

Permeability Coefficient of Proton-Irradiated Poly(ethylene Terephthalate) Thin Films*

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Synopsis

The principle of operation of an apparatus developed to study gas permeation through thin films is described, and the measurement method is discussed. Use is made of diffusion theory to obtain an expression for the permeability coefficient as a function of the rate of increase of the pressure in the receiving volume. The activation energy for permeation of helium through PET is determined. The permeability coefficient for helium is found to increase significantly with the range of the implanted protons although the incident charge has been kept constant. The hypothesis of structural modifications of the proton implanted PET seems to be confirmed by small-angle X-ray scattering experiments on the irradiated samples.

INTRODUCTION

Poly(ethylene terephthalate) thin films are widely used as entrance windows in nuclear physics detectors such as multiwire proportional chambers.

Various authors have already reported on the effects of radiation dose on the polymer properties. The changes of intrinsic viscosity which result from exposure to ^{60}Co γ -radiation and α particles of 23 MeV were presented by Moshkovskii et al.¹ The ultimate tensile strength of Mylar (E. I. DuPont de Nemours and Company, Inc.) films was measured, the samples being irradiated with 160 MeV protons,² ^{60}Co γ -rays,³ 1.2 MeV electrons,⁴ neutrons and γ -rays from reactor.⁵ Electron-beam-induced conduction⁶ and electron-beam charging⁷ studies have also been performed on poly(ethylene terephthalate) films. Since the above-mentioned detectors contain gases and are exposed to radiation, it appeared useful to study the behavior of the permeability coefficient of irradiated PET thin films. The present work is devoted to the determination of the permeability coefficient of 12- μm -thick Hostaphan (Kalle Films, Hoechst) films as a function of the incident energy of implanted protons. The incident charge has been kept almost constant and the permeating gas used was ultrapure Helium. The experimental apparatus and the measurement procedure are described, and the experimental results are presented and interpreted using a simple phenomenological model.

Small-angle X-ray scattering experiments support the hypothesis of structural modifications in the proton-implanted PET samples.

Part of these results constitute the MSc thesis of one of the authors.⁸

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EXPERIMENTAL APPARATUS AND MEASUREMENT PROCEDURE

Gases and vapors are known to permeate through polymers via diffusion in molecular scale, the mechanism being that of temporary voids created by the thermal movements of the polymeric chains.⁹ Using Fick's first law for steady state diffusion permeability,¹⁰ the amount Q of substance that has diffused in time Δt through the cross-sectional area A is found to be proportional to the constant gradient dc/dx of gas concentration in a film layer:

$$Q = - D \frac{dc}{dx} A \Delta t \quad (1)$$

where D is the diffusion coefficient.

The experimental method of Daynes and Barrer¹⁰ leads to a direct determination of the permeability coefficient K . In this method the linear growth of the pressure of the test gas in a receiving volume initially in vacuum is measured. This linear growth is due to the permeating gas stationary flow through the polymer, which takes place after a certain delay called the "time lag." Integrating eq. (1) over the thickness l of the film and making use of Henry's law, one gets

$$Q = D\sigma(p_1 - p_2)A \Delta t/l \quad (2)$$

where σ is the sorption coefficient and p_1 and p_2 are the pressures of the gas on both sides of the polymeric material. Since $p_1 \gg p_2$, the permeability coefficient $K = D\sigma$ may then be written as

$$K = Ql/p_1A \Delta t \quad (3)$$

Combining eq. (3) and the equation of state for a perfect gas, one finally obtains

$$K = \frac{\gamma}{p_1 T} \frac{\Delta P}{\Delta t} \quad (4)$$

where $\gamma = \frac{l}{A} V \frac{T_0}{P_0} \text{ cm}^2 \cdot \text{°K/atm}$, $T_0 = 273.15 \text{ °K}$, and $P_0 = 1 \text{ atm}$.

The ratio $\Delta P/\Delta t$ is the slope of the linear part of the experimental curve which gives the time dependence of the pressure in the receiving volume V .

In this experiment the area A of the polymer film has been set to $A = 19.63 \pm 0.08 \text{ cm}^2$ and the thickness $l = 12.07 \pm 0.06 \text{ }\mu\text{m}$ calculated by averaging weights of fixed area samples and using the density $\rho = 1.395 \pm 0.001 \text{ g/cm}^3$ of the polymer.¹¹ The receiving volume was found to be $292.84 \pm 10.70 \text{ cm}^3$ in the conditions of the experiment.

