LABORATÓRIO NACIONAL DE ENGENHARIA CIVIL

THE INFLUENCE OF WEATHERING CONDITIONS IN THE EVOLUTION OF MOLECULAR PROPERTIES OF PVC FOR OUTDOOR APPLICATIONS. AN ANALYTICAL STUDY USING TECHNIQUES OF SURFACE ANALYSIS (SEM AND XPS)

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A INFLUÊNCIA DAS CONDIÇÕES DE ENVELHECIMENTO NA EVOLUÇÃO DAS PROPRIEDADES MOLECULARES DO PVC ESTABILIZADO PARA APLICAÇÕES EXTERIORES. UM ESTUDO ANALÍTICO USANDO TÉCNICAS DE ANÁLISE DE SUPERFÍCIE (SEM AND XPS)

RESUMO

Procurou-se com a presente comunicação apresentar os resultados de um estudo para avaliar o estado de degradação de placas extrudidas em PVC rígido, para aplicações exteriores, submetidas a diferentes condições de envelhecimento, utilizando técnicas de análise de superfície, nomeadamente microscopia electrónica de varrimento (SEM) e de espectroscopia de fotoelectrão X (XPS). O desenvolvimento das formulações, o envelhecimento e a subsequente caracterização por microscopia electrónica de varrimento foi realizada no LNEC. A caracterização por espectroscopia de fotoelectrão X foi realizada no Centro de Química-Física Molecular do Instituto Superior Técnico.

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 deterioration condition of extruded hard PVC plates, for outdoor applications. The plates were subject to different ageing conditions, using techniques of surface analysis, namely scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The development of formulations, the ageing and the subsequent characterisation by scanning electron microscopy were done in LNEC. The characterisation by X-ray photoelectron spectroscopy was done at the Centre for Molecular Chemistry-Physics of *Instituto Superior Técnico* (Higher Technical Institute of Lisbon).

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.

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L'INFLUENCE DES CONDITIONS DE VIEILLISSEMENT SUR L'EVOLUTION DES PROPRIETES MOLECULAIRES DU PVC POUR DES APPLICATIONS EXTERIEURES. UNE ETUDE ANALYTIQUE UTILISANT DES TECHNIQUES D'ANALYSE DE SURFACE (SEM ET XPS)

RÉSUMÉ

L'objectif essentiel de cette communication est de présenter les résultats d'une étude visant à évaluer l'état de détérioration des plaques extrudées de PVC rigide, pour des applications extérieures. Les plaques ont été soumises à de différentes conditions de vieillissement, en utilisant des techniques d'analyse de surface, nommément la microscopie électronique de balayage (SEM) et la spectroscopie de photoélectron X (XPS). Le développement des formulations, le vieillissement et la caractérisation postérieure par microscopie électronique de balayage ont été effectués au LNEC. La caractérisation par spectroscopie de photoélectron X a été effectuée au Centre de Chimie et Physique Moléculaire de *l'Instituto Superior Técnico* (Institut Supérieur Technique).

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.

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THE INFLUENCE OF WEATHERING CONDITIONS IN THE EVOLUTION OF MOLECULAR PROPERTIES OF PVC FOR OUTDOOR APPLICATIONS.
AN ANALYTICAL STUDY USING TECHNIQUES OF SURFACE ANALYSIS
(SEM AND XPS)

Abstract

In the present work, four different TiO_2 pigmented PVC formulations, designed to outdoor applications, were submitted to the artificial accelerated ageing in xenon light, without and with spray of water, and to natural exposure in Lisbon. The influence of the combined action of water, temperature and radiation in the oxidative ageing is evaluated by means of molecular analysis, using X-Ray Photoelectron Spectroscopy (XPS) and Scanning Electronic Microscopy (SEM), permitting to compare the results obtained under different exposure conditions.

Keywords: Poly(vinyl chloride); titanium dioxide pigments; weathering; XPS; SEM.

1. INTRODUCTION

The low cost and the good performance of the poly(vinyl chloride) products make this polymer very suitable for applications in buildings, mainly in exterior applications, like window profiles, cladding structures and siding. 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 interest.

In the present work, we have used XPS and SEM analytical techniques to evaluate the influence of different photoxidation conditions in the degradation of stabilized PVC extruded samples on the surface.

X-ray photoelectron spectroscopy is a well established technique very useful for surface characterization. However its application to insulating samples and particularly to halogenated polymers, raises two major problems. One is the charge accumulation at the surface which has as the major consequence the difficulty of finding a reference for correcting the charge shifts appearing in spectra [1]. The other one is that the X-ray induces polymer degradation which, in halogenated polymers is usually measured as a decreasing of the ratio halogen/carbon as the irradiation time increases [2]. Nevertheless, charging effects have been used to good advantage by several authors [3, 4]. Also the degradation by X-ray can be used advantageously in the analysis of a polymer.

The main objective of this paper is to find information concerning the influence of the weathering conditions (thermal history and role of degradation agents) in the degradation level of stabilized PVC products for outdoor applications and compare the results from different exposure methods, considering the influence of each degradation agent and to show that programmed sequence of intervention of each degradation agent influences the final weathering state of samples.

As a tool to improve XPS data understanding, the following of the evolution of the X-ray induced degradation in PVC products, constitutes also a secondary objective.

2. EXPERIMENTAL

2.1. Samples: compounding and processing

In this study, we use 4 different types of TiO_2 pigmented PVC formulations, containing $CaCO_3$ and various additives, which are designed for outdoor applications. Particular care was taken to select thermal stabilisers with acceptable ecotoxicological characteristics.

The PVC formulations are referred to as PVC CZ and PVC S, according to the type of thermal stabiliser present (respectively based on calcium/zinc or dibutyltin-maleate). Formulations including additionally a benzotriazole type anti-UV additive (tinuvin P) are marked with a "T" (referred to as PVC CZT and PVC ST).

The compounding of the designed formulations and posterior extrusion was done at Baquelite Liz (Portugal). The extruded plates have 2 mm thickness.

Five extruded plates, around 1,5 mm of thickness, of each formulation were studied: non aged (U), 4900 hours of xenon irradiation without spray of water (AR), 7000 hours of xenon irradiation, the first 2650 hours without spray of water and the last 4350 hours with spray of water (AR/ARW), 4350 hours of xenon irradiation with spray of water (ARW) and naturally weathered during 5 years (N).

2.2. Experimental methods of analysis

Samples were analysed by X-Ray Photoelectron Spectroscopy (XPS) using a XSAM800 (KRATOS) X-Ray Spectrometer operated in the fixed analyser transmission (FAT) mode, with a pass energy of 20 eV and the non-monochromatised AlK_a X-radiation (hυ=1486.7eV) with a power of 130 W (10 mA and 13 kV) and using ultra high vacuum (UHV), under a pressure in the range of 10^{-7} Pa. They were analysed at room temperature, at take-off angle relative to the surface (TOA) of 90º. The roughness of surfaces did not allow for the angle resolved analysis. Spectra were collected with a step of 0.1 eV, using a Sun SPARC Station 4 with Vision software (Kratos). The curve fitting for component peaks was carried out with a non-linear least-squares algorithm using a mixture of Gaussian and Lorentzian peak shapes. Sensitivity factors used were 0.25 for C 1s, 0.73 for Cl 2p, . No charge compensation was used. Charge shifts were corrected using as reference the aliphatic carbon, C 1s, with a binding energy BE=285 eV as explained in the next section.

Samples were analysed by Scanning Electronic Microscopy (SEM) using a JEOL JSM 6400, operating with a power of 15 kV. The samples were previously recovered with carbon, to assure their conductivity, using a Vacuum Evaporator JEOL-JEE-4x.

2.3. Artificial weathering

The artificial simulated weathering was carried out in two different chambers: an Aralab Fitoclima 600 EDTU and an Atlas Weatherometer Ci 65, respectively equipped with a 6000 and 6500-Watt borosilicate glass-filtered xenon arc sources. The sample AR was artificially aged in the Aralab chamber, during 4900 h of continuous irradiation, using circulating air with a relative humidity of (60 ± 5) % . The samples AR/ARW and ARW was artificially aged in a continuous

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irradiation program performed in Atlas chamber, which was subdivided in two periods with different exposure conditions: a first period of 2650 h of irradiation without spray of water and a last one of 4350 h with cycles of spray of water for 18 minutes each two hours, using circulating air with a relative humidity of (10 ± 5) %. Although, the both chambers are equipped with water filters, an aquanizer and a cartridge deionizer, the quality of the water fluxing through the specimen and rack sprays was also controlled by means of a water purity meter. The intensity of radiation in both chambers was auto-adjusted to assure a global irradiation of 550 W/m^2, in the wavelength interval from 290 to 800 nm. The intensity of the radiation sources was frequently verified with both calibrated 340 nm and 295-400 nm radiometers. To assure the correct temperature of the circulating air, a calibrated black standard thermometer sensor was used, which was maintained at 65 ± 5ºC. The maximum temperature measured in the exposed surface was 53ºC.

