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ScienceDirect
Nuclear Instruments and Methods in Physics Research B 265 (2007) 276–280
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

Be careful when using X-ray exposure analysis for polymers

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Available online 6 September 2007

Abstract

The techniques of X-ray diffraction analysis (XDA) and X-ray photoelectron spectroscopy (XPS) for investigation of the structure and surface constitution of materials respectively are considered to be free from radiation-induced artifacts. But earlier a very strong effect of the X-ray flux on the surface constitution of the polytetrafluoroethylene (PTFE) was observed. Later we studied a crystalline structure of the PTFE by the methods of XDA and differential scanning calorimetry (DSC) simultaneously. Quite unexpectedly the values of crystallinity degree measured by the two methods for as-received samples of the same polymer differed more than two times (26% for DSC and 68% for XDA). It was established that during an analysis by XDA the samples were irradiated by the X-ray doses 0.1–1 kGy depending on exposure. The irradiation of PTFE with such small doses of both X-ray and ^{60}Co γ-radiation results in a significant increase of crystallinity that is identified by the DSC method but not by the XDA one. Only after irradiation with doses higher than 10 kGy the measured crystallinity degrees for the two methods become equal. We believe the reason of the observed difference is in the capability of the DSC method to register only thermodynamically stabilized crystallites while the XDA procedure fixes the total response from crystal and paracrystal phases.

PACS: 61.80.Jh; 61.82.Pv; 82.50.Gw

Keywords: Polymer; Ionizing radiation; X-ray diffraction analysis; Radiation effect

1. Introduction

It is widely accustomed to use X-ray diffraction analysis (XDA) for investigating the material structure and X-ray photoelectron spectroscopy (XPS) for studying the surface constitution. This technique is considered to be free from radiation-induced artifacts [1]. Nevertheless, there was an indication of damage to polymer surfaces by the X-ray flux in the XPS studies [2–4]. No detailed study has been made of the effect, however. This is the case with polytetrafluoroethylene (PTFE), a material known to be highly susceptible to radiation damage and extensively studied by XPS [1,5] with no mention of any damage by the X-ray flux.

But in [6] a very strong effect of the X-ray flux was observed on the surface constitution of the PTFE that was brought into accord with the mass spectrum of gaseous species evolved during irradiation. The authors observed the time dependence of the structure, magnitude and binding energy of the C(1s) and F(1s) signals. The X-ray absorbed doses on the surface were evaluated to be about 10^6 kGy. Similar radiation effects in PTFE were revealed in [7]. Later, the same authors of [6] exposed the PTFE to 3 keV electron irradiation [8] and concluded that similar surface radiation effects resulted from both X-ray and electron irradiation at the same dose.

There is now a generally accepted model [6] to account for the observations. The surface is thought to form a network of branched and/or cross-linked fluorocarbon chains with an accompanying loss of fluorine, and appearance of unsaturation. These results were confirmed by mass spectroscopy during X-ray irradiation [9].

The radiation dose and depth of damage by Mg Kα X-rays in PTFE were estimated in [6]. The authors incorrectly estimated the damage depth and hence the dose rate. A

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[1] A great loss for polymer radiation chemical society; Prof. Dr. Boris (Aronovich) Briskman passed away on August 22nd, 2007.

0168-583X/$ - see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.nimb.2007.08.059

corrected analysis was presented in [8]. We checked these results once more and also estimated radiation heating of the PTFE samples. The results of the analysis and our conclusions are treated in the Appendix.

It is evident that some sort of similar effects is very probable when using XDA. The X-ray exposure of polymer samples in this case can result in bulk degradation. The information, that we got, is presented below. We do not know any other information available on the problem.

2. Experiment

It is accustomed to use the methods of differential scanning calorimetry (DSC) and XDA for investigation of crystalline structure and crystallinity degree of various materials, including polymers. We used both methods simultaneously to study radiation effects in PTFE [10]. A comparison of the investigation data, that are the subject of our paper, resulted in unexpected conclusions.

2.1. Apparatus

100 and 50 μm thick PTFE films (Russian national standard 10007-80) were used. The films were irradiated by ^{60}Co γ-rays at absorbed dose rate of 6 Gy/s and temperature of 333 K up to dose of 300 kGy. The crystallinity degree was measured by the XDA method on the DRON-2 X-ray source through the Cu Kα X-rays scattering in the region of large angles. The source was operated at 30 kV and 30 mA. To decrease the film texture influence the sample was continuously rotated in its own plane.

