

Degradation of Polymers (PVC, PTFE, M-F) during X-ray Photoelectron Spectroscopy (XPS-ESCA) Analysis

G. Coullerez, Y. Chevolut, D. Léonard, N. Xanthopoulos and H.J. Mathieu

Materials Department - LMCH
Swiss Federal Institute of Technology (EPFL)
CH-1015 Lausanne, Switzerland

(Received September 28 1998; accepted January 11 1999)

This study reports on a comparison of degradation effects observed for unsupported polymer films such as poly(vinyl chloride) (PVC), poly(tetrafluoroethylene) (PTFE) and a melamine-formaldehyde resin (M-F) embedded in cellulose during X-ray Photoelectron spectroscopy (XPS-ESCA) analysis. Comparison of data reveals that degradation with time is larger for the standard than for the monochromatic Al K_{α} source. Decreasing the power of the monochromatic source from 350 W to 150 W reduces the influence of the X-rays. Results show a loss in Chlorine for PVC and PTFE forms additional C-F groups during X-ray damage. M-F shows little variation of the C/N ratio, only C-H groups typical for the cellulose are degraded. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) applied as an independent measure of surface composition confirms XPS results.

1. Introduction

X-ray photoelectron Spectroscopy (XPS-ESCA) is the most widespread technique for surface characterisation of polymers [1]. XPS allows to detect with high precision the binding state of solid materials. However, the analyzed sample is exposed to high fluxes of X-rays leading to a potential degradation of polymer materials reducing sensitivity and binding energy precision [2-4]]. Degradation studies show that X-ray bombardment may lead to a decomposition of Poly(tetrafluoroethylene) (PTFE) [5-7], Poly(methylmethacrylate) (PMMA) [6,8] Polyvinyl chloride (PVC) [2,9], Poly(ethylene terephthalate) (PET) [2,6,9,11], Poly(vinylidene fluoride) (PVDF) [12], Polystyrene (PS) [13-15], Poly(ether ether keton)s (PEEK) [16], Nylon6 [9] and biomedical Poly(amidoamine)s [17]. The main chemical changes in polymers are (1) main-chain scission, (2) cross-linking, and (3) volatile product formation and cyclization [8]. There is widespread agreement that in all cases where degradation of polymers has been observed, experimental conditions and the type of X-ray source are extremely important. Time-of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is used to confirm XPS analysis results. For the present study the polymers (PVC, PTFE) were chosen because of their known x-ray degradation and its chemical inertness, respectively. In addition, the behaviour with respect to the M-F resin is to be investigated. The aim of the present paper is therefore to compare the three different samples under identical conditions with non-monochromatized and monochromatized radiation within the same X-ray analysis

system.

2. Experimental

Three different samples were used, all in form a thin unsupported film with a thickness of 0.1 mm for PVC (-CHCl-CH₂-)_n and PTFE (-CF₂-CF₂-)_n and 0.2 mm for the partially cured Melamine-Formaldehyde resin (M-F) (-C₅H₁₀N₆O₂-)_n. The chemical structure of M-F is shown in fig. 1

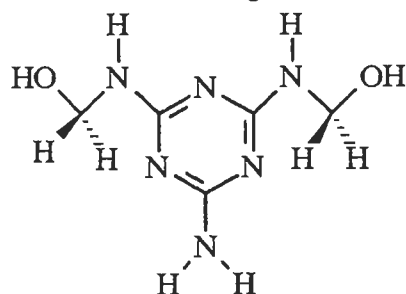


Fig. 1 Chem. structure of uncured Melamine-Formaldehyde.

The polymer films are commercially available: PVC-85 (without softener from Hoechst/Germany), PTFE (Maagtechnik /Switzerland cat. no. 245214). M-F (Perstorp G-7023-G) is embedded in a cellulose foil from Perstorp/Sweden. Prior to analysis, samples were washed for 30s in ethanol, dried with argon, followed by 30 s rinsing in n-hexane and drying with argon. Then the samples were immediately fixed on a sample holder stub, covered with a stainless steel mask and transferred into the UHV vacuum chamber for XPS analysis.