The apparatus used in this work (Fig. 1) is made of glass, copper, and brass. It is based upon the one developed by Sobolev.⁹ The pressure p_1 on the left side of the polymer film (5) is measured by means of the mercury

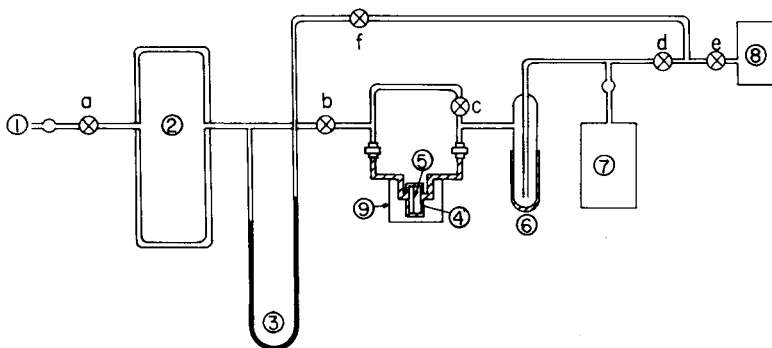


Fig. 1. Experimental apparatus: (1) gas entrance; (2) expansion volume; (3) mercury manometer; (4) permeability chamber; (5) polymer sample; (6) liquid-nitrogen-filled trap; (7) McLeod gauge; (8) rotary vacuum pump; (9) thermostated bath; (a-f) stopcocks.

manometer (3) and its constancy is ensured by the expansion volume (2) of the order of 1000 cm^3 . The permeability chamber (4) contains the sample under study and is immersed in the bath (9) whose temperature θ is electronically regulated. The receiving volume V is defined by the film (5), the stopcocks (c) and (d) and the McLeod gauge (7) which measures the pressure growth. The determination of K is done in the following way: First of all, a vacuum of the order of $1 \mu\text{bar}$ in the receiving volume is achieved by the rotary vacuum pump (8) and the liquid-nitrogen-filled trap (6). The pressure growth due to residual outgassing and leakages is then measured as a function of time, the results being shown in Figure 2 (curve I). Afterwards, the helium is allowed to diffuse through the polymer film, and the resulting increase of pressure is measured as a function of the permeation time (curve

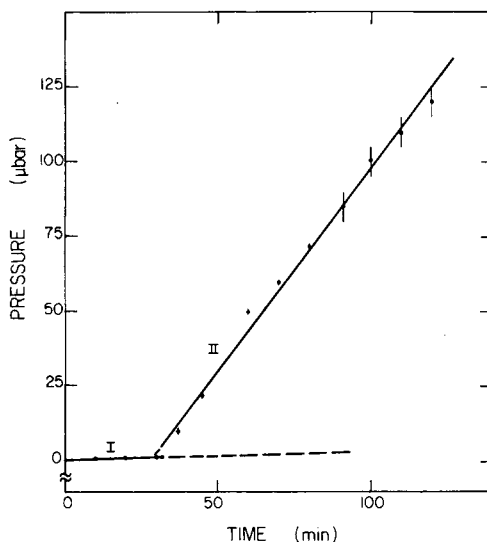


Fig. 2. Pressure growth vs. time for ultrapure He permeating through $12\text{-}\mu\text{m}$ PET films: (I) contribution of residual outgassing and leakages; (II) permeation of He plus residual outgassing and leakages. Both curves were fitted independently using the χ^2 method.

II of Figure 2). The above-mentioned time lag for helium being of the order of 0.05 s,¹² the nonlinear part of the curve II cannot be observed. Both curves are the results of independent straight-line fittings on the respective experimental sets of data using the standard χ^2 method. The factor $\Delta P/\Delta t$ in eq. (4) is obtained by subtracting the residual outgassing and leakages from the total pressure growth, i.e., $\Delta P/\Delta t = \alpha - \alpha'$, where α and α' are the χ^2 -adjusted angular coefficients of straight lines II and I, respectively.

Equation (4) may then be rewritten as

$$K = \gamma(\alpha - \alpha')/p_1T \quad (5)$$

where $\gamma = 4.92 \pm 0.22 \text{ cm}^2 \cdot \text{K}/\text{atm}$.

Figure 3 shows the chamber used to irradiate the PET films. The chamber itself is electrically insulated from the beam line terminal by means of the epoxy insulating flange (2). This allows measurement of the incident charge by the rear electrode (6). During exposure the defocussing of the beam is visualized on the fluorescent glass window (5) and care is taken that the cross-sectional area of the beam on the window is larger than the geometrical area of the sample being irradiated.