The test pieces were placed in a similar position relative to the radiation source and the differences in the distribution of the weathering parameters were compensated by rotation of the cylindrical sample rack.

2.4. Natural exposure

The specimens to be tested were exposed in March of 2000 to outdoor weathering in Lisbon (severe climate, according to [5]), in accordance with ASTM Method D 1435, [6], at an angle of 45º, facing South, and were removed periodically to perform the several analyses described above.

3. PREVIOUS FINDINGS

It was shown in some previous works [7, 8], by means of techniques of colourimetry and infrared spectroscopy, that there are high increases of conjugated double bond and carbonyl formation during time of accelerated artificial ageing with continuous xenon irradiation. It was found that the cyclic spraying of water during artificial ageing changes the stoichiometry of the degradation reactions in TiO$_2$-PVC composites, originating only a low increase in the conjugated double bonds and a medium increase in the carbonyl concentration. We found also that the PVC samples studied did not show yellowing during five years of natural exposure, and there was only a very low increase in the carbonyl concentration. More recently, it was found that an initial period of xenon irradiation, without spray of water, produces an unknown phenomenon that minimizes the internal degradation and the effects of erosion, and avoids the additive migration, during posterior artificial ageing with radiation and water. Indeed, samples AR/ARW, irradiated with xenon light during 7000 hours, using cyclic spray of water only in the last 4350 h, shows a constant concentration of unsaturation and carbonyl groups in the last 4300 hours of irradiation [8]. Moreover, these samples shows a better white appearance and less signs of weathering than samples ARW, that are weathered simultaneously in the same chamber, during 4350 hours,using xenon light and cyclic spray of water (figure 1). It was these unexpected results that motivate the present work and the recourse to surface analysis techniques.

PVC CZT →

PVC CZ →

PVC ST →

PVC S →

(a)   (b)
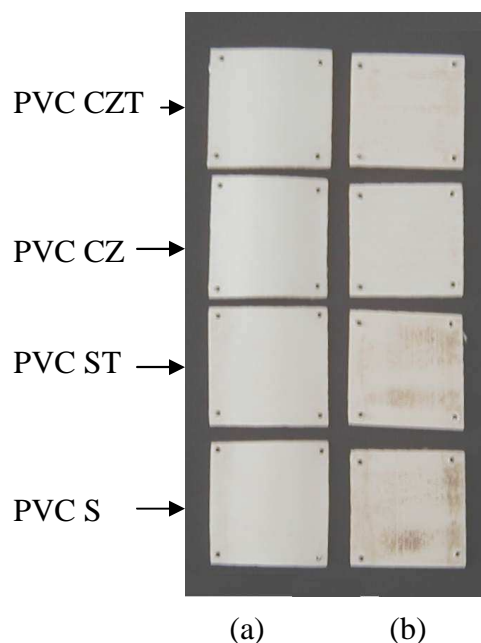
Figure 1: extruded plates of 4 TiO2 - PVC composites formulations: a) FTIR spectra for a PVC CZ film, in the carbonyl domain: a) samples AR/ARW, irradiated with xenon light during 7000 hours, using cyclic spray of water only in the last 4350 h; b) samples ARW, irradiated with xenon light during 4350 hours, using cyclic spray of water.

4. SEM RESULTS

The Scanning Electron Microscope (SEM) produces images by scanning the surface of a specimen with a beam probe of electrons. Low energy secondary electrons produce a signal that is strongly influenced by topography. The backscattered electron signal is also sensitive to local topography, but it allows mainly to differentiate between different phases. Figure 2 contains the SEM images, resulting from backscattered electrons, of samples of PVC S not weathered and at the end of weathering performed under four different exposure conditions.

(a)   (b)   (c)   (d)   (e)
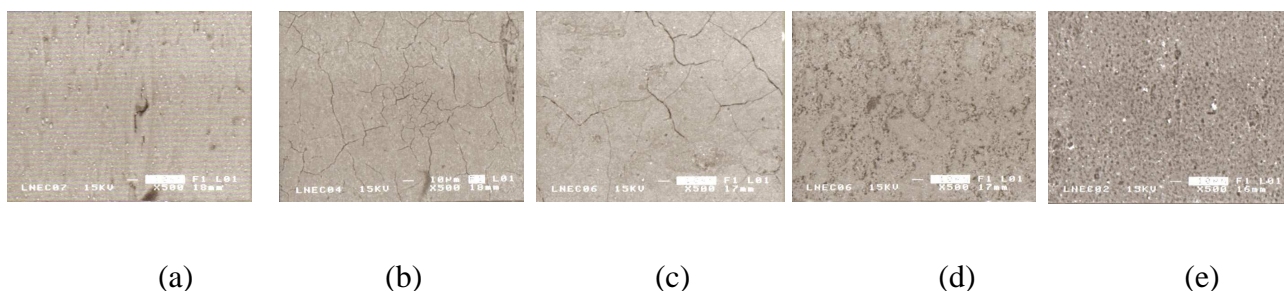
Figure 2: SEM backscattered electrons images of a PVC S (×500): a) sample U, after processing, not weathered; b) sample AR, irradiated with xenon light during 4900 hours; c) sample AR/RW, irradiated with xenon light during 7000 hours, using cyclic spray of water only in the last 4350 h; d) sample ARW, irradiated with xenon light during 4350 hours, using cyclic spray of water; e) sample N, submitted to natural exposure during 5 years.

Similar SEM images, resulting from secondary electrons, are presented in figure 3.

(a) (b) (c) (d) (e)
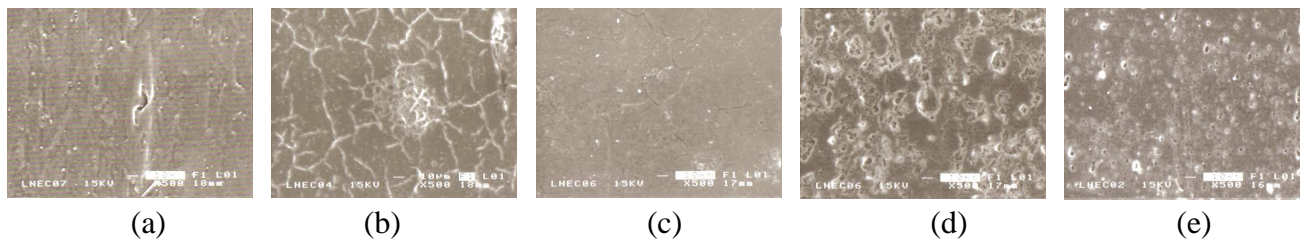
Figure 3: SEM secondary electrons images of a weathered PVC S (x 500). The order is the same that is used in figure 2

SEM observations of unweathered extruded sample U revealed some localised defects resulting from processing, but the surface is smooth with no significant discontinuities or flaws, whereas the exposed side of weathered samples revealed considerable change in texture and surface finishing, relatively to unweathered sample.

After Xenon irradiation the surface of sample AR becomes discontinuous, covered with a crack network, irregular and randomly branched. This sample presents more and deeper cracks than sample AR/RW, submitted to an initial period of xenon irradiation, but the cracks in this one are larger than in the first.

The sample ARW, submitted to cycles of water from beginning, presents cracked areas and evidences of the fast erosion originated by water, like holes and channels, which are regions of lower density.

The sample N, exposed outdoors, presents some surface defects and signs of the erosion originated by rain, but the surface is more continuous and less degraded than in sample ARW.

SEM images obtained with secondary electrons allows to reveals the significant differences between state of the surface of sample AR/RW and the surfaces of other weathered samples. It is evident that the texture of the surface of the sample AR/RW, submitted to a previous period of xenon irradiation, has less signals of degradation induced by weathering than any other surface.

