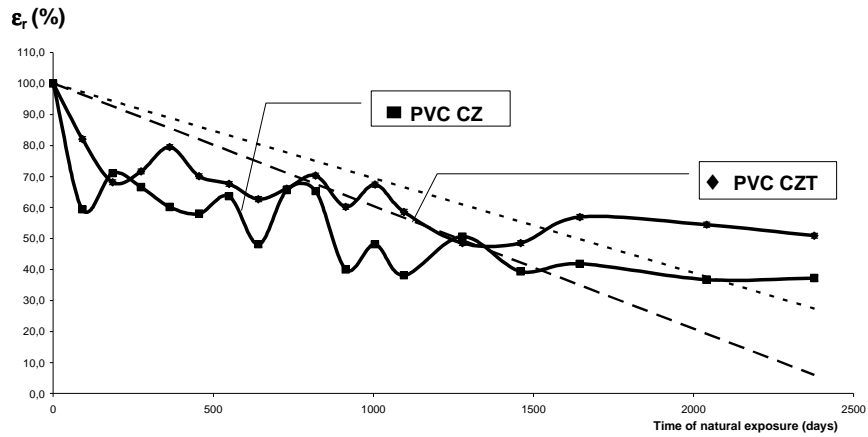


Fig. 7 - Evolution of the strain at break of specimens, extracted from PVC profiles stabilised with Ca/Zn, submitted to natural weathering (LISBON)

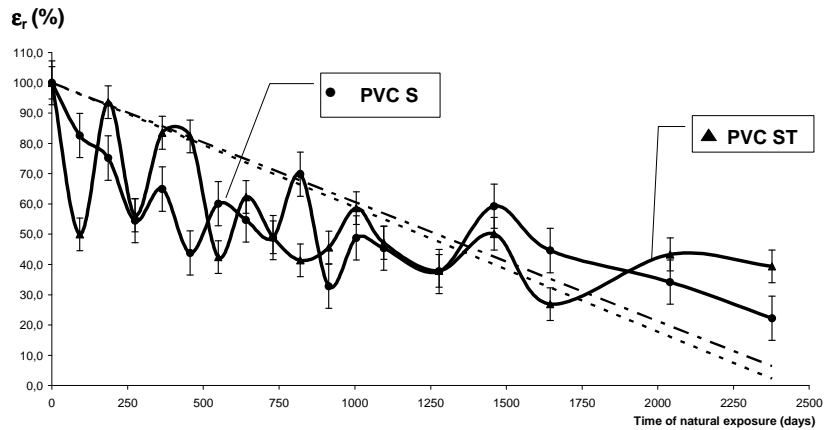


Fig. 8: Evolution of the strain at break of specimens, extracted from PVC profiles stabilised with DBTM, during 7 years of natural weathering (LISBON)

4. STATISTICS

All atmospheric parameters, like global irradiance, temperature, relative humidity and precipitation, follow normal distribution functions (95% CI). Accumulated values of these parameters, which are used to statistical purposes, fits best a Weibull distribution. For exemplificative purposes the probability plot for accumulated global irradiance is presented in figure 9.

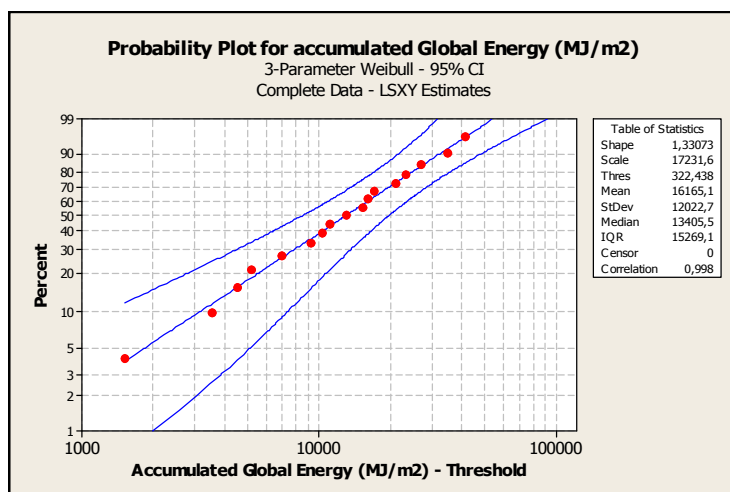
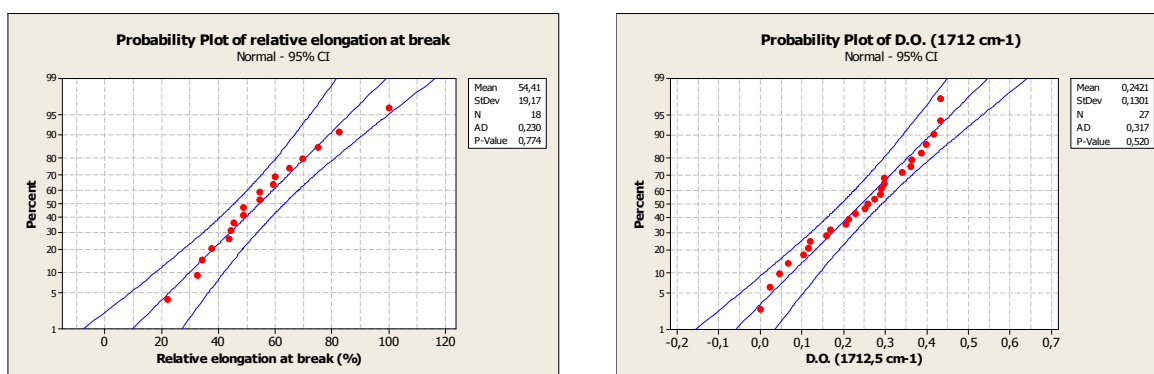


Fig. 9 - Probability Plot for accumulated global irradiance during the natural exposure (LISBON)

The data from elongation to break of each set of 15 specimens, taken periodically from natural exposure, follows a normal distribution, even considering a confidence interval of 95%, as indicated by several methods (Anderson-Darling, Wilks-Shapiro and Kolmogorov-Smirnov). The elongation at break and the optical density at 1712 cm^{-1} of the reported PVC formulation, present a trend decreasing or increasing during weathering, respectively. These data follows a lognormal or Weibull distribution (95% CI), instead to a normal distribution, like is presented in the figure 10 for exemplificative proposes¹.



a)

b)

Fig. 10 - Probability Plot for a typical PVC formulation, stabilised with calcium/zinc, during natural weathering (LISBON), concerning the data: a) of the strain at break (extruded plates); b) of the optical density at 1712 cm^{-1} (calendered films)

¹: Each data point results from average of each set of 15 tested specimens.