RESULTS AND DISCUSSION

All results presented here refer to ultrapure helium and poly(ethylene terephthalate)-based films of the RN Hostaphan type.¹¹ This aromatic polymer is known to be biaxially oriented.

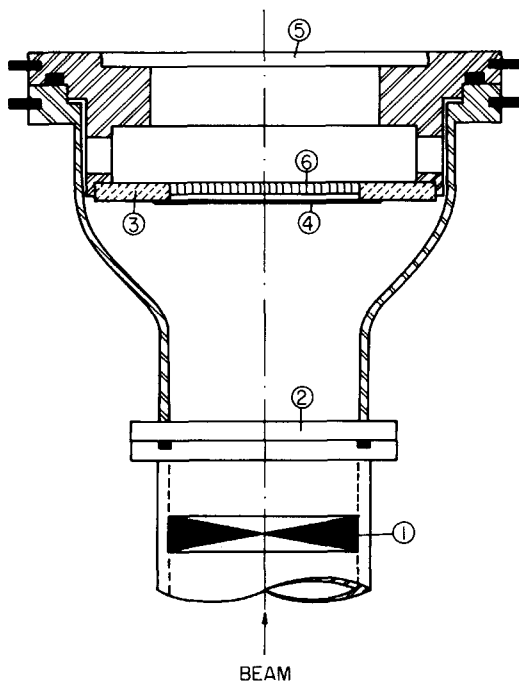


Fig. 3. Irradiation chamber: (1)-pipeline valve; (2) epoxy insulating flange; (3) polymer film support; (4) polymer film; (5) fluorescent glass window; (6) rear electrode.

The diffusion process being a thermally activated one, one expects a temperature dependence of the permeability coefficient of the form

$$K = K_0 e^{-\Delta E/R\theta} \quad (6)$$

where ΔE is the permeability activation energy.

The variation of K as a function of the temperature of nonirradiated PET film has been studied and the results are shown in Figure 4. The θ dependence of K [eq. (6)] was χ^2 -adjusted to the data, leading to the following results:

$$K_0 = (1.30 \pm 0.86) \times 10^{-5} \frac{\text{cm}^3 \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{atm}} \quad \text{and}$$

$$\Delta E = 4.58 \pm 0.38 \text{ kcal/mol}$$

This last result agrees quite well with the value $\Delta E = 4.7 \text{ kcal/mol}$ found by Michaels and co-authors¹³ for He in PET, the polymer used there containing a amorphous volume fraction of 0.70.

In order to study the influence of implanted protons on the permeability coefficient of the PET, film samples were exposed to the proton beam of a Van de Graaff accelerator (Pontificia Universidade Católica, Rio de Janeiro), using the irradiation chamber already described in the previous section. During the irradiation the pressure inside the chamber was of the order of 10^{-5} Torr and low-intensity currents (10–80 nA) were used in order to avoid perforation of the film due to thermal effects. Care was taken to keep the total incident charge constant and uniformly distributed over the whole area of the sample.

Before measuring the effect of implanted protons, the permeability coefficient was determined for crossing protons of 1.3 MeV which released 420 keV in the polymer film. Experimental conditions are listed in Table I. The permeability coefficient was found to be

$$K_{cp} = (5.96 \pm 0.34) \times 10^{-9} \frac{\text{cm}^3 \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{atm}}$$

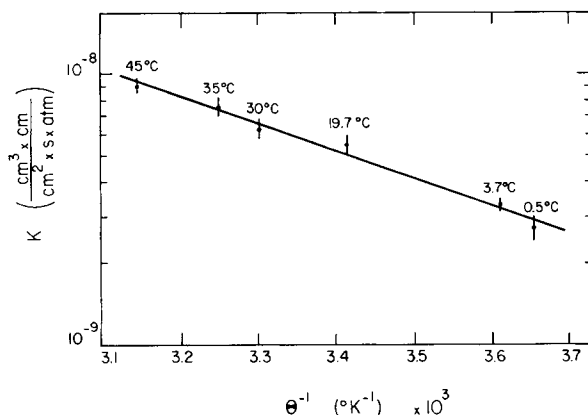


Fig. 4. Temperature dependence of the permeability coefficient for nonirradiated PET film. The straight line results from a χ^2 adjustment.

