Degradation studies of PVC films

A.M. Botelho do Rego¹, A.M. Ferraria¹ and L. Pimentel Real²

¹Centro de Química-Física Molecular, IST, Technical University of Lisbon, Av. Rovisco Pais, 1049-001 Lisboa (Portugal)
²Laboratório Nacional de Engenharia Civil, Departamento de Materiais, Núcleo de Materiais Plásticos e Compósitos, Av. do Brasil, 1700-066 Lisboa, Portugal

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 calendering). 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 5600 W boro silicate glass-filtered xenon arc source (cut-off at 280 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 boro silicate 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 boro silicate glass-filtered xenon arc source (cut-off at 280 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 boro silicate glass-filtered xenon arc source (cut-off at 290 nm).
- QUV: 1680 hours of ageing (208 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, ΔYI, vs. Cl¯ /Cl and Cl/C, both measured by XPS, displays a good correlation with Cl−/Cl but a very poor correlation with Cl/Cl. It can be correlated with colourimetry results: Cl¯ /Cl is a better parameter to measure PVC degradation than Cl/C.

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 there 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


CONCLUSIONS

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 CaCO₃) 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].
- CZT seems to be more resistant to weathering conditions than other formulations.
- 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.