A multivariate analysis was performed with the data from tensile and FTIR tests, taken during natural exposure, using the following simple equation:

$$Y = \sum_i^n C_i W_i$$

where Y is the property in analysis, W_i are the accumulated values of climatic variables and C_i are the regression coefficients.

To complete the multivariate analysis, a preliminary analysis of variability and a final residual analysis were performed. Using the Principal Component Analysis method it was concluded that the evolution of main properties during the natural weathering, like elongation at break and optical density at carbonyl domain, can be described only by radiation, temperature and humidity. These three parameters are responsible by 90% of the total variability of the weathering process.

The figures 11 and 12 present the graphic diagnostic of the linear multivariate residual analysis, showing both cases follows Gaussian distribution criteria.

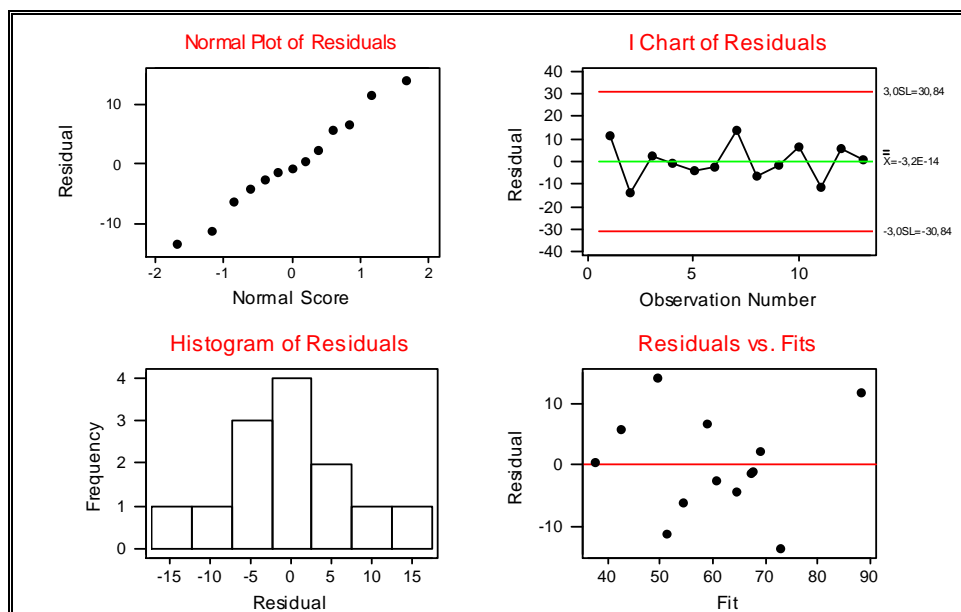


Fig. 11 - Residual analysis graphs of the multivariate linear regression that represents the evolution of the elongation at break of a typical PVC formulation during natural exposure (LISBON), in relation to atmospheric parameters

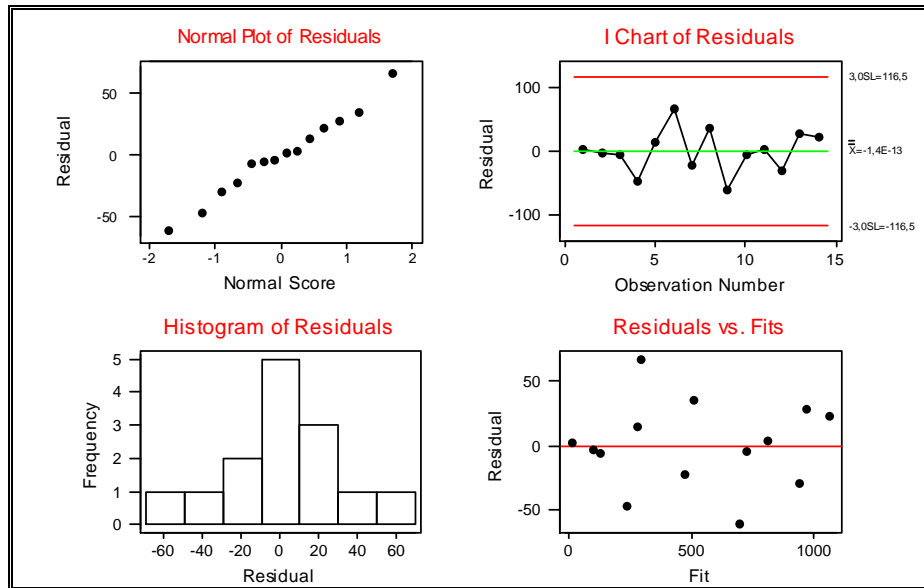


Fig. 12 – Residual analysis graphs from the of the multivariate linear regression that represents the logarithmic relation between optical density at 1712 cm^{-1} of a typical PVC formulation and time of natural exposure (LISBON)

5. ACCELERATION FACTORS. DURABILITY AND LIFETIME PREDICTION

Figure 13 presents the evolution of optical density at 1712 cm^{-1} of the reported PVC formulation during the weathering at different photo-oxidative conditions. The mathematical functions representing these plots are indicated in table 2.

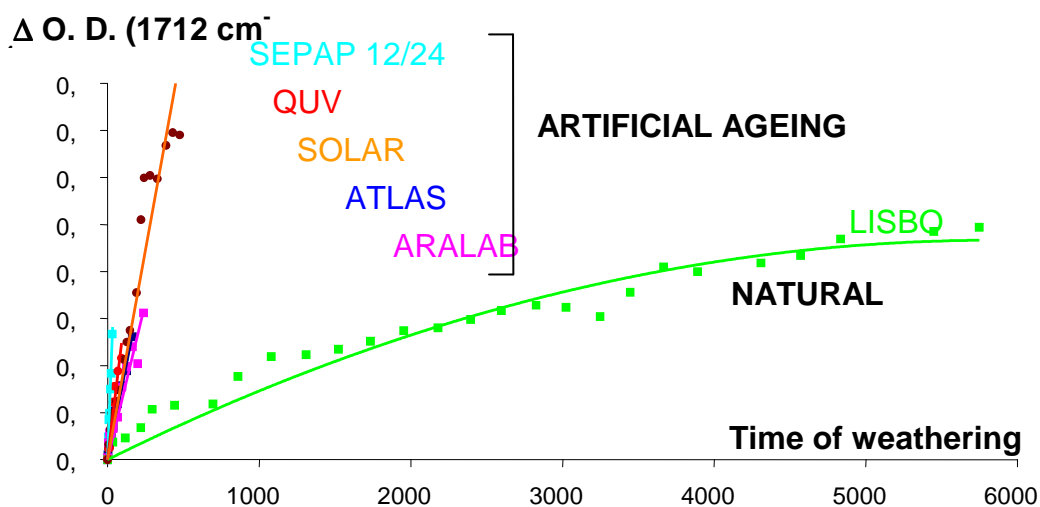


Fig. 13: Kinetic plots representing the evolution of the optical density at 1712 cm^{-1} during weathering under different photo-oxidative conditions