5. XPS RESULTS

X-ray irradiation is known to induce degradation on halogenated surfaces [1, 2]. This disadvantageous fact can be overcome and even give precious information about the surface if a systematic study of the degradation is performed. Carbon and chlorine XPS signals were then continuously measured 33 to 36 times for periods from 7700 to 8200 s. Another problem related with the use of XPS in the study of halogenated polymers is the choice of a reference for charging correction [1]. However, since the surface of the samples here studied revealed very poorly chlorinated surfaces (Cl/C<0,15 for all the samples), due to surface degradation during processing, the C 1s peak assignable to aliphatic component (B.E.=285 eV) [9]. was taken as reference. Carbon peak was fitted with 3 components (at 285, 286.7 ± 0.1 (286.4 ± 0.1 for S4 sample) and 288.8 ± 0.1 eV. Component at ~288.8 eV is assigned to carbonate [10]. Component at 286.4 eV is usually assigned to carbon bound to chlorine [1]. Chlorine peak was fitted with two components each of them being a spin-orbit doublet. The Cl $2p_{3/2}$ components of each doublet were located at 198.3 ± 0.1 and 200.2 ± 0.1 eV, the first one being assigned to chloride ion and the second one to Cl bound to

carbon [9].

The XPS results, presented in figure 4, show that the sample AR/RW, submitted to a previous period of xenon irradiation, presents an initial Cl/C ratio similar to the sample N, exposed to natural environment, and that this ratio is higher than in other weathered samples, which is consistent with a lower degradation, i.e. to an higher concentration of chlorine.

The results obtained from sample N confirm also that the processing is very aggressive to the surface of PVC materials, due to thermoxidative degradation, which decreases the concentration of Cl in extreme surface. A similar degradation occurred during storage and blending of PVC compounds and during preparation of pressed pellets for XPS analysis.
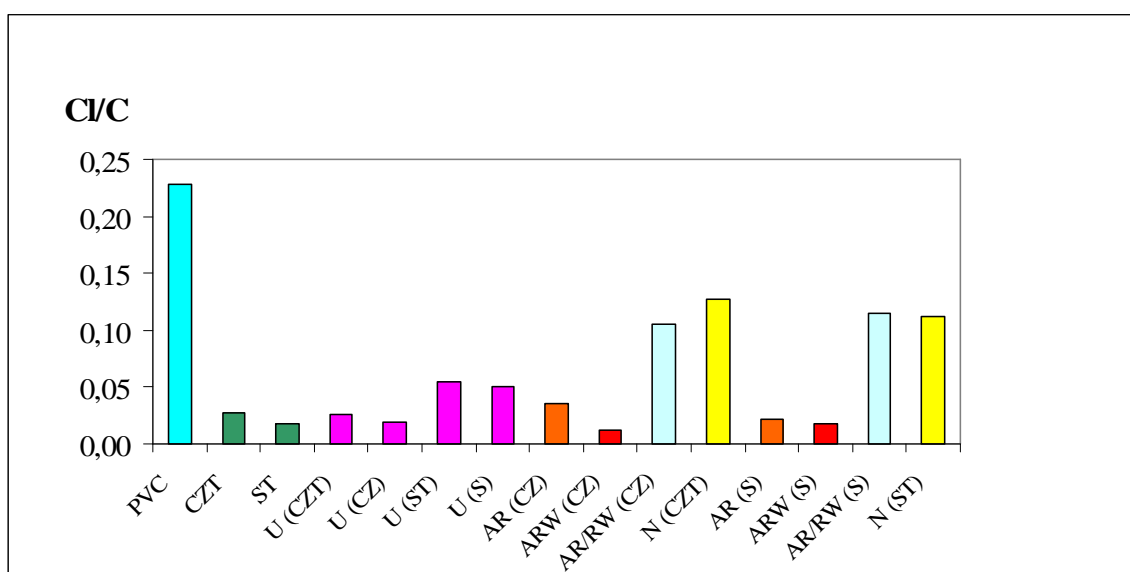
Figure 4: Initial Cl/C ratio measured by XPS in various samples from different formulations: virgin PVC, unweathered extruded plates and weathered under different conditions.

The XPS results, presented in figure 5, show that sample ARW, submitted to cycles of water during xenon irradiation, presents much more oxygen than other samples, suggesting that this element was already inside the holes and channels formed by the erosive action of water, in the form of entrapped oxygen or water. The results suggest also that tin thermal stabilizer segregates at surface as consequence of the prolonged action of xenon irradiation and it is not washed out by water.
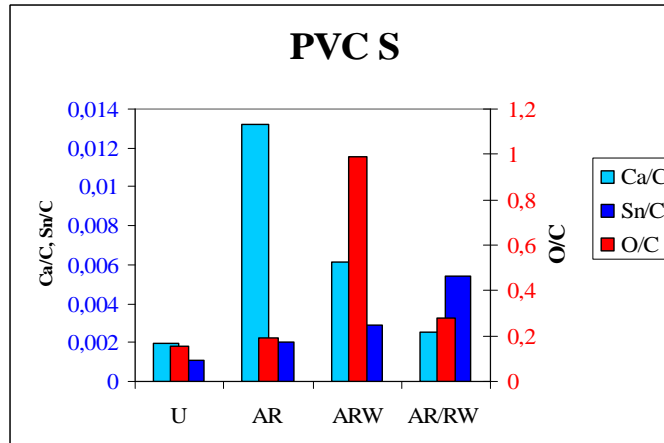
Figure 5: Initial Ca/C, Sn/C and O/C ratios of a PVC S, measured by XPS in the unweathered extruded plate and in samples weathered under different conditions.

The XPS results even suggest that the irradiation causes the migration of Ca to the exposed surface, and this additive is there partially washed out by water action, being the calcium concentration higher in more degraded samples. Indeed, there are more calcium in sample AR, submitted to continuous xenon irradiation without water, and less calcium in samples continuous irradiated with cycles of water (samples ARW and AR/RW). Finally, the samples less degraded presents the lowest concentration of calcium, confirming what is referred before.

Surprisingly was the high silicon concentration detected by XPS in all specimens. By means of a sequential analysis, we found that silicon was introduced in the processing and during artificial weathering, probably due to products used in the cleaning of blenders and extruders, and from silica present in water. These finds confirm that XPS can be used as processing optimization tool, detecting undesirable contaminative elements.

The degradation induced by X-ray irradiation is usually evaluated in PVC by means of Cl/C ratio decreasing rate. The follow-up of that degradation may be very instructive about the mechanism of chlorine loss (under the form of HCl or Cl_2), during degradation. To attain this target, we performed some XPS experiments in the same virgin PVC that is used in our PVC formulations As can be seen in the figure 6, the Cl migration rate to the surface is lower than the Cl escape rate to the vacuum.
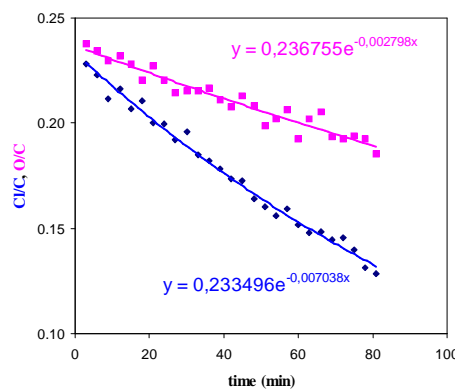
Figure 6: Evolution of Cl/C and O/C ratios of a virgin PVC, during XPS irradiation.

It is also interesting to know what kind of spectra changes take place during degradation (figure 7).

Initially we have more CH2 than C-C, and only one Cl component (Cl-C); at the end we have more C-C than CH2, and less Cl, as should be expected by the known mechanism of "unzip" reaction of PVC degradation.

We performed also similar XPS measurements in the various PVC formulated compounds. The results are presented in figures 8 and 9.

From figure 8, it can be seen that the evolution and whole quantities of Cl/C and C/O ratios are similar in both compounds, but different that is obtained from PVC resin. However, contrarily to PVC resin, the compounds present a different behaviour: Cl migration rate to the surface is higher than escape rate to the vacuum, resulting in an increase of Cl/C ratio during X-ray irradiation. So, part of chloride is trapped in the surface.

Like before, the spectra reported in figure 9 present differences from spectra of virgin PVC: initially there are two components in the Cl peak (two doublets): Cl⁻ and Cl-C. At the end of irradiation there is only one doublet: the Cl⁻ species. So, the peak of bound chlorine decreases and the peak of chloride increases.

