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PERMEABILITY COEFFICIENT OF PROTON IRRADIATED

POLYETHYLENE TEREPHATALATE THIN FILMS

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ABSTRACT

The principle of operation of an apparatus developed to study gas permation through thin films is described and the measurement method is dicussed.

Use is made of diffusion theory to obtain a expression for the permeability coefficient as a function of the rate of increase of the pressure in the receiving volume.

The Gibbs function for permeation of Helium through Polyethylene Terephtalate (P.E.T.) is determined. The permeability coefficient f̶o̶ of 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 P.E.T. seems to be confirmed by small angles X-rays scattering experiments on the irradiated samples. (Author)

I - INTRODUCTION

Nowadays Polyethylene Terephatalate 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 on the polymer properties. A common feature of these studies is that they were performed varying the radiation dose. The changes of intrinsic viscosity which result from exposure to ^{60}Co γ-radiation and α particles of 23 MeV were presented by N.S. Moshkovskii et al [1]. The ultimate tensile strength of Mylar 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 conduction [6] and electron-beam charging [7] studies have been performed on Polyethylene Terephatalate films. Since the detector above mentioned contain gases and are expos ed to radiation it appeared useful to study the behaviour of the permeability coefficient of irradiated P.E.T. thin films. The present work is devoted to the determination of the permeability coefficient of 12 µm thick Hostaphan** 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 ultra pure Helium. The experimental apparatus and the measurement procedure are described and the experimental results are presented and interpreted using a simple phenomenological model.

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* E.I. Du Pont de Memours and Company, Inc.

** Kalle Films - Hoechst

Small angles X-rays scattering experiments support the hypothesis of structural modifications in the proton implanted P.E.T. samples.

Part of these results constitutes the M.Sc thesis of one of the authors [8].

II - EXPERIMENTAL APPARATUS AND MEASUREMENT PROCEDURE

Gases and vapours 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

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

where D is the diffusion coefficient.

The experimental method of Dienes-Barrer [10] 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 "time lag". Integrating equation (1) over the thickness ℓ of the film and making use of Henry's law one gets:

$$Q = U \sigma (p_1 - p_2) A \Delta t / \ell \qquad\qquad (2)$$

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 measurements coefficient $K = D\sigma$ may then be written as:

$$K = \frac{Q \ell}{p_1 A \Delta t} \qquad\qquad (3)$$

Combining equation (3) and the state equation of a perfect gas one finally obtains:

$$K = \frac{\gamma}{P_1 T} \frac{\Delta P}{\Delta t} \qquad\qquad (4)$$

where

$$\gamma = \frac{\ell}{A} V \frac{T_o}{P_o} \quad cm^2 \ {}^oK/atm$$

$$T_o = 273.15 \ {}^oK$$

and

$$P_o = 1 \ atm$$

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 $A = (19.63 \pm 0.08) cm^2$ and the thichness $\ell = (12.07 \pm 0.06) \mu m$ measured averaging weights of fixed area samples and using the density $\rho = (1.395 \pm 0.001) g/cm^3$ of the polymer [11]. The receiving

volume was found to be $(292.84 \pm 10.70)cm^3$ 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 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) which temperature θ
is electronically regulated. The receiving volume V is delimited
by the film (5), the stopcoks (c) and (d) and the Mc Leod 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 µbar 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 II of
Figure 2). The above mentioned time lag for Helium being of the
order 0.05 seconds [12] the non linear part of the curve II
cannot be observed. Both curves are the results of independent
straigh-line fittings on the respective experimental sets of
data using the standard χ^2 method. The factor $\Delta P/\Delta t$ in equation
(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:

$$K = \gamma(\alpha - \alpha') / p_1 T \qquad (5)$$

where $\qquad \gamma = (4.92 \pm 0.22) \quad cm^2 \,^{\circ}K/atm$

Figure 3 shows the camber used to irradiate the P.E.T. films. The chamber itself is electrically insulated from the beam line terminal by means of the Epoxy insulating flange (2). This allows the measurement of the incident charge by the rear electrode (6). During the 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 be larger than the geometrical area of the sample being irradiated.