X-ray exposure and XPS analysis were performed at room temperature in a AES/XPS system with concentric hemispherical analyser (Perkin-Elmer, mod. PHI 5500). A standard non-monochromatized AlK α (1486.6 eV) X-ray anode operated at 14 kV and 350 W was used. In addition, in the same analysis system a monochromatic source at 350 W or 150 W with a radiation over a circular area of 4 mm diameter was applied. The sample was positioned at an angle of $\theta = 25^\circ$ between the input lens of the analyser and the surface normal. Incident X-ray angles for the standard and monochromatized sources were 34° and 70° , respectively. All angles are given with respect to surface normal. A charge neutralisation flood gun was operated at low voltage varying the electron current to minimise peak shifting. Data acquisition was controlled by an HP-Apollo computer using ACCESS software v. 5.2b on SR 10.3. Pass energy of the Analyzer was 23.5 eV for multiplex data corresponding to 500 meV energy resolution. Base pressure in the analysis chamber during analysis was in the low 10^{-9} mbar region. Presented spectral data $N(E)$ were corrected for charging of the sample referring to C-C/C-H (C1s) at 285.0 eV (PVC, M-F) or to C-F at 292.5 eV in case of PTFE. The XPS analyser was calibrated to the Au4f $_{7/2}$ peak and Cu 2p $_{3/2}$ peaks at 84.0 eV and 932.7 eV, respectively, before starting the present series of measurements. In order to control and determine the influence of the X-ray flux all samples were measured during consecutive time intervals. The first time interval was 8 minutes (case A), followed by 40 min X-ray bombardment into the same spot with simultaneous data acquisition giving a cumulated exposure of 48 min (case B), followed by six times 40 minutes XPS measurements with simultaneous acquisition reaching a total time of 288 min (case C).

ToF-SIMS analysis was performed on a PHI-Evans Trift I system using a pulsed 15 keV Ga $^+$ source. Samples were biased at ± 3 kV with respect to the grounded extraction electrode for positive and negative mode SIMS, respectively. The 1900 pA dc ion beam was pulsed at 5 kHz repetition rate (7 ns pulse width measured with the unbunched beam). The analyzed area was estimated to $94 \times 100 \mu\text{m}^2$ under so-called 'static' conditions with an ion dose of the order of 10^{12} ions/cm 2 . All measurements were performed in the high mass

resolution mode using a bunched ion beam. Further details are found elsewhere [18].

3. Results

The samples were irradiated for different times ranging from 8 min (A), 48 min (B) to 288 min (C). The high-resolution spectra of the C1s peaks are shown for cases A, B and C in fig. 2-4(a-c), respectively. Spectra are adjusted for their peak maximum and normalised for height intensity of the largest peak. Fig. 2(a-c) shows the results for PVC.