(a)   (b)
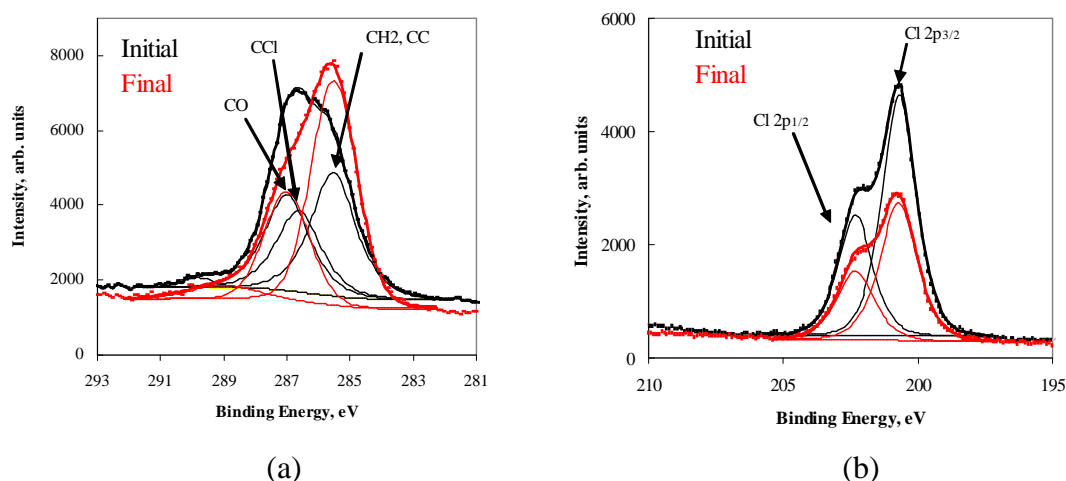
Figure 7: Initial and final bands of a virgin PVC, obtained from XPS measurements: a) Carbon bands; b) Chlorine bands.

(a)   (b)
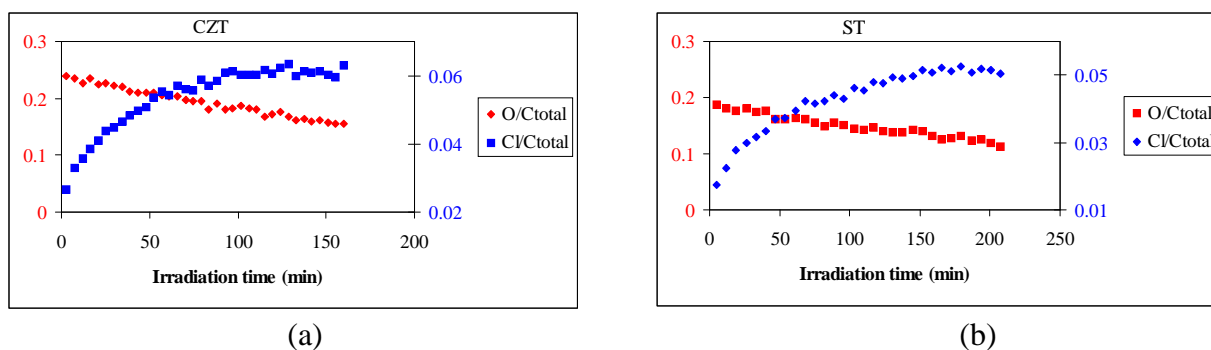
Figure 8: Evolution of Cl/C and O/C ratios of two stabilized PVC compounds, during XPS irradiation: a) PVC CZT; b) PVC ST.

(a)

(b)
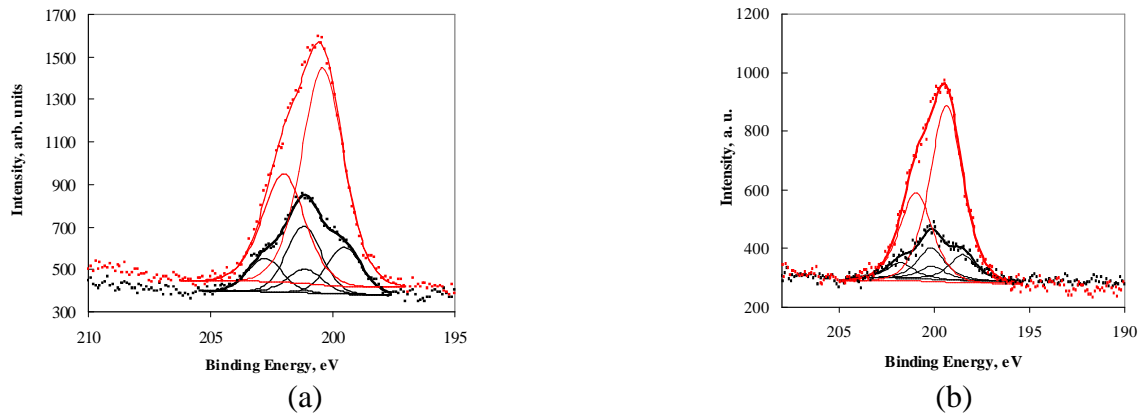
**Figure 9: Initial and final bands of a virgin PVC, obtained from XPS measurements: a) Carbon bands; b) Chlorine bands.**

Concerning the different PVC formulations, after extrusion, but yet not weathered, we performed also similar XPS measurements. Typical results, for two formulations, are presented in figures 10 and 11.

(a)

(b)
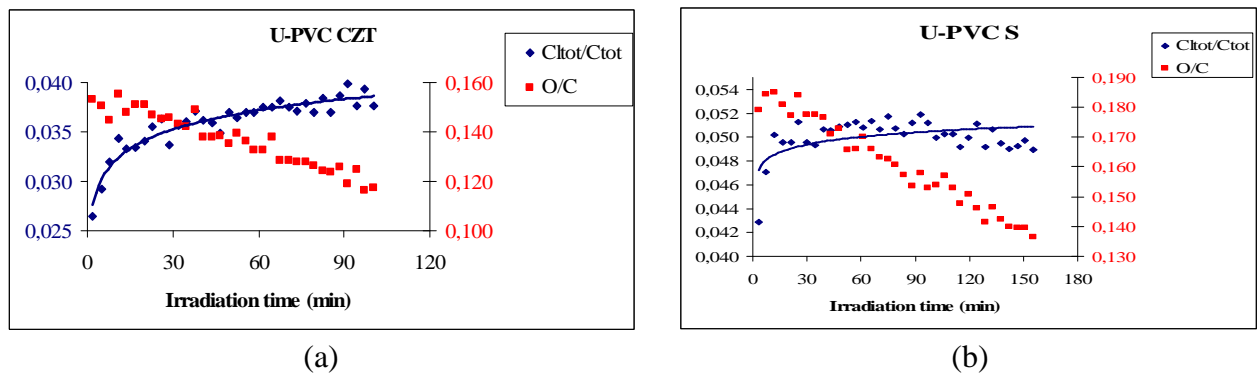
Figure 10: Evolution of Cl/C and O/C ratios of two stabilized PVC extruded plates, yet not weathered, during XPS irradiation: a) PVC CZT; b) PVC S.

(a)

(b)
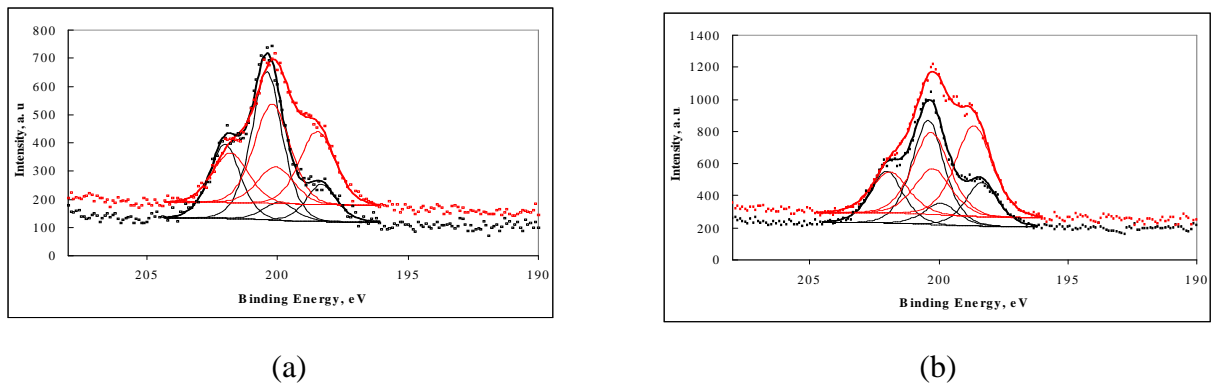
Figure 11: Initial and final bands of two stabilized PVC extruded plates, yet not weathered, obtained from XPS measurements: a) Carbon bands; b) Chlorine bands.