Table 2: Acceleration factors for the formation of carbonyl groups during artificial ageing of the reported PVC formulation in relation to natural weathering

Photo-oxidative conditions	Acceleration factor
(Xenon continuous irradiation) ATLAS	13
(Xenon continuous irradiation + cyclic spray of water) ATLAS	14
(Xenon continuous irradiation) ARALAB	14
(Xenon continuous irradiation) SOLAR BOX	14
(Mercury medium pressure vapour continuous irradiation) SEPAP	143
(Mercury low pressure vapour continuous irradiation + cyclic condensation without light) QUV UVB 313	58

The plots from regression and the equations correlating the properties of the same PVC formulation with irradiance, during natural exposure, are presented in figure 14.

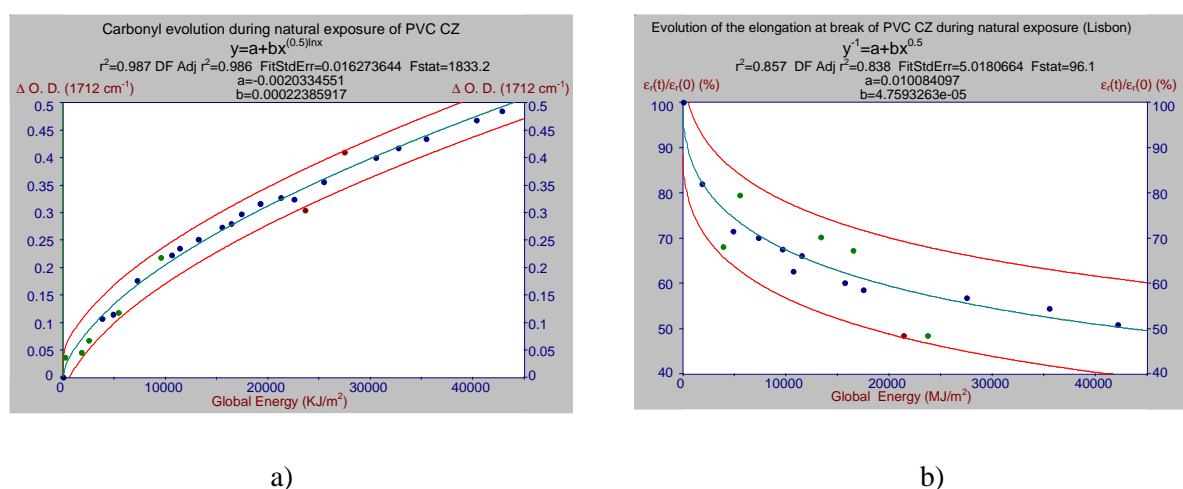


Fig. 14 - Plots of the best function correlating the accumulated global irradiation during natural exposure (LISBON) with: a) the optical density at 1712 cm⁻¹; b) the relative elongation at break (%)

The figure 15 shows the longevity functions of a calendered film and an extruded plate, both concerning the reported PVC formulation, during natural exposure.

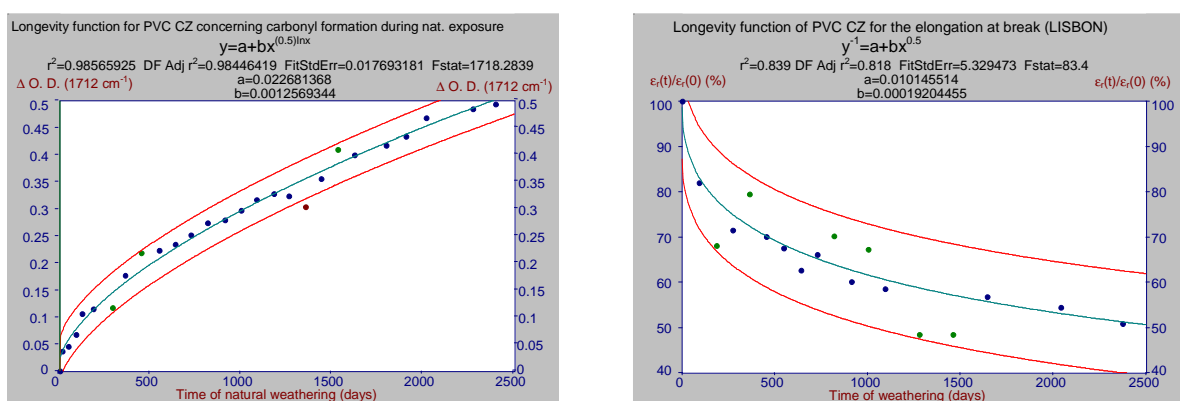


Fig. 15 - Longevity functions of the reported PVC formulation under natural exposure (LISBON): a) data from the evolution of the optical density at 1712 cm^{-1} ; b) data from the evolution of the elongation at break

Stipulating a critical value to the property considered it is possible to estimate the lifetime for each formulation. Supposing an application in Lisbon, where the mechanical properties of the PVC profile is critical, and considering admissible a variation up to 50% of the original elongation at break, the reported PVC formulation will have only a 2 years lifetime. Considering a similar application, but where the chemical properties of the PVC profile is critical, requesting a critical value of the carbonyl concentration limited to 0,3 absorbance units by FTIR, the same PVC formulation will have a 3 years lifetime.

6. CONCLUSIONS

The degradation process induced by weathering in the PVC formulations studied is the result of the known dehydrochlorination reactions, photo-oxidation and crosslinking, whose induces modification in the molecular structure of PVC and, consequently originates drastic changes in the mechanical properties of such polymers. The preponderance of each type of chromophore products, containing double bounds or carbonyls, depends mainly of the nature and intensity of degradation agents.

As expected, the measured values of all climatic agents follow a normal distribution. As confirmed by a principal component analysis, the climatic agent that has higher relevancy in the degradation of PVC is the radiation, followed by temperature and humidity. The combined action of these parameters, mainly radiation and temperature, gives place to the occurrence of synergistic phenomena.