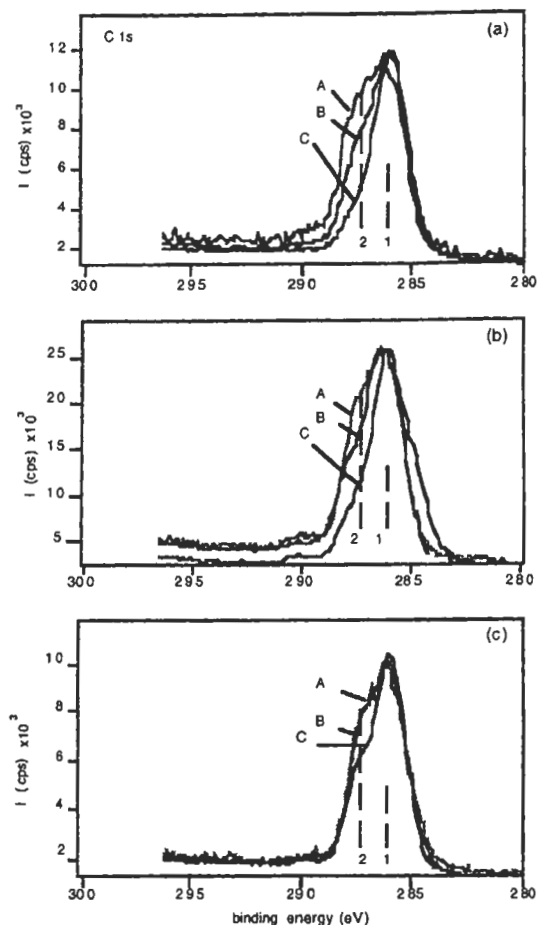


Fig. 2 High resolution XPS spectra of C1s for PVC using a non-monochromatic Al K α source operated at 350 W (a), monochromatic Al K α source at 350 W (b) and 150 W (c). The normalized intensity (counts per s) is shown as a function of the binding energy for a total x-ray exposure during XPS analysis of (A) 8 min, (B) 48 min and (C) 288 min. The energy position of the identified bands are indicated in the text.

The C-C (1) and C-Cl (2) bands are indicated with energy positions at 285.9 eV and 287.0 eV. Inspection reveals that during x-ray exposure the C-Cl (band no. 2) decreases with increasing exposure time. This effect is stronger for the non-monochromatic source and decreases for lower power.

Results of the thin PTFE foil measured under identical conditions as the PVC foil are shown in fig. 3(a-c). Normalisation is done for the C-F band at 292.5 eV. Contrary to the PVC foil, the band does not decrease but additional bands at the lower and higher binding energy sides appear. This effect is more pronounced for the non-monochromatic source and for increasing power.

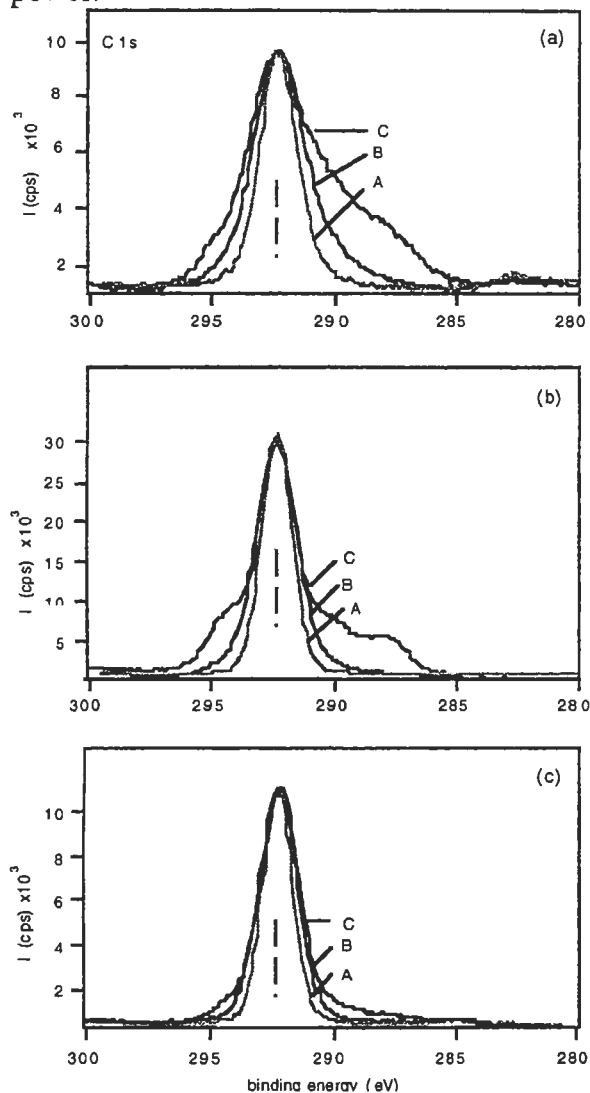


Fig. 3 High resolution XPS spectra of C1s for PTFE using a non-monochromatic Al K α source operated at 350 W (a), monochromatic Al K α source at 350 W (b) and 150 W (c). [20]. A,B,C as in fig. 2.