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From figure 10, it can be seen that the evolution and whole quantities of Cl/C ratio are similar in both formulations, and similar to is obtained from PVC compounds.

However, it can be seen from figure 11, that both extruded formulations (Ca/Zn or DBTM stabilised) present similar behaviour, but the spectra still different from compounds and virgin PVC: There are the same number of components in the Cl peak, before and after X-ray irradiation: Cl bonded and Cl⁻. So, the peak of bound chlorine decreases and the peak of chloride increases.

Finally, in the case of weathered samples, we found both kinds of different behaviour (figure 12). Taking as example the tin stabilized samples, the XPS results show that the behaviour of sample AR/RW is different from other weathered samples, as concerns to the level of degradation originated by X-ray irradiation, measured by means of the evolution of Cl/C ratio. The chlorine from C-Cl break during X-ray irradiation is not trapped at the surface and is released from the sample, probably as chlorine Cl_2 or hydrochloride acid HCl. In counterpart, the other samples present a different behaviour in terms of evolution of the chloride concentration during X-ray irradiation. In these samples the chlorine transforms into chloride and is trapped at the surface, perhaps due to the existence of delocalized double bonds, which are good electron acceptors and stabilize the Cl⁻ at outer surface. Moreover, as the Cl⁻ concentration in the surface of more degraded samples is low, this increases de Cl⁻ migration.
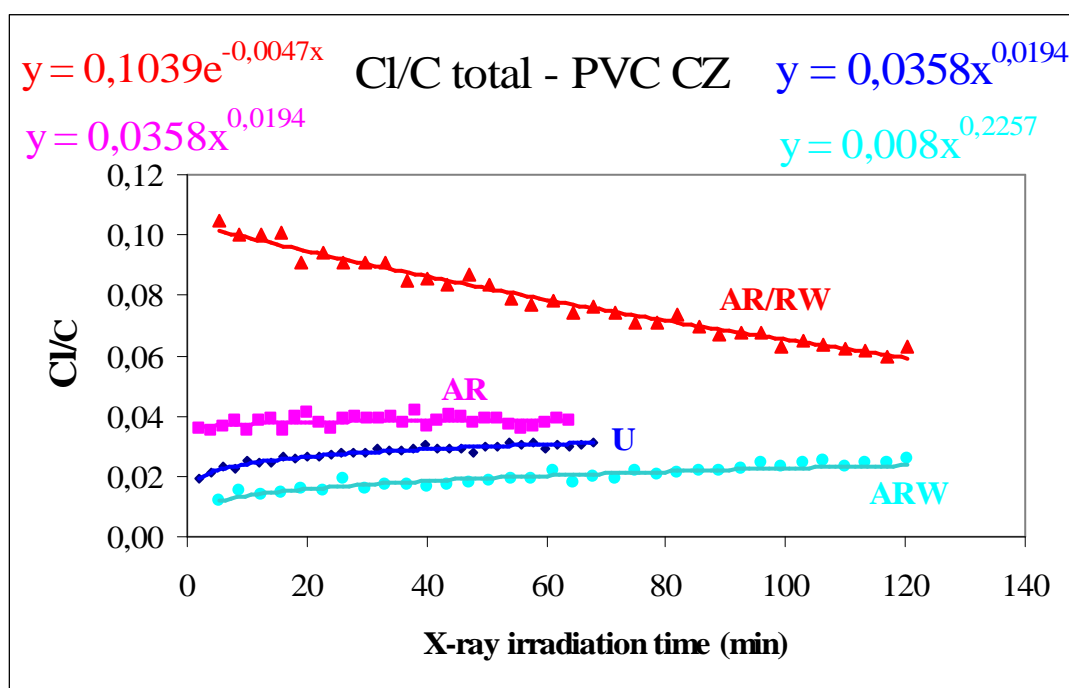
Figure 12: Evolution of Cl/C ratio of the unweathered extruded PVC S and weathered PVC S samples, during X-ray irradiation.

The evolution of Cl/C ratio of PVC plates stabilised with calcium/zinc, during X-ray irradiation, is similar to featured by PVC plates stabilised with tin maleate.

6. CONCLUSIONS

The initial Cl/C ratio, measured by XPS in the beginning of X-ray irradiation, agrees well with yellowing index of weathered samples, measured in previous works. Basically, high yellowing index correspond to low Cl/C ratios and vice-versa, as expected.

The SEM and XPS results also agree well with previous findings, obtained by FTIR spectroscopy, and are compatible with the following ageing mechanism:

1. Long irradiation periods (sample AR) induce a generalized degradation of the surface, 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 micro-cracks all over the surface.

2. The first action of water consists in the formation of oxidation products of carbonyl type (C=O), originated by OH* radical attack to any unsaturation in the polymer, due to photo-activity of TiO_2 pigments in the presence of water, resulting in whitening of the surface [8].

3. The subsequent action of water consists essentially on the remotion of this low adhesion defect-region overlayer (by erosion), uncovering deeper, more uniform regions of the sample, richer in Cl, having less conjugated double bonds (lower yellowness index). This region, with more uniform distribution of defects is not so easily degraded as other weathered samples, presenting more localized weak points.

4. When that previous xenon irradiation period is absent, the mechanical degradation of the surface is still concentrated around defects (not generalized to all surface) and the erosion by the water is most localized. However, the effect on the double bonds still exists, decreasing the yellowing but keeping the Cl/C ratio.

The XPS results allow to suggest that the increasing or decreasing of the Cl/C ratio during irradiation seems to be only dependent of the initial concentration of chlorine present in the sample. So, samples presenting low values of this ratio (less than 0,05) show a increasing evolution of the Cl/C ratio, and vice-versa. Intermediate values of this ratio (near 0,05) gives rise to a behaviour of slow initial increase followed by slow decrease. This can be explained by a diffusion mechanism, which is directly related with the concentration gradient of Cl. When the Cl/C ratio increases, the initial composition contains always two Cl components (Cl bound to C and Cl$^-$) and the component responsible for the total increase is Cl$^-$. When the Cl/C ratio decreases, the initial composition contains a large bound Cl component and a small or negligible Cl$^-$ component which stays essentially constant during X-Ray irradiation.

Other XPS findings were that XPS technique can help to improve the polymer processing because it allows an elemental chemical analysis. This allows to measure degradation levels of PVC compounds induced by the various stages of processing (by means of Cl/C and O/C ratios) and, therefore, to optimize the formulation before starting the production at an industrial scale. Also the contamination levels can be evaluated. For instance, in this work, we have shown that Si is introduced during processing and during artificial irradiation, probably by water.

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SLIDES
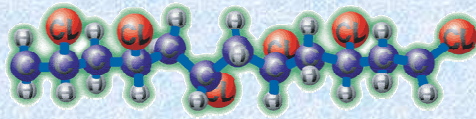
THE INFLUENCE OF WEATHERING CONDITIONS IN THE EVOLUTION OF MOLECULAR PROPERTIES OF POLY(VINYL CHLORIDE) FOR OUTDOOR APPLICATIONS. AN ANALYTICAL STUDY USING TECHNIQUES OF SURFACE ANALYSIS (SEM AND XPS)

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Objective

Main: to find information concerning the **influence of the weathering conditions** (thermal history and role of degradation agents**)** in the degradation level of stabilized PVC products for outdoor applications.

Secondary: as a tool to improve XPS data understanding, to follow the evolution of the **X-ray induced degradation** in PVC products.

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Experimental: processing

1. Formulation design. Selection and weighting of additives.

PVC and Additives

2. Blending

Compounds CZ, CZT, S, ST

Preliminary stability study

3. Extrusion

Extruded Plates PU

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Experimental: weathering conditions

Artificial weathering with xenon borosilicate filtered continuous irradiation sources

1. continuous irradiation without water (60% RH)

2. continuous irradiation with cyclic spray of water (18 min every 2 hours)

3. Programme 1, followed by programme 2
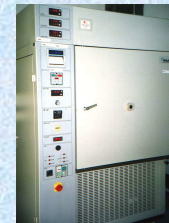
Natural weathering

Lisbon, 45º facing South

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Experimental: samples

1. **PVC resin**
2. **Compounds:** formulations for outdoor applications containing PVC, $CaCO_3$, TiO_2, DBTM (or Ca/Zn/ESO), UV-light absorber, lubricants and a processing aid. Specimens: CZT, CZ, ST, S
3. **Extruded plates (~ 1,5 mm):**
   a. **SAMPLE PU**: processed, but not aged (reference)
   b. **SAMPLE PAR**: 5000 h of continuous xenon irradiation (60% RH – humid conditions) – Prg. 1
   c. **SAMPLE PARW**: 4000 h of continuous xenon irradiation (5% RH) and cyclic spray of water (18 min in each 2 hours) – Prg. 2.
   d. **SAMPLE PAR+RW**: 7000 h of continuous xenon irradiation (5% RH – dry conditions), using cyclic spray of water in the last 4000 h (18 min in each 2 hours) - Prg. 3.
   e. **SAMPLE PN**: 4 years of natural weathering in Lisbon.