The elongation at break and the optical density in carbonyl domain are good representations of

degradation induced by weathering. It was also found a good correlation between these two parameters during weathering, which means that an increased concentration of carbonyl, induced by weathering, gives place to a decreasing of elongation at break.

The comparison of the characteristics of the FTIR spectra of differences, resulting from the ageing under different photo-oxidative conditions, indicates that stoichiometry of PVC degradation reaction are different in each system. In consequence, it is not found a good correlation between two different systems for the set of all formulations, which means that there is an inherent variability in accelerated weathering tests, not only related with the type of radiation sources, but also with other factors like the composition of the PVC final product. By other hand, it is also found antagonism resulting from the interaction of climatic agents with additives present in the PVC formulations (like water that catalyses the photochemical activity of TiO₂).

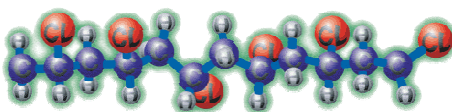
The chambers equipped with mercury radiation sources produce more acceleration of degradation, but they have a lower level of natural exposure simulation. The best correlation with natural exposure was obtained using artificial ageing with borosilicate filtered Xenon radiation, using a cyclic spray of water or condensation periods at dark conditions. This means that a better simulation of the natural weathering of such PVC materials in laboratory conditions needs to consider the intervention of water and humidity.

7. REFERENCES

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SLIDES



STUDY OF THE INFLUENCE OF THE AGEING CONDITIONS IN THE DURABILITY OF PVC FORMULATIONS USED IN OUTDOOR APPLICATIONS

Luís Pimentel Real



EWS, September 2007

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Objectives of the research

1. Analysis of the evolution of the PVC properties. Influence of ageing conditions.
2. Evaluation of the role of specific additives in the PVC formulations.
3. Correlation between the microscopic and macroscopic properties of specimens.
4. Comparison of the degradation level of final products induced by different processing conditions (calendering vs. extrusion).

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Objectives of the research



5. Comparison of different weathering systems. Evaluation of the simulation capability of the artificial ageing, carried out in different photooxidation conditions.
6. Correlation between artificial weathering and natural exposure (acceleration factors and lifetime prediction).
7. Complementary: Statistical analysis of PVC properties and climatic parameters.

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Experimental: samples

SAMPLES: calendered **films** (150 µm) and extruded **plates** (2 mm)

COMPOSITION	PVC TYPE			
	CZT	CZ	ST	S
PVC	100	100	100	100
TiO ₂	4	4	4	4
CaCO ₃	4	4	4	4
Internal lubricant	1	1	1	1
External lubricant	0,2	0,2	0,2	0,2
Processing aid	1	1	1	1
Thermal Stabiliser Ca/Zn	4	4	-	-
Costabiliser epoxidized soybean oil	3	3		
Thermal Stabiliser (DBTM)	-	-	3	3
UV absorber	0,4	-	0,4	-

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Experimental: processing



Mixing of compounds:

- Films: 8 l Mixer with temperature controller
- Plates: 200 l Mixer with temperature control

Rheological characterization of compounds

(optimization of formulations):

- Torsion rheometer with a malaxer (190 °C, 100 rpm)

Processing of compounds:

- Calendering of Films (180 °C)
- Extrusion of Plates (142 - 169 °C)

Initial Characterization of processed samples:

- FTIR, colour, gloss, UV-VIS, Tensile, Flexion, Impact, DSC, Infrared Microscopy

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Experimental: Ageing conditions

ARTIFICIAL THERMOXIDATIVE CONDITIONS

below T_g (55 et 65 °C/50% Hr), near T_g (80 °C) and above T_g (95 et 110 °C)

ARTIFICIAL PHOTOXIDATIVE CONDITIONS

- Xenon sources with different powers and combinations of filters: borosilicate with cut-off at 280 nm, borosilicate/borosilicate (cut-off at 290 nm) and borosilicate/quartz (cut off < 290 nm)
- Mercury arc vapour sources: MA-40 medium-pressure lamps and fluorescent UV-B lamps of low pressure

NATURAL WEATHERING: LISBON,
45° facing SOUTH

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Experimental: weathering conditions (reported)

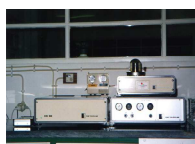
Photoxidative condition	Irradiation Source	Cyclic spray of water and relative humidity of air	Dark Period	Time of weathering	
ATLAS 1	Continuous 6500 watt borosilicate filtered xenon arc	No; Hr ≈ 10%	No	4755 h	
ATLAS 2		18 min each 2 hours		3350 h	
ATLAS 3		No; Hr ≈ 10%		2660 h	
ATLAS 4		18 min each 2 hours only in last 3500 h (after ATLAS 3)		6010 h	
ARALAB 1	Continuous 6000 watt borosilicate-quartz filtered xenon arc	No; Hr ≈ 60%		4 h each 12 h with condensation	1400 h
ARALAB 2	Continuous 6000 watt borosilicate filtered xenon arc	No; Hr ≈ 10%			5360 h
SOLAR BOX	2500-Watt borosilicate glass filtered xenon arc	No; Hr ≈ 10%			4750 h
QUV 313	313 nm low-pressure mercury vapour	No	No	910 h	
SEPAP	Medium-pressure mercury vapour	No; Hr ≈ 10%	No	820 h	
LISBON	Sun	Natural rain and dew	Yes (night)	7 years	

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Experimental: ageing and characterization

METHODS AND APPARATUS FOR CHARACTERIZATION AND EVALUATION OF THE DEGRADATION

- UV-VIS spectroscopy and colorimetry
- Infrared microscopy
- Gloss measurements
- Impact Charpy
- DSC



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Experimental: ageing and characterization

METHODS AND APPARATUS FOR EVALUATION OF THE DEGRADATION (reported here)

- Infrared spectroscopy (FTIR)
- Tensile Properties



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Evolution of the PVC properties



Objectif 1

Confirmation of known degradation process caused by weathering

- ✓ **Dyhydrochlorination: liberation of HCl and formation of conjugated double bonds (colourimetry, UV-VIS and FTIR)**
- ✓ **Photoxidation: attack to the double bonds, dealing to the formation of oxidation products with carbonyl and hydroxyl groups (FTIR)**
- ✓ **Crosslinking and chain breaking (tensile, impact, DSC)**

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Evolution of the PVC properties

Effects of the global weathering process (confirmed)



- ✓ Loss of mechanical properties
- ✓ Partial recovery of mechanical properties due to crosslinking and/or renovation of surfaces
- ✓ Colour (yellowing) and gloss changes
- ✓ Partial recovery of the whitening due to oxidation, leading to the decrease of the adhesion of the degraded surface and consequent erosion