Results of the Melamine-Formaldehyde are shown in fig. 4(a-c) measured under the same experimental conditions as the polymer foils.

Four bands have been identified corresponding to (1) C-N (288.0 eV), (2) C-OH (286.7 eV), (3) C-H (285.0) and (4) the aromatic shake-up peak at 294.3 eV. The shape of peaks (1) and (2) remains remarkably constant. The band (3) is most pronounced when the monochromator

is operated at 150 W. The band which corresponds to the C-H cellulose peak decreases with increased power as well as for the case of the non-monochromatic source shown in fig. 4(a).

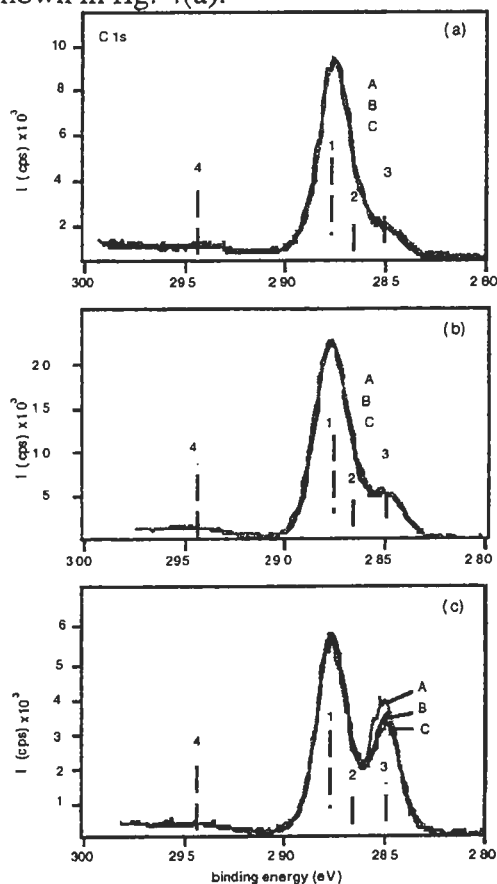


Fig. 4 High resolution XPS spectra of C1s for Melamine-Formaldehyde using a non-monochromatic Al K α source operated at 350 W (a), monochromatic Al K α source at 350 W (b) and 150 W (c). The energy position of the identified bands are given in the text. A,B,C as in fig. 2.

Fig. 5 shows the concentration ratio of carbon to X (X= Cl, F or N) of the elemental atomic concentrations c_A calculated with the help of eq. (1)

$$c_A = \frac{I_A/S_A}{\sum_{i=1}^n I_i/S_i} \quad (1)$$

where I_A and I_j are the peak area intensities, S_A and S_j are the PHI-ACCESS elemental sensitivity factors of C1s (0.296), Cl2p (0.891), F1s (1.0) and N1s (0.477) [19]. Inspection reveals that for the PVC foils C/Cl is a strong function for X-ray radiation time with its lowest value at C/Cl = 2.6. The effect is strongest for the standard source compared to the monochromatic source at the same power (350 W). The loss of chlorine corresponds to

the continuous decrease of the C1s band of C-Cl during X-ray measurements.