Experimental: methods of characterization

Scanning electronic microscopy (SEM)

X-ray photoelectron spectroscopy (XPS)

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Previous findings (FTIR and colourimetry)

YELLOWING

IRRADIATION → C=C   C=O

WATER → WHITENING   EROSION

SAMPLE PAR →
Increase of C=C (yellowing)
Increase of C=O (oxidation)

SAMPLE PARW →
Very low increase of C=C
Medium increase of C=O

SAMPLE PN →
C=C constant (no yellowing)
Very low increase of C=O

SAMPLE PAR+RW →
1 - Increase of C=C and C=O
2 - Decrease of C=C and C=O
3 - C=C and C=O constants

Previous findings

extruded plates

SAMPLE PAR+RW more weathering time (7000 h) and maintenance of original whitening!

CZT

CZ

ST

S

SAMPLE PARW less weathering time (4 000 h), but more yellowing and stains!

SEM of extruded PVC S (DBTM stabilised)

Backscattered electrons (500x)

Sample PU, 0 h
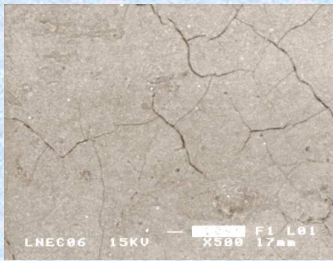
Sample PAR, 5000 h
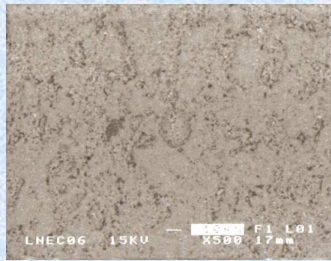
Sample PAR+RW, 7000 h
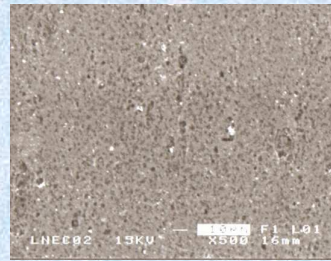
Sample PARW, 4000 h

Sample PN, 4 years

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SEM of extruded PVC S (DBTM stabilised)
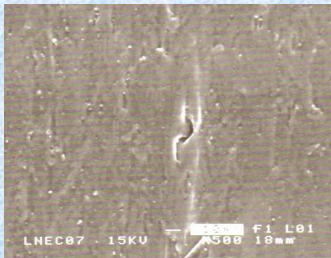
Secondary electrons (500x)
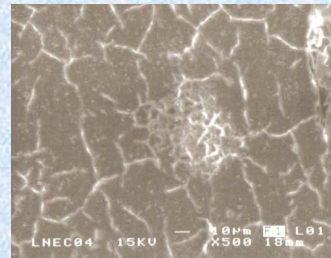
Sample PU, 0 h
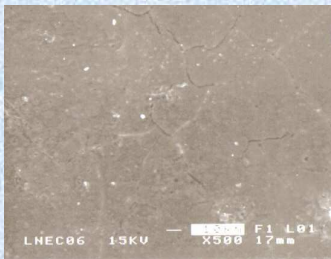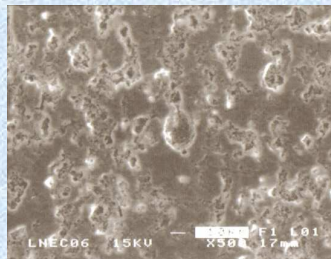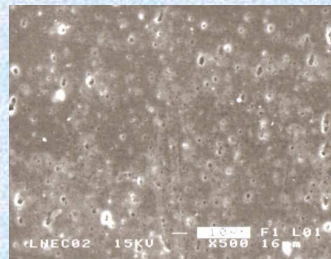
Sample PAR, 5000 h

Sample PAR+RW, 7000 h

Sample PARW, 4000 h

Sample PN, 4 years

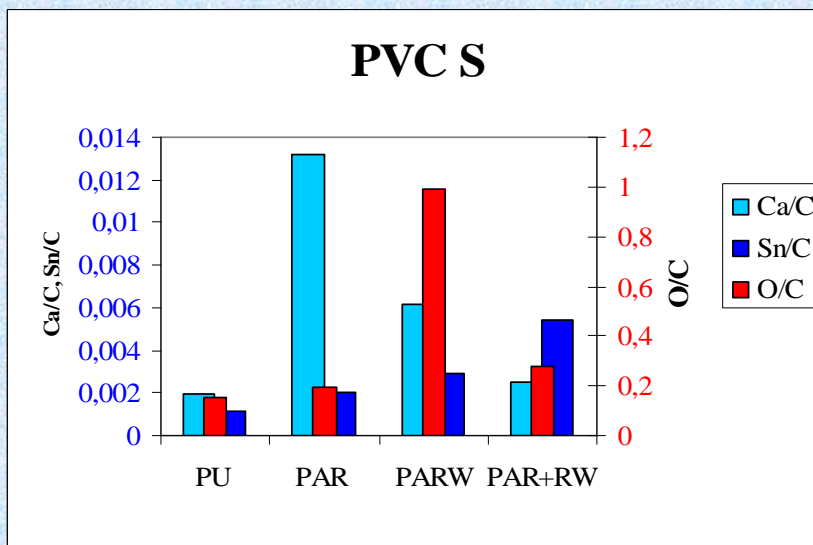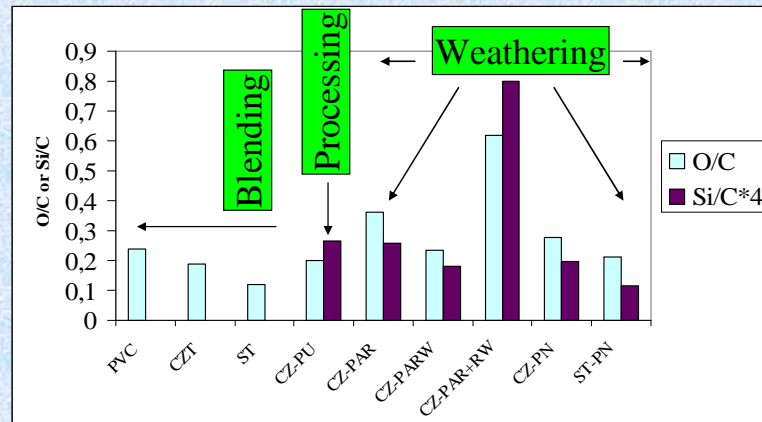September 2005

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Cl/C
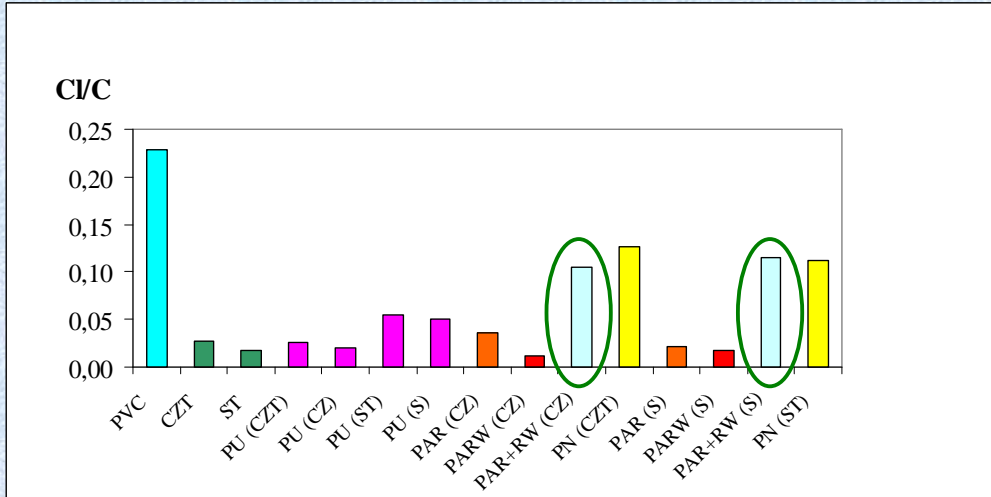
XPS atomic ratios