Evolution of the PVC properties

~~$E, \sigma_e, \epsilon_c, \sigma_R$~~

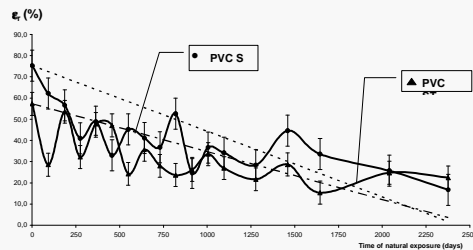
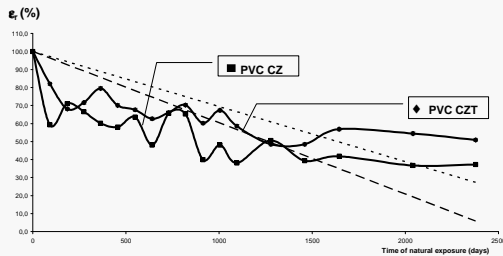
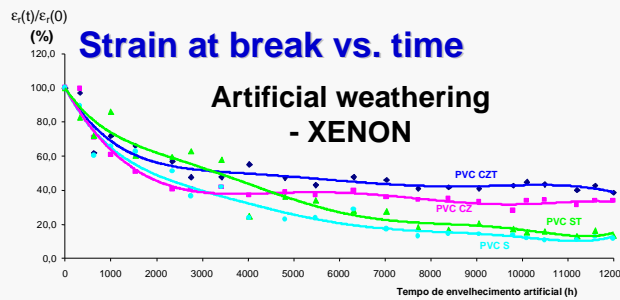
ϵ_r



$\epsilon_r(t)/\epsilon_r(0)$

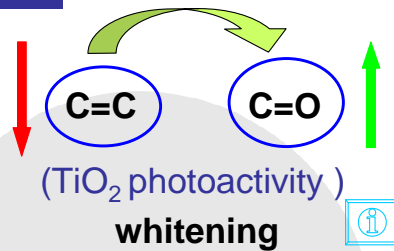
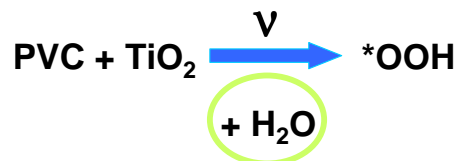
Strain at break vs. time

Artificial weathering - XENON



Natural weathering - SUN

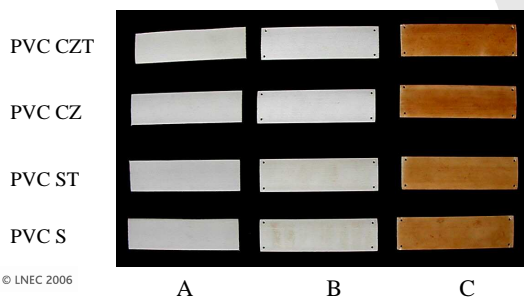
Evolution of the PVC properties



Change of stoichiometry

- ✓ The water contributes to the maintenance of white colour of stabilised PVC.

Specimens picture



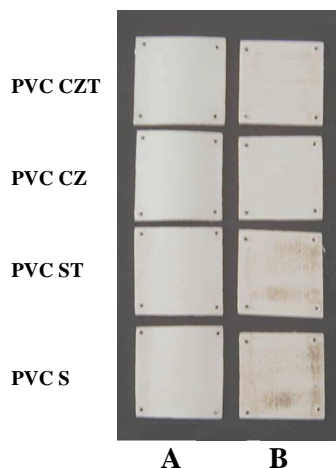
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- A) Reference samples, exposed at Lisbon
- B) 6000 h irradiated (xenon) using rain cycles (white specimens, showing stains in samples stabilised with di-butyl tin maleate)
- C) 8000 h irradiated (xenon) without rain cycles (total yellowing)

Evolution of the PVC properties

Another interesting phenomena related to the PVC ageing

Specimens picture



- A) **7000 h**: 2650 h of continuous irradiation (xenon) without rain cycles + 4350 h of continuous irradiation (xenon) using rain cycles (weather resistant white specimens)
- B) **3350 h** of continuous irradiation (xenon) using rain cycles (specimens showing stains)

- ✓ A previous period of irradiation (without water) enables the mechanical destruction of surface by water jets or rain, discovering a much more homogeneous surface and thence much more resistant to the ulterior action of radiation.

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Role of the additives

Objective 2

- ✓ Influence of the thermal stabiliser: FTIR spectra, colour, gloss, T_g , impact, tensile properties

➔ Best behaviour of Ca/Zn/ESO thermal stabiliser (decreasing colour and gloss changes; no plasticization nor “staining”)

- ✓ Role of TiO_2 : protection to UV radiation

➔ It shows photochemical activity in the presence of water (oxidation and whitening)

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Role of the additives

Objective 2

- ✓ Influence of anti-UV absorber

Positive (decreasing yellowing and oxidation), during processing and during artificial and natural weathering

Negative (decreasing of E_a): thermoxidation

Possibility of occurrence of antagonistic effects in cases of interaction of UV absorber with other additives (like thermal stabilisers), like formation of Hydrogen bonding, which inhibits the tautomeric rearrangement of benzotriazoles.

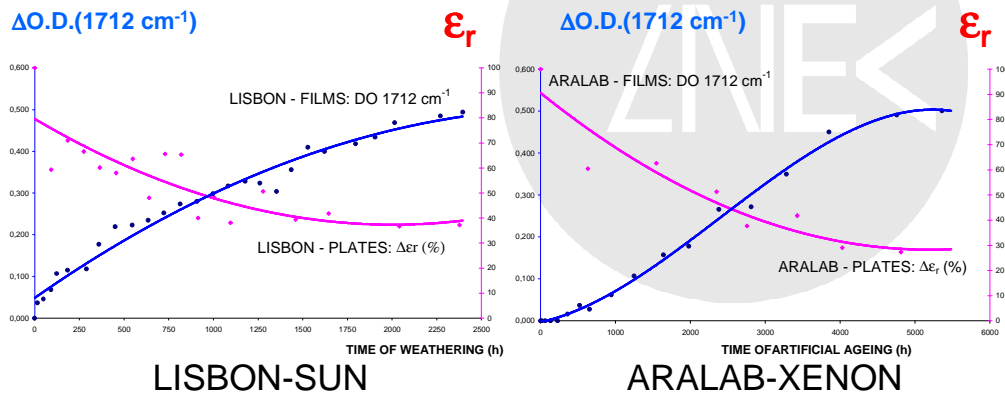
➔ *Fx: more variability in the case stabilised polymers*
Need of reference data from natural exposure