TABLE I
Experimental Conditions for 1.3-MeV Crossing Protons

Incident charge (μC)	33 ± 2
Dose (mrad)	38.1
Film temperature θ ($^{\circ}\text{C}$)	30 ± 0.5
Room temperature T ($^{\circ}\text{C}$)	24 ± 0.5
Gas Pressure p_1 (mm Hg)	53.3 ± 0.2

a value which, surprisingly, is compatible with the one obtained under the same experimental conditions (film and room temperature and gas pressure) for nonirradiated PET film:

$$K = (6.33 \pm 0.53) \times 10^{-9} \frac{\text{cm}^3 \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{atm}}$$

This agreement may be explained by assuming that crosslinking and degradation effects occur simultaneously¹ and cancel each other. Crosslinking, due to the presence of an aliphatic branch,¹⁴ would contribute to a decrease of K while degradation, associated with the C_4 atom,¹⁵ would increase its value. An alternative hypothesis is that protons crossing the polymer would be responsible for only temporary deformations of its chains, or permeation is not sensitive to the damage done under these conditions.

Protons of different energies were then implanted inside PET films. Table II shows the experimental conditions during the irradiations.

The maximum proton ranges¹⁶ were calculated using tables in the existing literature.¹⁷ The permeability coefficient of the proton implanted films has been determined using the above-mentioned experimental method. The results are presented in Table III and illustrated in Figure 5. The sample temperature θ was 30°C except in the case of sample no. 10, for which it was 24°C . For this sample the value of K_{ip} quoted in Table III and plotted

TABLE II
Experimental Conditions for Proton Implantations

Sample no.	Energy (keV)	Range (μm)	Incident charge (μC)	Dose (mrad)
1	300	4.10	29.0	80.2
2	380	5.20	30.0	80.1
3	450	6.15	29.7	80.2
4	500	6.80	29.0	80.6
5	530	7.30	30.1	79.6
6	600	8.45	29.4	77.8
7	630	9.10	30.1	75.9
8,9	670 ^a	9.60	30.1	76.5
10	700	10.25	25.3	74.8
11	750	11.20	33.0	73.4
12,13	780 ^a	11.80	30.1	72.4

^a At each of these proton energies two PET films have been irradiated (see Table III and the discussion of the results in the text).

TABLE III
Experimental Conditions and Results for Proton-Implanted PET Film

Sample no.	Proton energy (keV)	Room temp (°C)	Gas pressure (mm Hg)	K_{ip} ($\text{cm}^3 \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{atm}$) $\times 10^{-9}$
1	300	23.0 ± 0.5	53.4 ± 0.2	6.57 ± 0.51
2	380	26.9 ± 0.5	47.9 ± 0.2	7.01 ± 0.65
3	450	25.5 ± 0.5	53.0 ± 0.2	7.81 ± 0.59
4	500	23.7 ± 0.5	50.4 ± 0.2	7.93 ± 0.58
5	530	26.0 ± 0.5	54.8 ± 0.2	8.55 ± 0.90
6	600	25.5 ± 0.5	52.5 ± 0.2	8.59 ± 0.63
7	630	26.0 ± 0.5	50.9 ± 0.2	9.12 ± 0.68
8	670	26.0 ± 0.5	54.2 ± 0.2	36.0 ± 2.1
9	670	28.5 ± 0.5	47.6 ± 0.2	7.15 ± 0.66
10	700	24.0 ± 0.5	100.7 ± 0.2	14.45 ± 0.81
11	750	23.7 ± 0.5	49.5 ± 0.2	22.25 ± 1.31
12	780	25.0 ± 0.5	53.2 ± 0.2	7.40 ± 0.64
13	780	26.8 ± 0.5	52.0 ± 0.2	7.80 ± 0.72

in Figure 5 was calculated using the K vs. θ dependence as given by eq. (6). The 17% discrepancy of the incident change (see Table II) for sample no. 10 has not been taken into account. The results show that the permeability coefficient K_{ip} depends on the energy of the implanted protons, but the striking feature is that while the first seven experimental points behave quite smoothly (Fig. 5), the six remaining ones behave chaotically (see, for example, the incompatible values of K_{ip} obtained for the same proton

