

Degradation studies of PVC films

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INTRODUCTION

The outdoor degradation of poly(vinyl chloride) (PVC) products is complex and not completely understood for most of the technical formulations. Furthermore, it is known that the behaviour of such materials is dependent of the photo-oxidation conditions, namely source of radiation, temperature, presence of water and humidity. In the present work, we have used X-ray photoelectron spectroscopy (XPS) to evaluate the influence of different photo-oxidation conditions on the surface degradation of stabilized PVC, low thickness calendered samples (~ 150 µm). The main objective is the study of the influence of the weathering conditions on the degradation level of stabilized PVC products for outdoor applications trying to go deeper in the understanding of the mechanism of both the degradation and the stabilization of the surface under different environmental conditions, different polymer formulations and different processing methods (extrusion or calendaring). Comparisons are made with previous results obtained using colourimetry and infrared spectroscopy. The role of PVC formulation and of radiation source and water were studied using artificial weathering. Results were compared with degradation induced by natural weathering in Lisbon.

EXPERIMENTAL

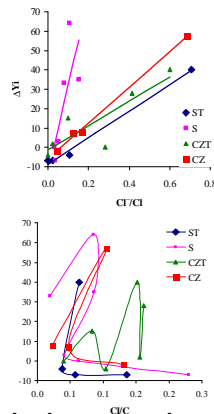
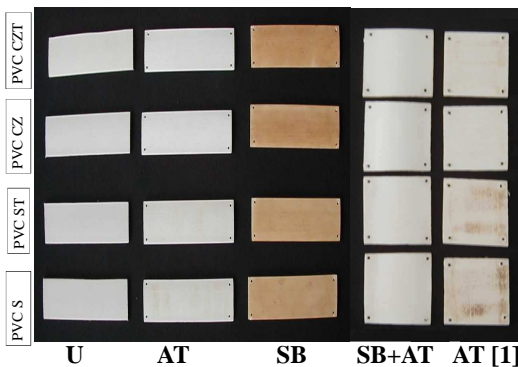
PVC formulations:

- S: Dibutyltin-maleate as thermal stabilizer.
- CZ: Calcium/Zinc as thermal stabilizer.
- ST and CZT: Tinuvin P as anti-UV additive

Ageing treatments:

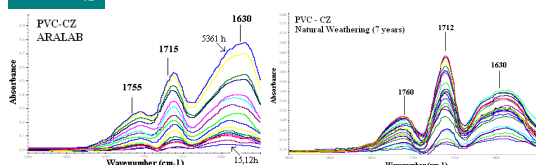
- ❖ U: Unweathered.
- ❖ AR: 5360 h continuous Xe irradiation in an ARALAB weatherometer equipped with 6000-W borosilicate glass-filtered xenon arc source (cut-off at 290 nm).
- ❖ AT: 3350 h continuous Xe irradiation with spray of water for 18 minutes each two hours in an ATLAS weatherometer equipped with 6500 W borosilicate glass-filtered xenon arc source (cut-off at 290 nm).
- ❖ SB: 4750 hours of continuous Xe irradiation in a Solar Box weatherometer equipped with 2500 W borosilicate glass-filtered xenon arc source (cut-off at 280 nm).
- ❖ QUV: 1820 hours of ageing (228 cycles of 8 hours, each one comprising 4 h of continuous irradiation and 4 hours in dark conditions) in a QUV PANEL apparatus equipped with four low-pressure Hg fluorescent lamps, with a maximum of emission at 313 nm.
- ❖ N: submitted to natural exposition for 66 months.
- ❖ Un: Unexposed face of the N samples

COLOURIMETRY



Yellowing index variation, ΔY_i , vs. Cl^-/Cl and C/C , both measured by XPS, displays a good correlation with Cl^-/Cl but a very poor correlation with $C/C \Rightarrow Cl^-/Cl$ is a better parameter to measure PVC degradation than C/C .

FTIRS



FTIR spectra, in the region of C=O and C=C stretching, of PVC CZ under artificial weathering (ARALAB ageing method) and submitted to Natural exposition for 7 years.