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Correlation between chemical and mechanical proprieties

Objective 3

Correlation between strain at break of plates and formation of oxidation products of carbonyl type in films

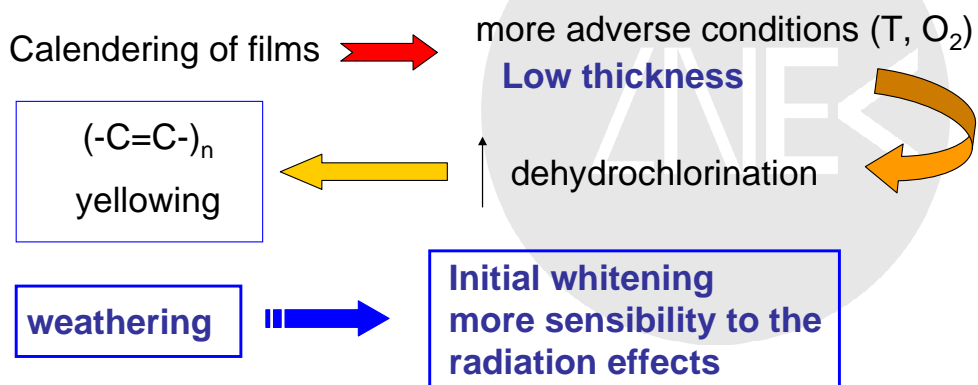


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Influence of thickness and processing conditions

Objective 4

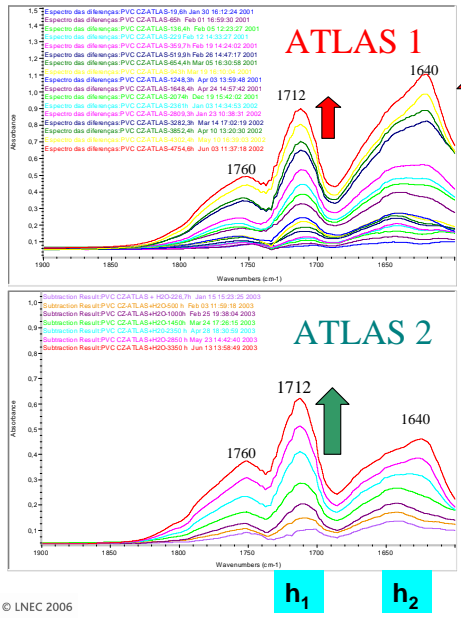
- ✓ The processing conditions influences the proprieties of the final products and the behaviour of PVC materials during weathering



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Comparison and simulation capability

Objective 5



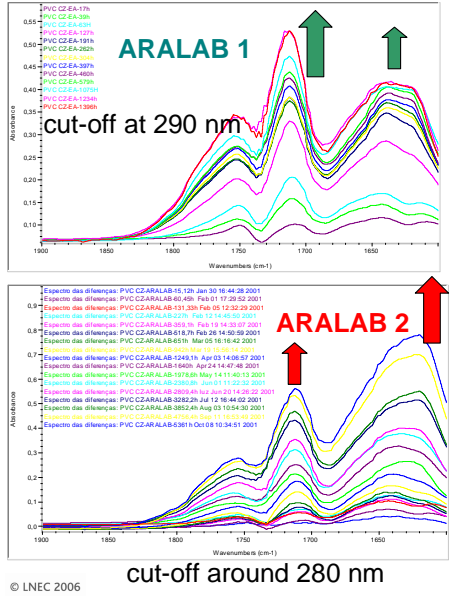
Effect of water

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Comparison and simulation capability

Objective 5

Effect of the filter type of glass filter from Xenon sources

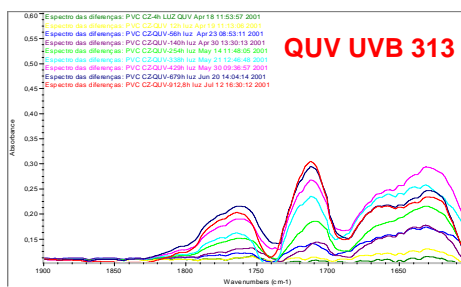
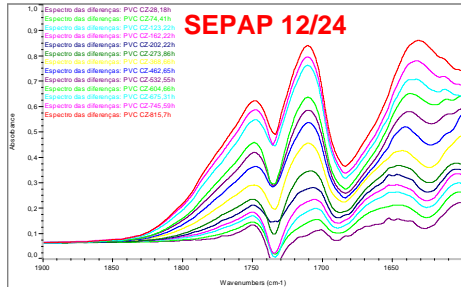


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Comparison and simulation capability

Objective 5

Comparison between mercury vapour pressure sources

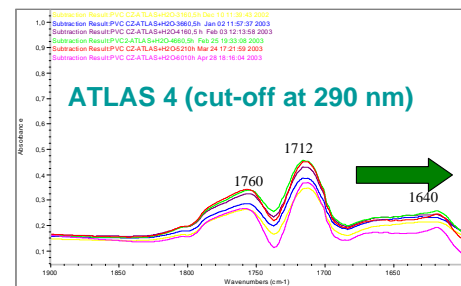
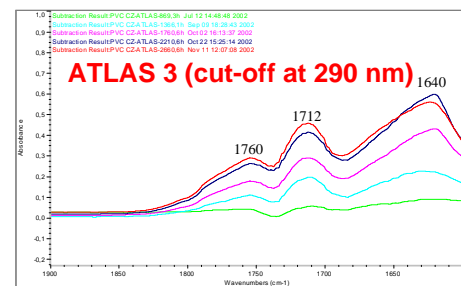


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Comparison and simulation capability

Objective 5

Effect of initial period of continuous irradiation

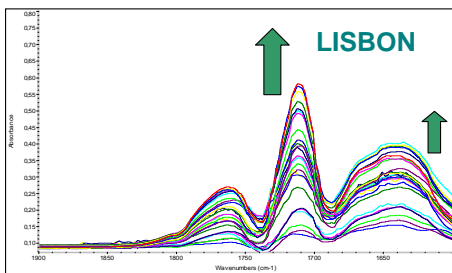
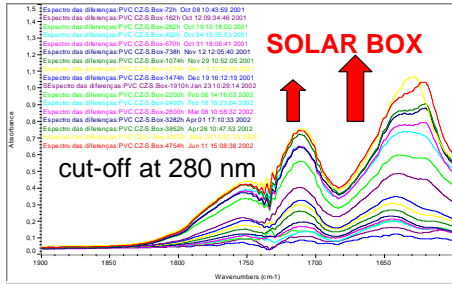