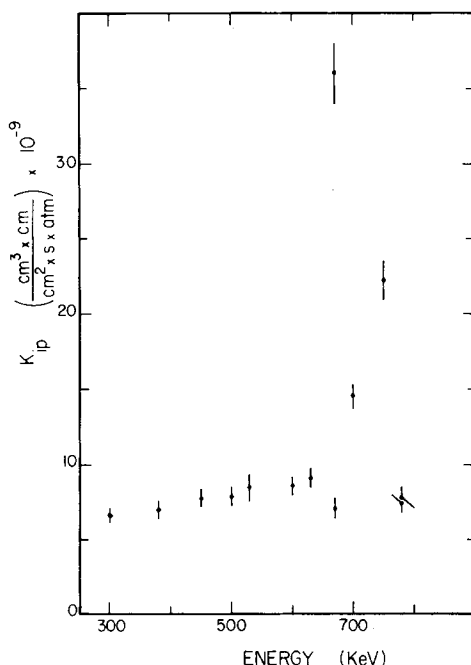


Fig. 5. Permeability coefficient of PET films as a function of the incident energy of the implanted protons.

energy of 670 keV). In addition, for proton energies above 630 keV, it was very difficult to obtain nonperforated irradiated films. This fact will be discussed later.

In the energy range 300–630 keV the smooth behavior of the permeability coefficient suggests a simple model already proposed by Crank¹⁸ for several films of different constitution. This model assumes that the actual irradiated film of total thickness l and permeability coefficient K_{ip} is the superposition of two films, an irradiated one of thickness l_1 equal to the proton range and permeability coefficient K_1 , and a nonirradiated one of thickness $l_2 = l - l_1$ and permeability coefficient K_2 . For a steady state of gas diffusion through the film, it can easily be shown that the following relation holds:

$$\frac{l}{K_{ip}} = \frac{l_1}{K_1} + \frac{l_2}{K_2} \quad (7)$$

Since $l = l_1 + l_2$, (7) reduces to

$$\frac{1}{K_{ip}} = al_1 + b \quad (8)$$

where $a = (1/l)(1/K_1 - 1/K_2)$ and $b = 1/K_2$.

Equation (8) has been χ^2 -adjusted to the experimental data in the energy range 300–630 KeV (samples 1–7), leading to the following results:

$$K_1 = (11.80 \pm 1.59) \times 10^{-9} \text{ cm}^3 \cdot \text{cm/cm}^2 \cdot \text{s} \cdot \text{atm}$$

$$K_2 = (5.52 \pm 0.52) \times 10^{-9} \text{ cm}^3 \cdot \text{cm/cm}^2 \cdot \text{s} \cdot \text{atm}$$

According to the model the parameter K_2 may be interpreted as the permeability coefficient of a film not irradiated and K_1 is the mean permeability coefficient for protons implanted through the whole thickness of the film.

Figure 6 shows the dependence of $1/K_{ip}$ on the range l_1 of the protons. The straight line comes from the above-mentioned adjustment.

Whatever the proton energy, the permeability coefficient K_{ip} of a p -implanted film is larger than the permeability coefficient K of a nonirradiated one. This fact leads to conclude that degradation phenomena predominate over crosslinking effects.

The chaotic behavior of the permeability coefficient K_{ip} for proton energies above 630 keV (Figs. 5 and 6) could be due to the presence of the rear electrode, which was used during the irradiations in order to determine the value of the implanted electric charge (see Fig. 3). Indeed, in the experimental conditions two phenomena are to be considered: emission of electrons by field effect and Paschen breakdowns. During irradiation, electric fields of the order of 10^7 – 10^8 V/m exist in the 5-mm gap between the rear electrode and the polymer film, and such field values allow cathode emission for contaminated cathodes.¹⁹ Electron discharges provoking breakdown inside the nonirradiated region of the film may occur when the range l_1 of the protons is larger than a certain threshold value which appears to be

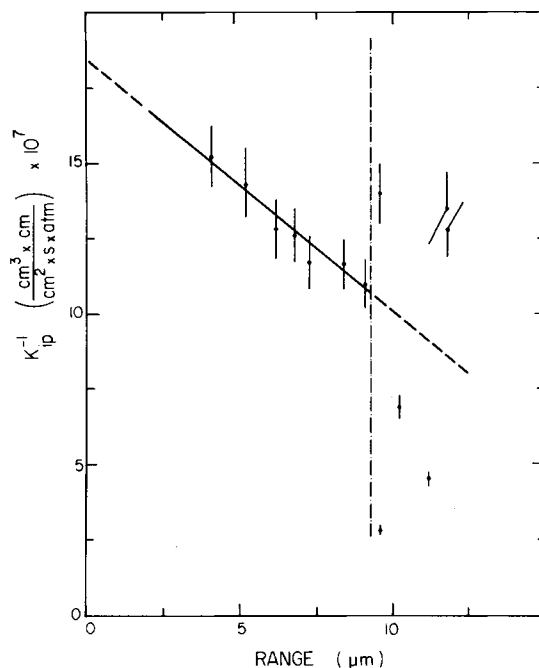


Fig. 6. Inverse of the permeability coefficient of PET films as a function of the range of the implanted protons. The straight lines have been adjusted only on the experimental points lying on the left side of the dotted vertical line.