PVC S

Global quantification

## XPS Elemental analysis: detection of pollutants

1. The Si is introduced during processing (silicones from cleaning of machines, etc.)
2. During artificial irradiation, more Si is introduced on surface by water (SiO_2 from moisture or rain)

XPS degradation of virgin PVC

X-ray induces polymer degradation. The follow-up of that degradation may be very instructive about the mechanism of chlorine loss during degradation.
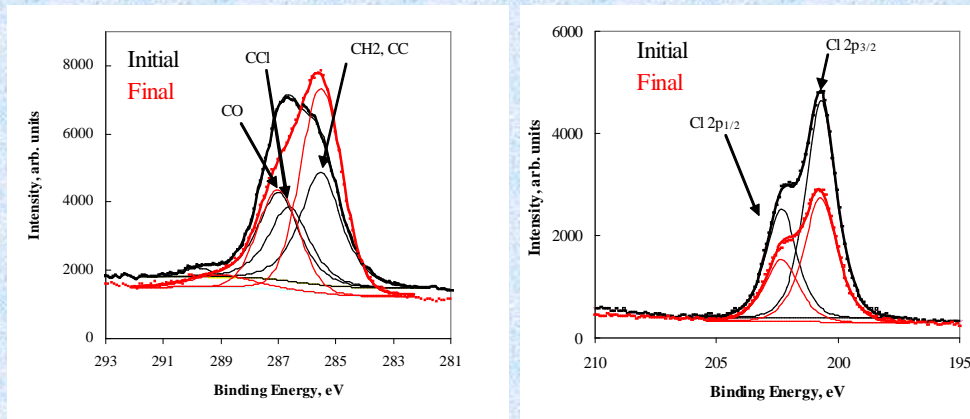

$y = 0,236755e^{-0,002798x}$

$y = 0,233496e^{-0,007038x}$
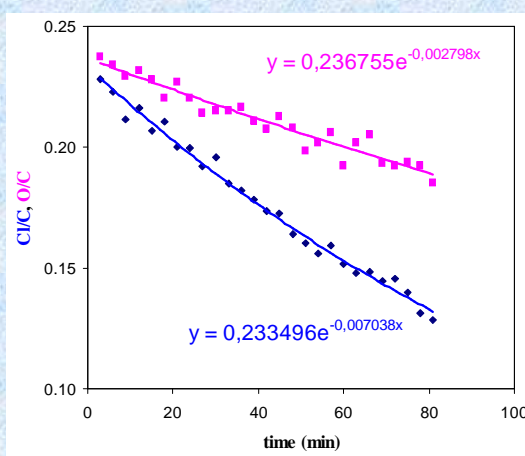
Cl migration rate to the surface is lower than the Cl escape rate to the vacuum (under the form of HCl or Cl_2).

XPS degradation of virgin PVC
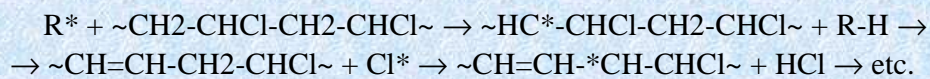
Initial
Final

CCl   CH2, CC
CO

Intensity, arb. units

293 291 289 287 285 283 281
Binding Energy, eV

Initial
Final

Cl 2p$_{3/2}$
Cl 2p$_{1/2}$

Intensity, arb. units

210   205   200   195
Binding Energy, eV

These findings agree with the known mechanism of "unzip" reaction of PVC degradation

R* + ~CH2-CHCl-CH2-CHCl~ → ~HC*-CHCl-CH2-CHCl~ + R-H →
→ ~CH=CH-CH2-CHCl~ + Cl* → ~CH=CH-*CH-CHCl~ + HCl → etc.

XPS degradation of stabilized PVC compounds

Destruction of C=O and C-Cl bonds by X-ray irradiation.

CZT

O/Ctotal
Cl/Ctotal

Irradiation time (min)
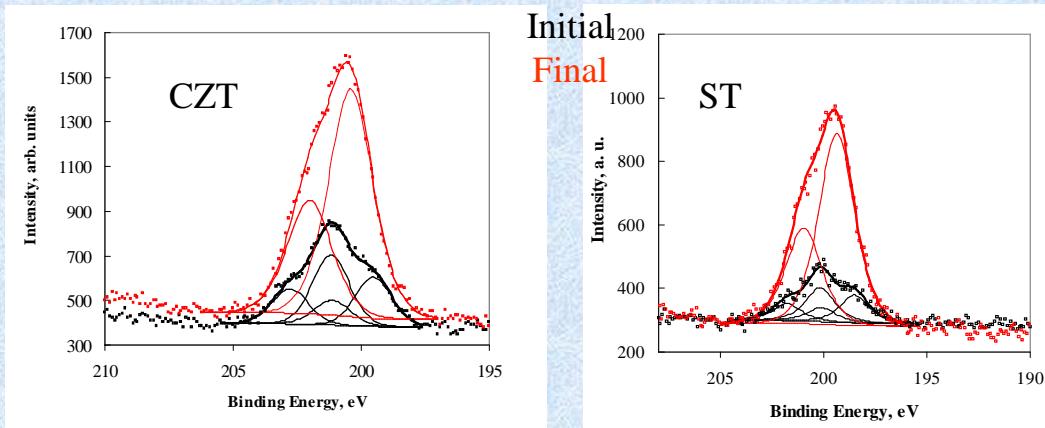
ST

O/Ctotal
Cl/Ctotal

Irradiation time (min)
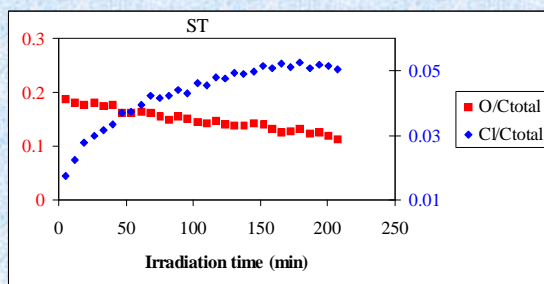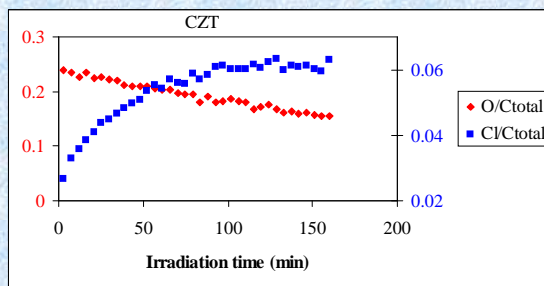
Similar evolution in both compounds, but different of PVC resin.

Cl migration rate to the surface is higher than escape rate to the vacuum. Part of Cl is retained in the surface by Cl traps!

XPS degradation of stabilized PVC compounds

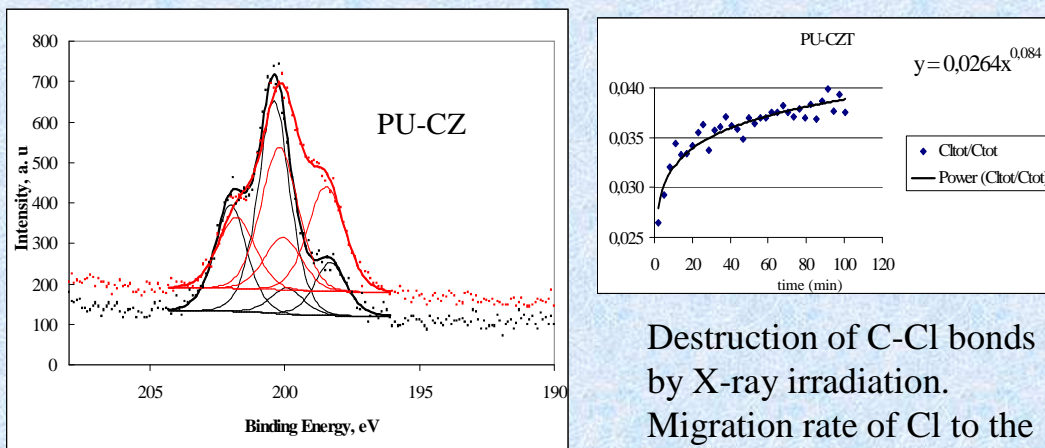Comparing to virgin PVC there are differences in spectra: initially there are two components in the Cl peak (two doublets): Cl⁻ and Cl-C. At the end of irradiation there is only one doublet: the Cl⁻ species!