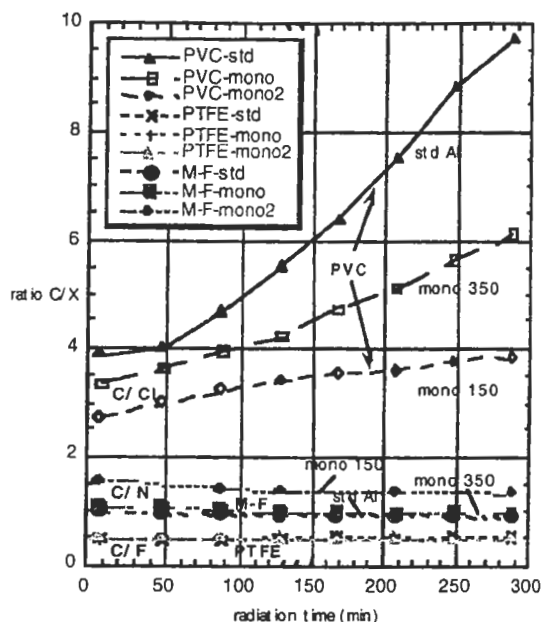


Fig. 5 Ratio of atomic concentrations of C/X (X= Cl, F or N) for the three samples (PVC, PTFE and M-F) as a function of non monochromatic radiation AlK_{α} (std 350 W) and monochromatic AlK_{α} (350 W (labeled mono) and 150 W (mono2)).

For PTFE the C/F-ratio is close to 0.5 and is almost constant during the entire exposure time for all three conditions (A, B, C) of standard and monochromatized radiation (compare fig. 3(a-c)). M-F reveals an increase of the C/N ratio from 0.85 for the standard source compared to 1.0 and 1.4 for increasing exposure times. This is mainly due to the decrease of the C-H group at 285.0 eV.

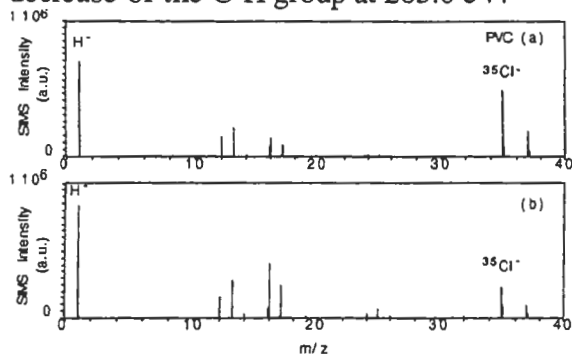


Fig. 6 Negative mode ToF-SIMS spectra of PVC (a) as received (b) after 288 min X-ray exposure of non-monochromatic irradiation (350 W).

ToF-SIMS spectra (fig. 6-8) confirm the XPS findings. Fig. 6 shows the ToF-SIMS data in the negative mode of PVC (a) without and (b) after 288 min X-ray exposure. The results of fig. 6(b) are obtained on the same sample that

was already analyzed for 288 min by XPS. The signatures of the presence of Cl (Cl^- as well as chlorinated peaks observed in the positive mode spectra (not shown)) decrease in intensity after massive X-ray irradiation. The ToF-SIMS spectra of PTFE (positive mode) shown in fig. 7a-b illustrate a structural modification following long X-ray irradiation.

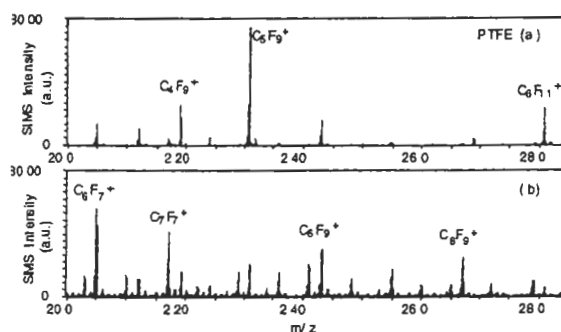


Fig. 7 Positive mode ToF-SIMS spectra of PTFE (a) as received (b) after 288 min X-ray exposure of non-monochromatic irradiation (350 W).

While before irradiation rather saturated fluorocarbon peaks such as $C_4F_9^+$ and $C_5F_9^+$ dominate the 200-300 amu range, less saturated peaks such as $C_6F_7^+$ are the most intense after X-ray exposure. This is also observed in other parts of the mass spectra as well as in the negative mode (not shown). Fig. 8a-b confirms the stability for C-N fragments of the M-F resins.