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Comparison and simulation capability

Objective 5

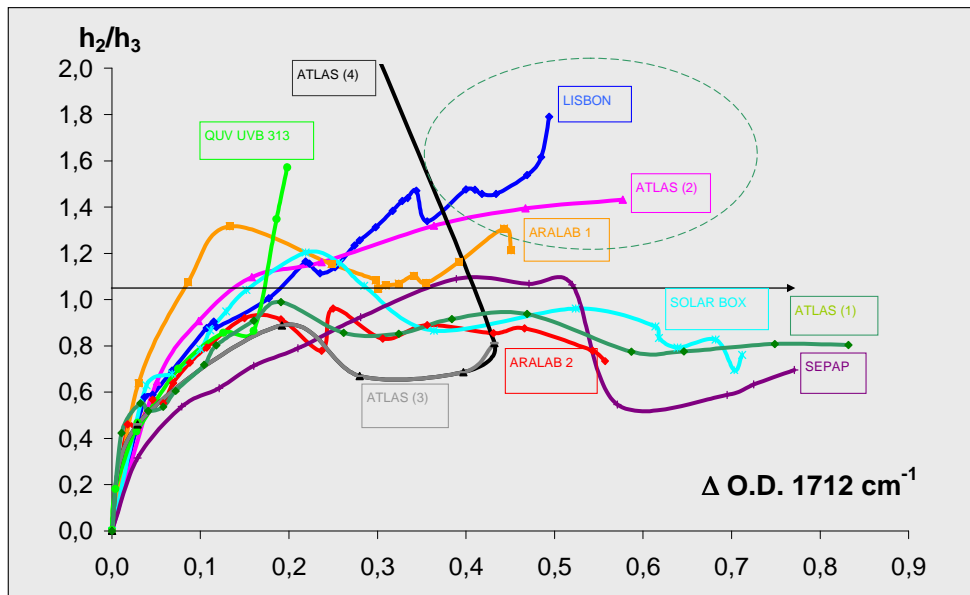
Comparison between an artificial simulated and the natural light sources



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Comparison and simulation capability

Objective 5



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Comparison and simulation capability

Objective 5

Statistical method of Spearman ranking

FTIR Spectroscopy (films): parameter h_2/h_3

- ✓ **Stoichiometry differences**
- ✓ **There aren't couples of systems showing a perfect correlation to the group of four formulations (due to different stoichiometry of the photoxidation mechanism).**

colourimetric parameters (films and plates)

- Evolution of colourimetric parameters (ΔE^* , ΔYI , $\Delta OD(450 \text{ nm})$) during weathering
- End values of a group of parameters

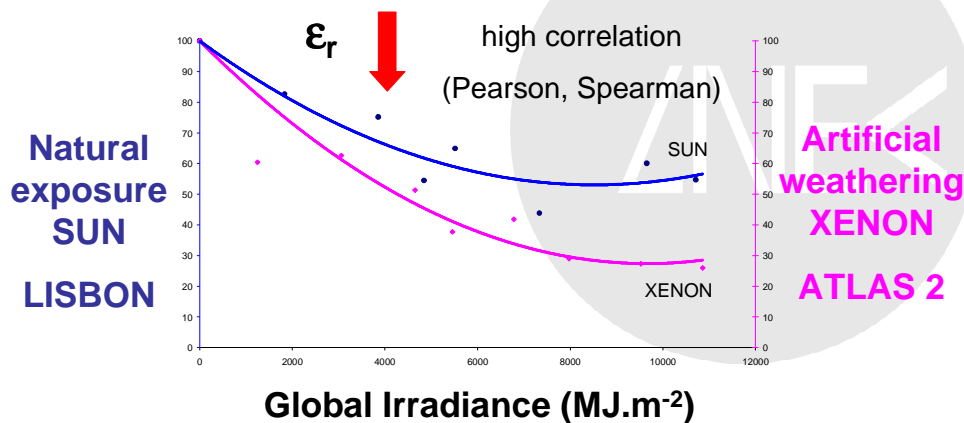
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Correlation between artificial and natural weathering

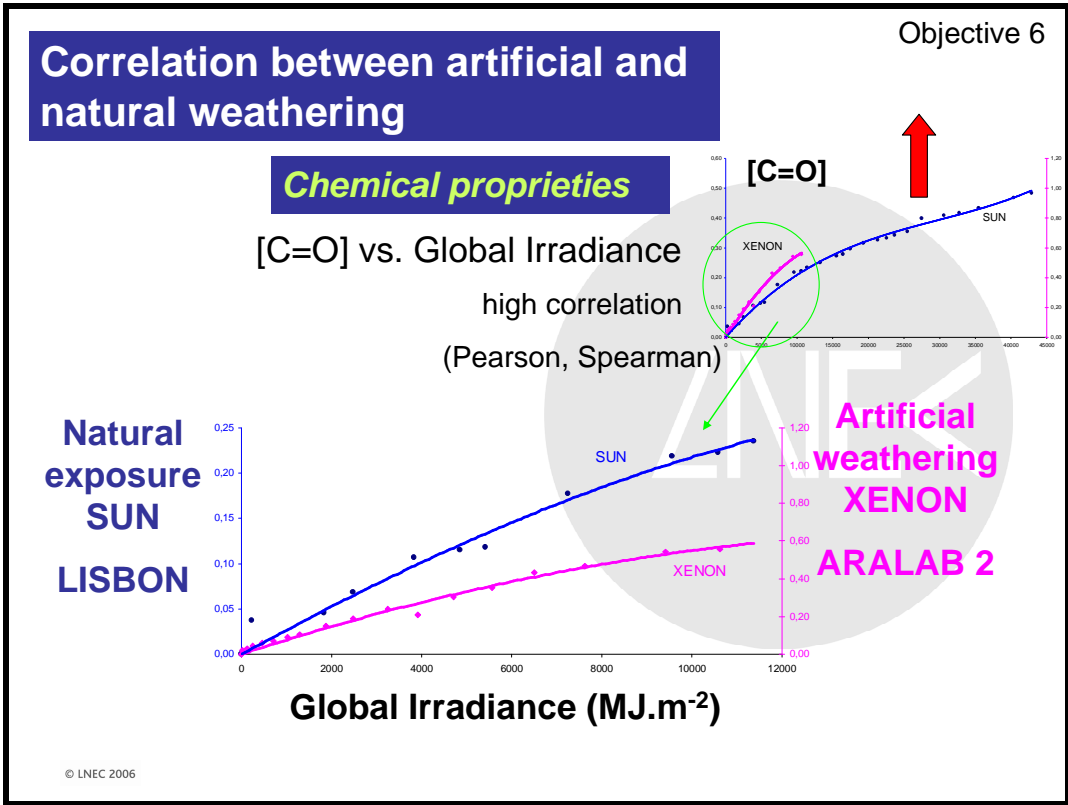
Objective 6

Tensile proprieties

Strain at break vs. Global Irradiance



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Objective 6

Correlation between artificial and natural weathering

Impact of the weathering conditions in the polymer degradation:
*natural exposition < artificial irradiation source
 (to the same dose of energy)*

