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GLOW DISCHARGE EFFECTS ON POLYTETRAFLUOROETHYLENE POLYMERS  
INVESTIGATED BY SECONDARY ELECTRON MICROSCOPY AND X-RAY PHOTOELECTRON SPECTROSCOPY

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Abstract

A glow discharge treatment of Polytetrafluoroethylene avoids charging effects and permits observation of the sample in Scanning Electron Spectroscopy; X-ray Photoelectron Spectroscopy has been used to study changes in the surface chemical composition and electronic structure of the polymer produced by this treatment.

Key words: SEM and X-ray Photoelectron Spectroscopy analysis, polymer surface radiation effects, glow discharge.

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Introduction

Studying organic or mineral insulators by means of an electronic probe is very difficult owing to charge build up which occurs under the beam (3, 6, 12). In Scanning Electron Microscopy (SEM), this effect hampers any high magnification observation. On Polytetrafluoroethylene (Teflon, PTFE), this problem can be partly overcome by putting the sample in a glow discharge.

This paper deals with this phenomenon. In order to understand the physical and chemical process induced on the samples by the discharge which leads to better observation conditions, PTFE surface sample were studied in X-ray Photoelectron Spectroscopy (XPS). Impurity metal atoms are deposited on the treated surface and other structural modifications occur which change the surface conductivity.

Experimental

Samples

Technological PTFE (TF 7 synthesized by Dupont de Nemours) was used in the form of  $\varnothing$  15 mm x 2 mm cylindrical disk samples. Firstly, the samples were cleaned in acetone in an ultrasonic bath. Glow discharges in Argon were generated by a JEOL 111 Fine Coat. The experimental conditions were: vacuum  $10^{-1}$  torr, current: 4 mA, voltage: 800 V, time 5 to 8 min. To check the spatial resolution some metal coated samples (Au Pd) were also prepared.

Methods

Secondary Electron images were obtained with a JEOL Scanning Electron Microscope JSM 840. The accelerating voltage used for the observations was 1, 2 or 3 keV. X-ray Photoelectron Spectroscopy was performed in a V.G. Instruments ESCALAB MK II. This instrument is equipped with a non-monochromatized X-ray source



Fig. 1. S.E. images of PTFE samples.

- 1a) PTFE-nt - magnification  $10^3$ .
- 1b) PTFE-t - magnification  $10^3$ .
- 1c) PTFE-m - magnification  $10^4$ .
- 1d) PTFE-m - magnification  $10^3$ .
- 1e) PTFE-m - magnification  $10^4$ .

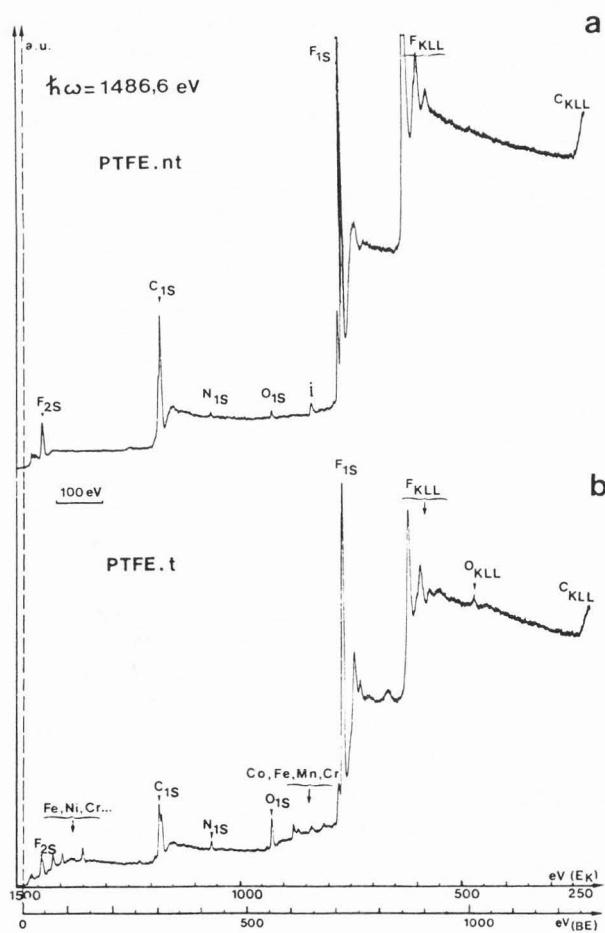
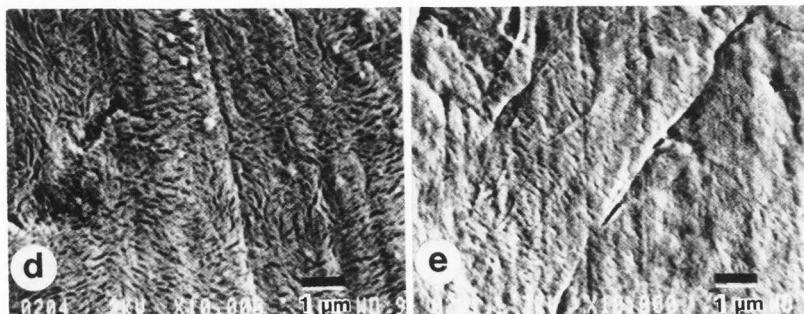