III - <u>RESULTS AND DISCUSSION</u>

All results presented here refer to ultra pure Helium and Polyethylene Terephtalate-based films of the RN Hostaphan type [11]. This aromatic polymer is known to be biaxially orient ed, which fact makes the difference between amorphous and crystal line states vanish [13].

The diffusion process being thermally activated one expects a temperature dependence of the permeability coefficent. The actual dependence is of the form [14]

$$K = K_o \, e^{-\Delta G/R\Theta} \qquad (6)$$

where ΔG is the permeability free activation energy (Gibbs funct

ion)

The variation of K as a function of the temperature of non-irradiated P.E.T. film has been studied and the results are shown in Figure 4. The θ dependence of K (equation 6) was x^2-ajusted to the data, leading to the following results:

$$K_o = (1.30 \pm 0.86) 10^{-5} \cdot \frac{cm^3 \cdot cm}{cm^2 \cdot s \cdot atm}$$

and

$$\Delta G = (4.58 \pm 0.38) \quad Kcal/mol$$

This last result agrees quite well with the value $\Delta G = 4.7$ Kcal/mol found by Michaels and co-authors [15] for "He-P.E.T.", 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 P.E.T., 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 irradiations the pressure inside the chamber was of the order of 10^{-5} Torr and low intensity currents (10 to 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 uniformely 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 1.

Table I: Experimental conditions for 1.3 MeV crossing protons

Incident change (µC)	33±2
Dose (mRad)	38.1
Film Temperature $\Theta(^{\circ}C)$	30±0.5
Room Temperature T $(^{\circ}C)$	24±0.5
Gas Pressure p_1 (mmHg)	53.3±0.2

The permeability coefficient was found to be

$$K_{cp} = (5.96\pm0.34)10^{-9} \frac{cm^3.cm}{cm^2.s.atm.}$$

value which, surprisingly, is compatible with the one obtained under the same experimental conditions (film and room temperature and gas pressure) for non-irradiated P.E.T. film:

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

This agreement may be explained by assuming that crosslinking and degradation effects occur simultaneously [1] and cancel each other. Crosslinking, due to the presence of an aliphatic branch [16], would contribute to a decrease of K while degradation, associated with the C_4 atom [17], would increase its value. An alternative hypothesis is that protons crossing the polymer would be responsible for only temperary deformations of its chains

Protons of different energies were then implanted

inside P.E.T. films. Table II shows the experimental conditions during the irradiations.

Table II: Experimental conditions for proton implantations

Sample n⁹	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*	9.60	30.1	76.5
10	700	10.25	25.5	74.8
11	750	11.20	33.0	73.4
12,13	780*	11.80	30.1	72.4

* At each of these proton energies two P.E.T. films have been irradiated (see Table II and the discussion of the results in the text).

The proton ranges were calculated using tables in the existing literature [18]. The permeability coefficient of the proton implanted films has then 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 $30^{\circ}C$ except in the case of sample n⁹ 10 for which it was $24^{\circ}C$. For this sample the value of K_{ip} quoted in Table III and plotted in Figure 5 was calculated using the K vs Θ dependence as given by equation (6). The 17% discrepancy of the incident

Table III: Experimental conditions and results for proton implanted P.E.T. film:

Sample nº	Proton Energy (KeV)	Room Temperature (°C)	Gas Pressure (mm Hg)	$K_{ip}(\frac{cm^3 \cdot cm}{cm^3 \cdot s \cdot atm})10^{-9}$
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±0.53
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

change (see Table II) for this 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 (Figure 5), the six remaining ones behave chaotically (see for example the incompatible values of K_{ip} obtained for the same proton energy of 670 KeV). In addition, for proton energies above 630 KeV, it was very difficult to obtain non perforated irradiated films. This fact will be discussed later.