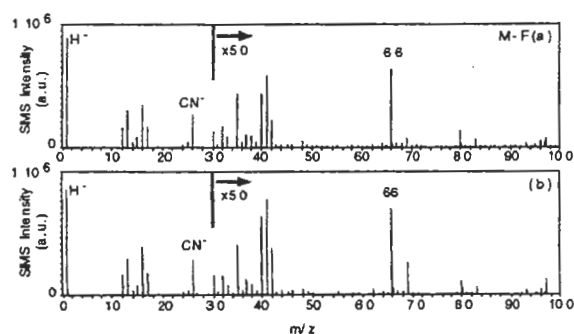


Fig. 8 Negative ToF-SIMS spectra of Melamine-Formaldehyde M-F (a) as received (b) after 288 min X-ray exposure of non-monochromatic irradiation (350 W).

These negative mode spectra indicate practically no change after exposing the sample to massive X-ray irradiation. The same result is found in the positive mode for the main peaks of M-F. The peak at $m/z = 66.019$ may be assigned to $C_3H_2N_2^-$.

4. Discussion

Experimental data obtained under identical conditions for all samples show that not only both polymers react differently but that in the case of the M-F resin embedded in cellulose it is the cellulose matrix which suffers mostly from X-ray irradiation. The XPS results for PVC are in agreement with earlier findings [2, 9] which indicated a loss of Chlorine during X-ray exposure. One notices that not only the type of x-ray source, but also the x-ray primary influences the degradation. The initial C/Cl value of $C/Cl > 2$ in fig. 5 for the three different radiations indicates that the PVC film has already lost Chlorine. Irradiation results in chlorine-carbon and hydrogen-carbon bond scission, leaving alkyl-radicals [9]. The first step seems to be dehydrochlorination. The reaction proceeds spontaneously by the formation of p-p double bonds, since the free radical produced by photo-dehydrochlorination cannot be compensated by an extrinsic reaction in vacuo.

Compared to PVC, PTFE shows the appearance of additional bands. This confirms earlier findings by Wheeler and Pepper as well as Takahagi *et al.*, respectively [5,10]. These authors explain qualitatively this effect by a change of C/F bindings within the irradiated surface. On the higher binding energy side (compare fig. 3(a-b)) for case C, carbon seems to be bound to three fluorine atoms and one carbon atom, as revealed by the chemical shift of approx. 2 eV. On the lower binding energy side, the appearance of two additional bands can be explained by the replacement of fluorine with a ligand of lower electronegativity, for example carbon. Such carbon ligands may be available from either carbon radicals terminating a chain, implying a branched structure, or carbon radicals internal to the chain, implying a crosslinked structure.

Systematic investigation of M-F degradation during x-ray exposure has not been reported yet. M-F seems to be stable with respect to C-N and C-O bands. Considering only the former bands a C/N ratio of 0.85 is obtained which is close to the theoretical C/N-ratio of 0.83 for the pre-polymer. The cellulose C-H groups are removed under the influence of the X-rays. This effect is more pronounced when either power or flux density is increased.

5. Conclusions

Three different samples (PVC, PTFE and M-F) in form of thin foils have been exposed to non-monochromatic and monochromatic X-ray

irradiations. The power of the latter was either 350 W or 150 W. XPS narrow band spectra at different times of X-ray exposure and ToF-SIMS data of samples (a) as received and (b) after the XPS exposure indicate different types of damage. Decreasing the primary X-ray flux when changing from non-monochromatic to monochromatic radiation reduces this effect. The effect is further reduced when decreasing the power of the X-ray source. This leads to the following conclusions:

1. PVC: immediate loss of Chlorine is observed in all cases.
2. PTFE: during X-ray radiation CF_3 -end groups as well as multiple cross-linked molecules are created
3. M-F resin: high stability of C-N and C-O bindings. Only C-H groups of the cellulose matrix are influenced.

6. Acknowledgements

Financial support from the Melcomp Group for Advanced Polymers of Perstorp AB in Perstorp/Sweden (G.C., H.J.M.) and the Swiss Priority Program for Materials SPPM (Y.C., D.L., H.J.M.) is acknowledged.

7. References

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