Fig. 2. X-ray photoelectron lines.  
2a) PTFE-nt sample.  
2b) PTFE-t sample.

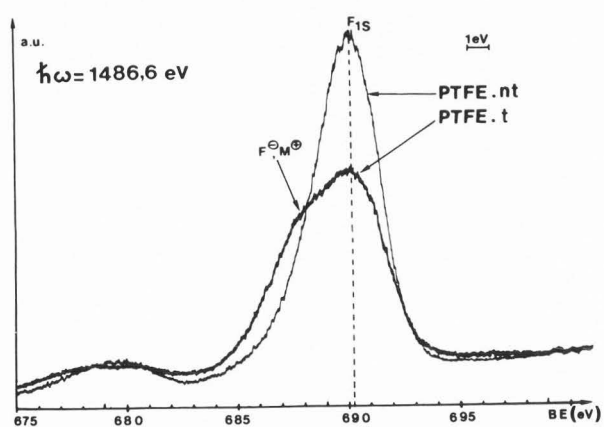


Fig. 3.  $F_{1s}$  lines for the PTFE-nt and PTFE-t samples.

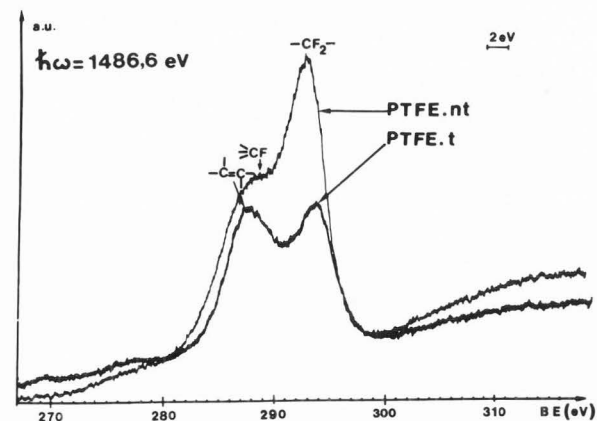


Fig. 4.  $C_{1s}$  lines for the PTFE-nt and PTFE-t samples.

(Aluminum  $K_{\alpha}$  = 1486.6 eV). The base pressure is normally around  $5 \cdot 10^{-11}$  Torr. Because of out-gassing effects due to the PTFE samples, the pressure rose to about  $10^{-9}$  Torr at the end of the experiment. The analysis chamber is fitted with a 150 mm spherical sector analyzer operating in constant pass energy mode and equal to 50 eV. In this experiment, the energy calibration was made by using the  $4f_{7/2}$  = 84.0 eV X-ray photoelectron line of clean bulk polycrystalline gold.

### Results

S.E. images: Three PTFE samples were investigated by means of a scanning electron microscope at a magnification of  $10^3$ . The first sample was cleaned in an ultrasonic bath (PTFE-nt), the second one was submitted to a glow discharge (PTFE-t), the last one was coated with metal (PTFE-m). It is interesting to note that the "non-treated" polymer (Fig. 1a) charged up under the electronic probe even at a low accelerating voltage. However, the PTFE-t (Fig. 1b) and the PTFE-m (Fig. 1c) samples present a good imaging contrast and a clear topography. At a higher magnification ( $10^4$ ), it was quite impossible to get an useful image on the non-treated polymer (PTFE-nt). On the two other samples (Fig. 1d and 1e), we obtain good details of the surface. The PTFE-t sample shows some morphological surface modifications: etch pits and crosslinking like features.