↓

- synergistic effects between climatic parameters (radiation and temperature) or chemicals (water, oxygen), or with additives
- importance of the instantaneous dose of photons received by the molecules (higher electronic excitation in artificial conditions)

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Correlation between artificial and natural weathering

Acceleration factors (FTIR Data)

Time
Fx ± u_{95%}

System	Fx (PVC CZT)	Fx (PVC CZ)	Fx (PVC ST)	Fx (PVC S)
ATLAS 1/3	15 ± 5	15 ± 3	16 ± 3	23 ± 10
ATLAS 2	14 ± 6	14 ± 3	18 ± 3	27 ± 12
SOLAR BOX	14 ± 6	21 ± 7	15 ± 3	29 ± 17
ARALAB 2	14 ± 6	12 ± 3	13 ± 3	30 ± 14
SEPAP	143 ± 89	98 ± 22	67 ± 13	133 ± 66
QUV 313	58 ± 23	132 ± 62	16 ± 3	124 ± 79

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Correlation between artificial and natural weathering



Different
acceleration
factors



The acceleration factors are dependent of the photoxidation conditions (source, filters, climatic parameters, nature of polymer and stabilisation degree)



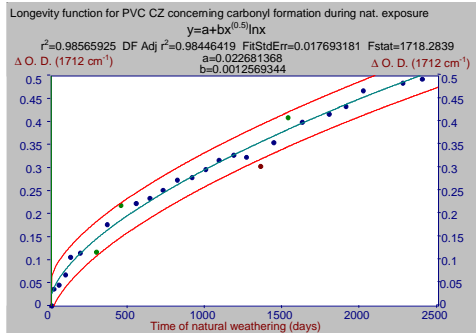
Need of observations in reference
conditions (natural exposure)

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Lifetime prediction. Durability

Chemical and mechanical proprieties of PVC

Non linear regression residual analysis distribution analysis



Definition of the best empirical equations to lifetime prediction

$P = f(t)$

Durability: depending of the propriety that is considered to establish the critical value



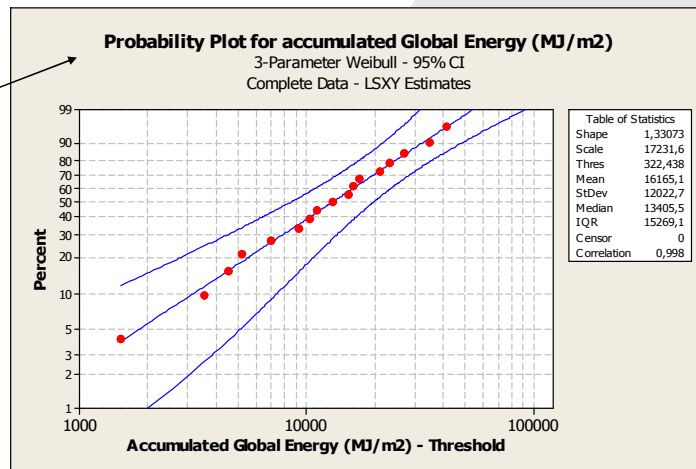
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Distribution function of the climatic data

Distribution analysis of the ageing parameters

Normal distribution (95%)

Natural weathering



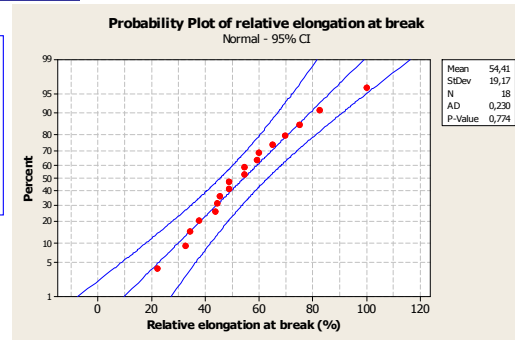
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Distribution function of the Polymer data proprieties

FTIR Analysis of the films in the carbonyl domain. Impact and tensile tests on extruded plates.



Statistical analysis of normality (Anderson-Darling and Wilk-Shapiro) and distribution analysis



Traction: Normal (E , σ);
Log normal, Weibull (ϵ_r)
FTIR: Weibull



Statistical Analysis of the influence of climatic parameters in the polymer degradation



Principal Component Analysis of climatic data and experimental results (FTIR and tensile) during artificial and natural weathering.



1. *Radiation*
2. *Temperature, water (rain)*

Conclusions from the thermoxydative study :

low contribution of temperature and humidity (by themselves) to the formation of oxidation products , but can be important (if $T > 65^{\circ}\text{C}$) to the formation of unsaturation



Polymer properties as functions of climatic data

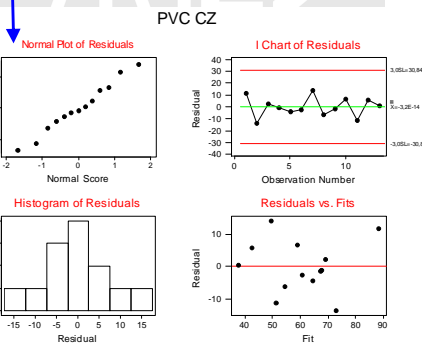
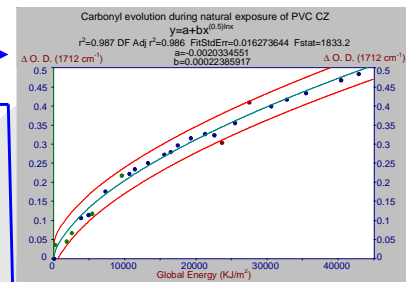
Non linear regression

Residual analysis

Empirical equations traducing the chemical and mechanical proprieties in function of climatic parameters

$$P = f(I, T, Hr, \dots)$$

Logarithmic functions



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