Both C=O and C=C IR absorption increase during weathering. However, C=C (1630 cm^{-1}) increases faster than C=O (~1715 cm^{-1}) in the artificial weathering and vice-versa in the natural weathering. This means that are differences in the stoichiometry of the degradation reaction. Natural weathering leads to a much lower yellowing probably because water reacts with C=C bonds to yield C=O groups breaking the π delocalization. So, the artificial ageing, in that conditions, are not entirely representative of real world.

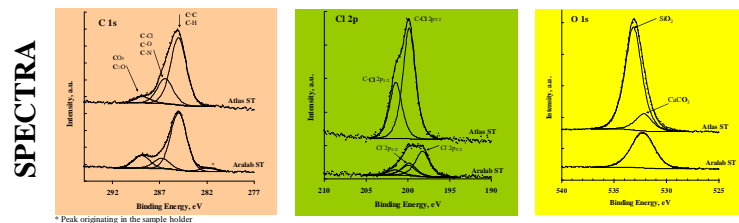
REFERENCES

- [1] L.P. Real, A.M. Ferraria, A.M. Botelho do Rego, *Polymer Testing*, 2007, 26, 77.
- [2] Starnes, Jr., W. H., *Prog Polym Sci*, 2002, 27, 2133.

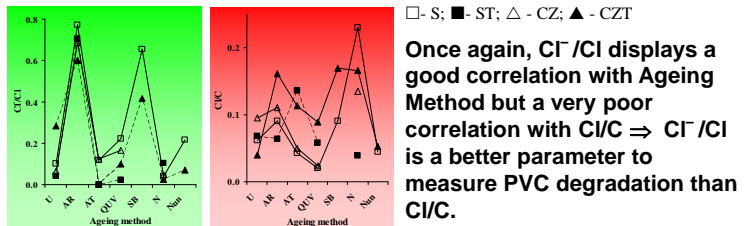
ACKNOWLEDGEMENTS

The authors wish to thank FCT for the Programa de Financiamento Plurianual and for A.M. Ferraria Grant SFRH/BPD/26239/2006.

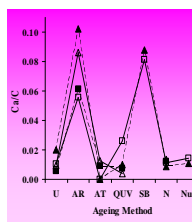
XPS RESULTS



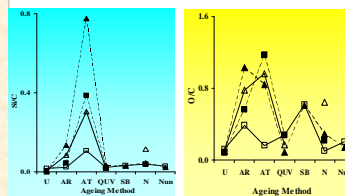
Quantitative Results



Once again, Cl^-/Cl displays a good correlation with Ageing Method but a very poor correlation with $C/C \Rightarrow Cl^-/Cl$ is a better parameter to measure PVC degradation than C/C .



A clear correlation exists between Ca/C and Cl^-/Cl suggesting that the reason for the chlorine resulting from degradation staying trapped at the surface under the form of chloride ion is the existence of the inorganic charge (mainly $CaCO_3$).



Most of the detected oxygen is bound to silicon or under the form of $CaCO_3$. Large amounts of silica, come from the water jet in Atlas chamber. It is preferentially adsorbed on surfaces with the anti-UV additive.

CONCLUSIONS

\rightarrow The Cl^-/Cl ratio is a good measure of PVC degradation:

- It can be correlated with colourimetry results: Cl^-/Cl increases with the variation of the Yellowing Index;
- It is sensitive to the ageing method for all the formulations used.
- It presents a clear correlation with the Ca/C ratio, indicating the importance of the inorganic charge (mainly $CaCO_3$) in the Cl^- trapping.
- The detection of Cl^- as a degradation product gives strength to the hypothesis of an ionic mechanism for polyene propagation involving ion pairs [2].

\rightarrow CZT seems to be more resistant to weathering conditions than other formulations.

\rightarrow The FTIR spectra obtained under different photooxidation conditions present peaks at same wavelength, which means that the degradation mechanism is equivalent under artificial and natural weathering.