X-ray photoelectron lines: Owing to the positive charge created by X-ray irradiation ( $10$ ) a correction of the energy position of the photoelectron and Auger lines is necessary. Comparison with previous work (1, 7) on PTFE led us to choose the value of 690.2 eV for the  $F_{1s}$  line. This value enabled us to evaluate the  $F_{1s}$  shift due to the charging of the sample as 7.0 eV for the PTFE-nt and 5.8 eV for the PTFE-t. In the following we will only consider the corrected values of the binding energies.

a) Elemental analysis of the PTFE-nt surface (Fig. 2a) - We note the presence of oxygen ( $O_{1s}$ ) due to atmospheric contamination and a very small photoelectron line located at 625 eV and probably due to the presence of iodine ( $I_{3d_{5/2}}$ ) used to fluorinate the compound before polymerization ( $IF_4$ ).  $C_{1s}$  line appears as a convolution of two peaks. If we compare the complete spectrum (Fig. 2a) to that obtained for the PTFE-t sample (Fig. 2b) we observe some modifications: splitting of the  $C_{1s}$  line shape, and a higher concentration of oxygen. Other photoelectron and Auger lines are found which are due to the

presence of metallic atoms (Co, Fe, Mn, Cr) on the PTFE-t.

b)  $F_{1s}$  lines (Fig. 3) - For the PTFE-nt sample, we only get a simple  $F_{1s}$  line at 690.2 eV. On the other hand, the  $F_{1s}$  line of the PTFE-t reveals a main structure at 690.2 eV which corresponds to the fluorine photoelectron line in PTFE and a second one at lower binding energy (689.2 eV) which can be attributed to metallic fluoride compounds due to deposited metal atoms (2, 9).

c)  $C_{1s}$  lines (Fig. 4) - The  $C_{1s}$  line corresponding to the PTFE-nt sample reveals two distinct structures at 292.4 eV and 288.2 eV which are respectively attributed to the  $-CF_2-$  and  $>CF$  groups in the polymer (2, 8, 11); photoelectron  $C_{1s}$  line of the PTFE-t exhibits a less prominent structure at 293.6 eV ( $-CF_2-$ ) and a new structure at 287.8 eV which can be explained by the presence of a double bond ( $>C=C<$ ) in the modified polymer.

### Discussion

Two effects can explain the good contrast of the S.E. image made on PTFE-t: low concentration deposit of metallic atoms and partial graphitization of the polymer surface.

The metal atoms were deposited during the short glow discharge and were extracted from the stainless steel surface of the sample holder of the JFC-111. Their concentration is very low (<1%) as the line intensity is very weak and as they could not be detected with an Auger microprobe. At this low concentrations, metal atoms cannot produce a conductive surface layer but they can make trapped electron surface sites disappear, leading to a better conductivity.

On the other hand, the energy position, the chemical shifts and the shapes of the photoelectron lines of PTFE ( $C_{1s}$ ,  $F_{1s}$ ) reveal structural modifications after the glow discharge treatment. Appearance of  $-C=C-$  groups is correlated to the decrease of  $-CF_2-$  and "F" lines. This shows that the glow discharge induced carbon-fluorine bonds to break with the formation of  $C=C$  bonds and this partial graphitization leads to reticulation on the PTFE surface (4, 5). This phenomenon has also been observed after much more energetic ion bombardment ( $> 1$  keV) (2, 11). The effect is apparent on the S.E. image at high magnification ( $10^4$ ).

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#### Discussion with reviewers

T.J. Shaffner: Have you been able to repeat the experiments on other organic and plastic materials?

Authors: We did not repeat these experiments on other organic materials, but we started a program on polymers modification by electronic excitation.

T.J. Shaffner: Could not one deposit gold, silver or other metal of choice instead of the stainless steel? What properties of such a metal would be the most desirable?

Authors: The stainless steel was accidentally deposited during the RF glow discharge. It is known that non oxidizable metals like gold, platinum or non-metallic compounds like graphite sputtered onto metal insulator materials led to good SEM observations because of the disappearance of the superficial charging effects.

T.J. Shaffner: How does the time of exposure to glow discharge affect the apparent conductivity of the PTFE and your ability to form images free from charging?

Authors: A glow discharge in an inert gas is generally used to clean a sample surface, but this method applied to polymer compounds alters the polymer itself because of the temperature increase of the sample during the treatment. This temperature increase generally leads to partial carbonization or graphitization of the polymer and in this case improves the conductivity.

T.J. Shaffner: The images of Fig. 1d and 1e show that glow discharge has altered the surface morphology. Although this reduces charging for high magnification work, the image one obtains does not correctly portray the original surface. Does this not invalidate practical application of the method for reducing charging?

Authors: As the glow discharge alters the original surface, it must be used carefully to get correct images of the surface.

R. Holm: What is the reason for the etch pits and other inhomogeneities after the rather short low voltage glow discharge treatment?

Authors: We suggest that during the glow discharge, inert gas ions interact with the atoms of the polymer surface to initiate radicals and ions. These species rapidly evolve and give backbone fragmentations, cross-linking and volatile species. These modifications can explain the new topography of the surface.

R. Holm: What happens to the sample after extended treatment or in the case of other discharge parameters?

Authors: We did not modify the parameters of the surface treatment of the sample, as our aim was only to understand the modifications of the SEM imaging.