of the order $8 \mu\text{m}$ for this experiment. In addition, the field emission effect is certainly enhanced because of the film deformation which reduces the "film-rear electrode" gap. This deformation results from the electrostatic force between the positive charge implanted and the negative charge induced on the rear electrode. The existence of a threshold effect in electron irradiated dielectrics was already reported.^{20,21}

The second phenomenon is the Paschen breakdown which may occur during the increase of the chamber pressure, from 10^{-4} – 10^{-5} mm Hg to atmospheric pressure, once the irradiation has been completed.

Both phenomena result in a parasitic irradiation of the polymer film by electrons of energies up to several keV. In opposition to the uniform and continuous proton irradiation the electron irradiation is nonuniform and of the burst type, a fact which may explain why several PET samples have been perforated.

Moreover, even for nonperforated films, implanted electrons may recombine with free implanted protons and form hydrogen atoms which provoke an additional degradation of the polymer, leading then to larger permeability coefficients (see, for example, samples nos. 8, 10, and 11 in Table III and Figs. 5 and 6).

Concerning sample no. 13, the unexpected low value of K_{ip} may arise because a nonnegligible fraction of the incident protons pass through the film. Indeed the values of the permeability coefficient for crossing protons K_{cp} and 780 keV implanted protons K_{ip} (Table III) are quite compatible, taking into account the respective doses.

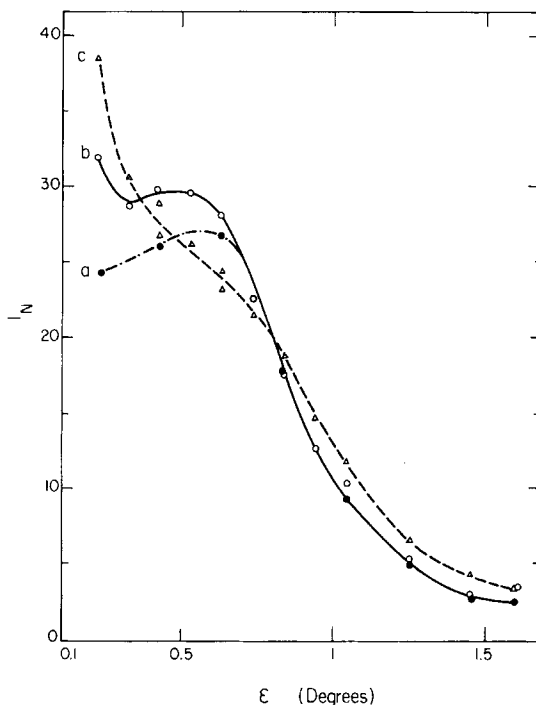


Fig. 7. Normalized intensity of the X-ray beam as a function of the scattering angle for nonirradiated (a), 6.15 μm (b), and 9.1 μm (c) implanted-proton PET films.

The permeability coefficient of several proton-implanted PET films has been remeasured several months after the first measurements were reported. The excellent agreement of the results prove that the effects of implantation remain for a long time after the irradiation.

Three PET films, one nonirradiated and two proton implanted, have been submitted to small-angle X-ray diffraction analyses. The results shown in Figure 7 suggest that the protons implanted actually provoke structural modifications of the poly(ethylene terephthalate) such as variation of the density and of the size of the voids.²² The wavelength ($\lambda = 1.54 \text{ \AA}$) of the X-rays indicates that the size of the diffraction centers is of the order of several \AA .

CONCLUSIONS

The results presented in this work show that protons implanted in poly(ethylene terephthalate) thin films cause an increase of the permeability coefficient of the polymer. This increase is a function of the incident energy of the protons, and it may be understood assuming that "degradation" or "predominant degradation plus crosslinking" phenomena occur as a consequence of the presence of the protons in the PET.

Modification of the polymer structure is confirmed by preliminary studies of the implanted samples by means of small-angle X-ray diffraction experiments.

The chaotic behavior of the permeability coefficient for "long range" protons is explained. It might be avoided by the suppression of the rear electrode, which has been used during irradiation of the samples.

As a possible application, charged particle implantation could be used to produce polymer films of fixed thickness and tunable permeability coefficient.

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