## XPS degradation of extruded PVC formulations

$$y = 0,0264x^{0,084}$$

There are the same number of initial and final components in the Cl peak: Cl bonded and Cl⁻.

Destruction of C-Cl bonds by X-ray irradiation. Migration rate of Cl to the surface is higher than the rate of liberation to the exterior. Part of Cl is retained in the surface by Cl- traps!

XPS degradation of extruded PVC formulations

PU-S

$y = 0{,}0461x^{0{,}0197}$

Cltot/Ctot
Power (Cltot/Ctot)
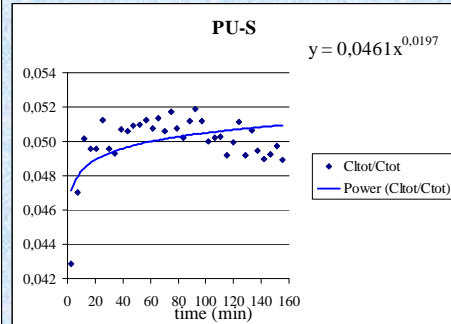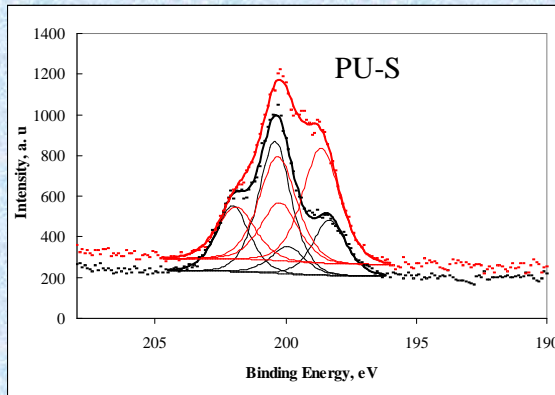
Similar results for the DBTM stabilized PVC compound

Destruction of C-Cl bonds by X-ray irradiation. Migration rate of Cl to the surface is higher than the rate of liberation to the exterior. Part of Cl is retained in the surface by Cl- traps!

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XPS of PVC plates: influence of weathering

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

$y = 0{,}1128e^{-0{,}0058x}$ Cl/C total - PVC S $y = 0{,}055e^{-0{,}0019x}$

$y = 0{,}022x^{0{,}0119}$ $y = 0{,}0121x^{0{,}1088}$

PAR+RW

PU

PAR

PARW
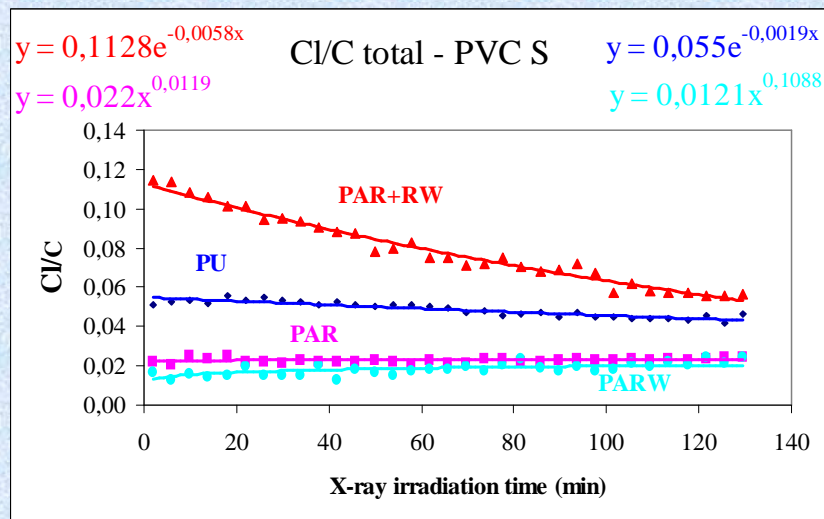
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XPS of extruded PVC CZ (Ca/Zn stabilized): influence of weathering

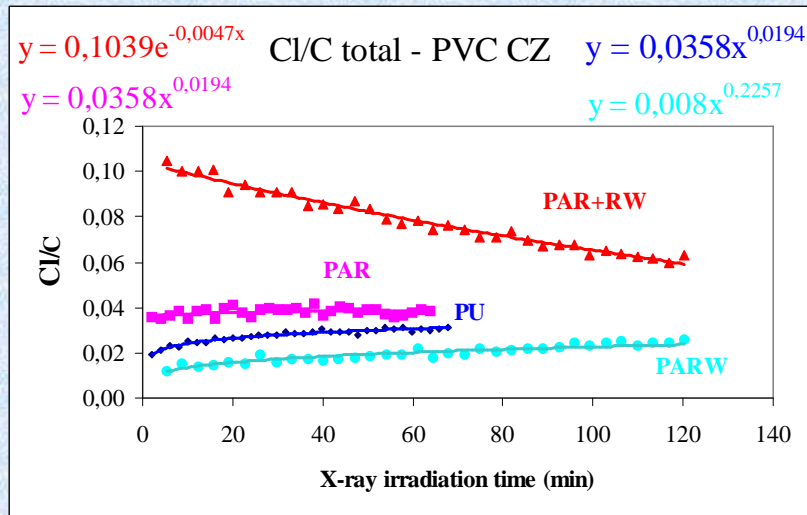**Cl/C atomic ratios: degradation during X-ray irradiation**

$y = 0{,}1039e^{-0{,}0047x}$ Cl/C total - PVC CZ $y = 0{,}0358x^{0{,}0194}$

$y = 0{,}0358x^{0{,}0194}$ $y = 0{,}008x^{0{,}2257}$

Conclusions

1. Weathering:

The initial Cl/C ratio, measured by XPS in the beginning of X-ray irradiation, agree well with yellowing index of weathered samples, measured in a previous work

XPS vs. yellowing index:

	Bound Cl/C	YI
PARW (CZ)	0.00(6)	12
PARW (S)	0.01(0)	20
PAR (S)	0.01(7)	51
PAR (CZ)	0.02(1)	31
PAR+RW (CZ)	0.10	7
PN (ST)	0.11	8
PAR+RW (S)	0.11	12
PN (CZT)	0.12	9

- Basically, high (low) yellowing index correspond to low (high) Cl/C ratios, as expected.

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Conclusions

- The SEM and XPS results also agree well with previous findings, obtained by FTIR spectroscopy, and are compatible with the following ageing mechanism:

a) Long irradiation periods (PAR) induce a generalized degradation of the surface, namely, loss of Cl, double bond (DB) and cross-link (CL) formation. DB and CL induce the shrinking of the surface material and consequent formation of micro-cracks all over the surface.

b) The first action of water consists in the formation of oxidation products of carbonyl type (C=O), originated by OH* radical attack to any unsaturation in the polymer, due to photo-activity of TiO2 pigments in the presence of water, resulting in whitening of the surface (previous work).

Conclusions

c) The subsequent action of water consists essentially on the remotion of this low adhesion defect-region overlayer (by erosion), uncovering deeper, more uniform regions of the sample, richer in Cl, having less DB (lower YI). This region, with more uniform distribution of defects is not so easily degraded as other weathered samples, presenting more localized weak points.

d) When that previous xenon irradiation period is absent, the mechanical degradation of the surface is still concentrated around defects (not generalized to all the surface) and the erosion by the water is very localized. However, the effect on the DB still exists, decreasing the YI but keeping the Cl/C ratio.

Conclusions

2. X-Ray induced degradation:

- Cl/C ratio decreases (increases) during irradiation if the initial Cl/C ratio is larger (lower) than ~0.05. This can be explained by diffusion mechanisms of Cl radical to the surface due to concentration gradients.

- When Cl/C increases, the initial composition contains always two Cl components (Cl bound to C and Cl$^-$) and the component responsible for the total increase is Cl$^-$.

- When Cl/C decreases, the initial composition contains a large bound Cl component and a small or negligible Cl$^-$ component which stays essentially constant during irradiation.

Conclusions

3. Other XPS findings:

→ XPS technique can help to improve the polymer processing because it allows an elemental chemical analysis. This allows to measure degradation levels of PVC compounds induced by the various stages of processing (by means of Cl/C and O/C ratios) and, therefore, to optimize the formulation before starting the production at an industrial scale.

→ Also the contamination levels can be evaluated. For instance, in this work, we have shown that Si is introduced during processing and during artificial irradiation, probably by water.

Acknowledgements

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- A special thanks to Prof. Ana Rego that has performed all XPS tests, which was a lot of hard work.

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