The crystallinity degree was also measured by DSC method in a DSM-2 calorimeter at scanning rate 12.5 K/min. The melting heat ΔH of original PTFE was assumed to be equal 82 J/g [11,12]. This ΔH value is recommended for the data base of macroscopic thermodynamical properties of linear macromolecules. It is by 24% lower than the ΔH value presented in [13] and by 23% higher than the ΔH value recommended in [14].

2.2. Dosimetry

Complicated X-ray spectrum for a tube with a copper anode in the energy range 6–30 keV has Kα and $K\beta$ characteristic radiation maximums at 8–9 keV. We calculated the absorbed energy in PTFE for such spectrum and found that the dose part corresponding to the characteristic radiation maximums reaches 75%. The dosimetry of such a low energy photon radiation is highly complex. With that end in view, we used a capacitor dosimeter KD-2mp with a diaphragm chamber suitable for the energy range 10–60 keV. Its validity was evaluated through measuring the aluminium half-value-attenuation layer. This layer was found to be equal 50 μm. This value was used to measure the chamber calibration factors. The measurement error did not exceed 20%.

At the same time the accumulation of peroxide radical during irradiation of PTFE films was used for dosimetry. With that end in view, we compared the content of radicals in the samples, irradiated by a specified dose of ^{60}Co γ-rays and unknown dose of X-rays. The main assumption is that the radiation-chemistry yield of the radicals was the same in both cases. The content of radicals was measured by the ESR method on the RE-1306 radiospectrometer.

3. Results

As follows from numerous publications, the crystallinity degree of PTFE amounts to 50–90% [15,16]. For PTFE samples of different molecular mass M the crystallinity degree, determined by the DSC method, amounts 33–66%, and for the samples with molecular mass $M > 10^7$ this value is about 100% (the XDA, NMR and IR-spectroscopy methods) [11].

The following values of mass crystallinity degree X were received for our original samples: $X = 26\%$ (the DSC method) and 68% (the XDA method). This discrepancy (~2.6 in ratio) demanded a detailed verification of the experimental data. At first, the X measurements for the same samples were repeated in another laboratory (Dr. Yu. K. Godovsky, Karpov Institute of Physical Chemistry, Moscow) in the "Perkin–Elmer" calorimeter. The data from DSM-2 calorimeter were completely reproduced. Second, using the value of crystal phase density $\rho_k = 2.30$ g/cm^3 [15] in the limits of the two-phase polymer structure model, it is possible to calculate the X value from the following correlation

$$\rho = 2.0 + 0.3X, \tag{1}$$

which was presented for PTFE in [17] and approved in [15,18]. We measured $\rho = 2.08$ g/cm^3 for the film at 293 K. This value corresponds to $X = 27\%$, that is in a very good agreement with the X, measured by the DSC method.

Then we irradiated the samples up to doses of 10, 30, 100 and 300 kGy of the ^{60}Co γ-radiation and found the X values. The experimental results are presented in Fig. 1. It

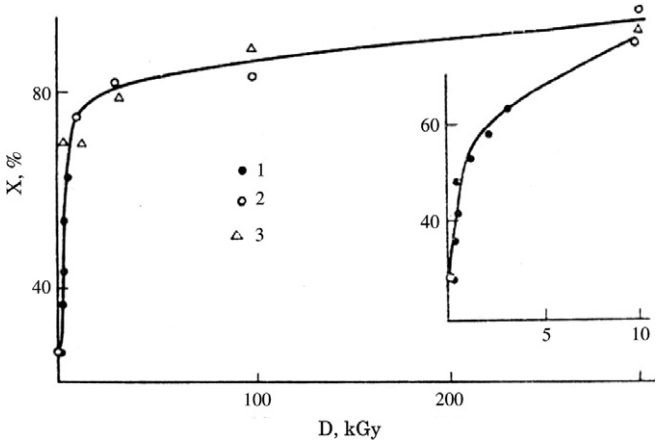

Fig. 1. PTFE crystallinity degree versus γ-radiation absorbed dose. DSC method: $P = 6$ (1) and 0.5 (2) Gy/s; XDA method: $P = 6$ Gy/s (3).