In the energy range 300 to 630 KeV the smooth behaviour of the permeability coefficient suggests a simple model already proposed by Crank [19] 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 non-irradiated one of thickness $\ell_2 = \ell - \ell_1$ 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

$$\frac{\ell}{K_{ip}} = \frac{\ell_1}{K_1} + \frac{\ell_2}{K_2} \tag{7}$$

Since $\qquad \ell = \ell_1 + \ell_2$, (7) reduces to

$$\frac{1}{K_{ip}} = a\ell_1 + b \tag{8}$$

where
$$a = \frac{1}{\ell}(\frac{1}{K_1} - \frac{1}{K_2})$$

$$b = \frac{1}{K_2}$$

Equation (8) has been x^2-adjusted to the experimental data in the energy range 500 to 630 KeV (samples 1 to 7), leading to the following results:

$$K_1 = (11.80 \pm 1.59)10^{-9} \frac{cm^3 . cm}{cm^2 . s . atm.}$$

$$K_2 = (5.52 \pm 0.52)10^{-9} \frac{cm^3 . cm}{cm^2 . s . atm.}$$

According to the model the parameter K_2 may be interpreted as the permeability coefficient of a film superficially 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 of the above mentioned adjustment.

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

The chaotic behaviour of the permeability coefficient K_{ip} for protons 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 Figure 3). Indeed, in the experimental conditions two phenomena are to be considered: Emission of electrons by field effect and Paschen breakdowns. During the irradiations electric fields of the order of 10^7-10^8 V/m exist in the 5mm gap between the rear electrode and the polymer film and such field values allow cathode emission for contaminated cathodes [20]. Electron discharges provoking breakdown inside the non-irradiated 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 of the order 8 μm 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 elctrostatic forces 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 a already reported [21], [22].

The second phenomenon is the Paschen breakdown which may occur during the increase of the chamber pressure, from $10^{-4} - 10^{-5}$ mmHg 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 non-uniform and of the burst type, fact which may explain why several P.E.T. samples have been perforated.

Moreover, even for non-perforated 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 nº 8, 10 and 11 in Table III and Figures
5 e 6). .

Concerning sample nº 13 the unexpected low value
of K_{ip} may arise because a non negligible fraction of the incident
protons passes through the film. Indeed the values of the permea-
bility coefficient for crossing protons K_{cp} (Table I) and 780 KeV
implanted protons K_{ip} (Table III) are quite compatible, taking
into account the respective doses.

The permeability coefficient of several proton
implanted P.E.T. films has been re-measured several months after
the first meas rements here reported. The excellent compatibility
of the results prove that the effects of the implantations
remain for a long time after the irradiation.

Three P.E.T. films, one non irradiated 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 modifica-
tions of the Polyethylene Terephatalate such as variation of the
density and of the size of the voids [23]. The wavelength
($\lambda = 1.54$ Å) of the X-rays indicate that the size of the diffraction
centers is of the order of several Å.

IV - CONCLUSIONS

The results presented in this work show that
protons implanted in Polyethylene Terephatalate thin films
cause an increase of the permeability coefficient of the polymer.
This increase is a function of the incident energy of the pro
tons, 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 P.E.T.

Modification of the polymer structure is confirm
ed by preliminary studies of the implanted samples by means of
small-angle X-rays diffraction experiments.

The chaotic behaviour of the permeability coeffi
cient for "long range" protons is explained. It might be
avoided by the suppression of the rear electroctrode which has
been used during irradiations of the samples.

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

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FIGURE CAPTION

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) Mc Leod gauge - (8) Rotary vacuum pump - (9) Thermostatized bath
(a) to (f) stopcoks

FIG.2.: Pression growth vs. time for ultra pure He permeating through 12 µm P.E.T. film. (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.

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.

FIG. 4.: Temperature dependence of the permeability coefficient for non-irradiated P.E.T. film. The straight line results from a χ^2 adjustement.

FIG. 5.: Permeability coefficient of P.E.T. films as a function of the incident energy of the implanted protons.

FIG. 6.: Inverse of the Permeability coefficient of P.E.T. films as a function of the range of the implanted protons. The straight line have been adjusted only on the experimental points lying on the left side of the dotted vertical line.

FIG. 7.: Normalize intensity of the X-ray beam as a function of the scattering angle for non-irradiated (a), 6.15 μm (b) and 9.1 μm (c) implanted protons P.E.T. films.

BEAM