Dynamical Properties of the New "Rubber-like" Irradiated Polyethylene

A. A. RADY

Faculty of Science, Ain Shams University, Abbasia, Cairo, Egypt

1. Introduction

Polyethylene grade 20 irradiated with different doses from 0 to 149 units of radiation has been examined. The dynamic properties have been measured in a frequency range extending from 0.0005 cycles/sec. to 50 kilocycles/sec. and in a temperature range from −50 to 100°C. It was found that a rubbery attitude occurs when the specimen attains a dose lying roughly between 8 and 12 units. A specimen of 8 units was chosen to represent this attitude here.

One unit of radiation is assumed to be equivalent to the flux of 10^{17} slow neutrons/cm.^{2} plus the associated fast neutrons and gammas. The last two are considered to be proportional to the slow neutron flux.[3]

2. Apparatus and Method

Rods of irradiated polyethylene, about 8 inches long and $^1/_2$ inch in diameter, were used in this work. The resonance method was chosen for the frequency range between 1 to 50 kilocycles/sec., and the rotating cantilever method for the frequency range 0.0005 to 2.5 cycles/sec. The details of the apparatus and the method employed will be published elsewhere. E_1, the real part of Young's modulus and E_2/E_1, the internal friction coefficient, were measured; E_2, the imaginary part of the elasticity modulus; and η the real part of the dynamic viscosity were deduced.

3. Results and Discussion

(a) Young's Modulus

At room temperature the real part of Young's modulus is found to increase slightly with increase of frequency in the audio frequency range (Fig. 1). In the low frequency range it shows a relaxation at about 0.01 cycles/sec., but there are no other relaxations in the intermediate uninvestigated range

shown by the dotted lines. The same thing is expected below 0.0005 cycles/sec., the lowest limit in the low frequency range, since this material is crosslinked and the value of the modulus at this frequency is not far from the static. The relaxation in the dynamic modulus is accompanied by a peak in the damping curve at the same frequency of 0.01 cycles/sec.

With respect to temperature, the modulus decreases with increase of T (Fig. 2). When the specimen was cooled below room temperature, the modulus increased rapidly and had an abrupt rise in a definite range of temperature below which little additional increase occurred. It increased about 500% in the range 25–0°C. The curve tends to take the familiar S shape and flatten at about +50 and −50°C., reaching minimum and maximum values of the order of 10^8 and 10^{10} dynes/cm.^{2}, respectively. The latter value at low temperature may be compared with the value obtained by Flinn[5] at the megacycle range as 0.4×10^{10} dyne/cm.^{2}. The E_1 curve for a certain fixed frequency was shifted as a whole in the direction of increasing temperature when the frequency increased. The parallelism between low temperature and high frequency may be carried to the high temperature and low frequency, where the modulus approached a limiting value of the order 10^8 dyne/cm.^{2}.

For E_2, the imaginary part of Young's modulus, it is seen in Figure 1 that it increases with frequency at room temperature, having a peak in the low frequency region. According to the Debye relaxation theory, it is expected that the maximum of E_2 with respect to frequency may lie at a point where the derivative of E_1 with respect to log frequency is a maximum. This is the case in Figure 1. With decrease of frequency toward zero, it is supposed that E_2 tends to zero also, since the condition will be static and a state of equilibrium is attained. A plot of E_2 against temperature (Figs. 2 and 3) shows a relaxation plateau at low temperatures.
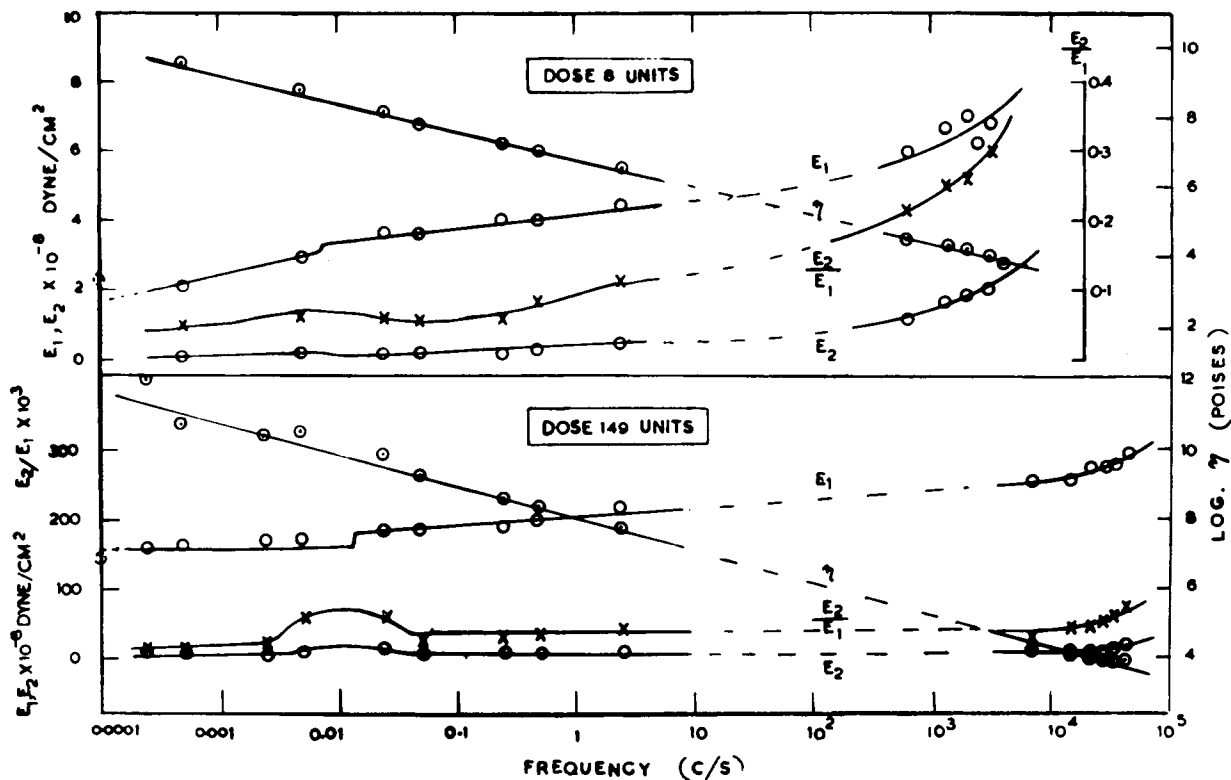
Fig. 1. E_1, E_2, E_2/E_1, and η vs. frequency at room temperature.

(b) Internal Friction

The peak found in the internal friction–temperature curve (Fig. 2) lies in the region where the slope of E_1 reaches a maximum. This result is repeated for each fixed frequency chosen in the plot, i.e., 0.0005, 0.01, and 1000 cycles/sec. It is evident that the peaks of these curves shift toward higher temperatures with increase of frequency in the manner characteristic of a relaxation phenomenon.
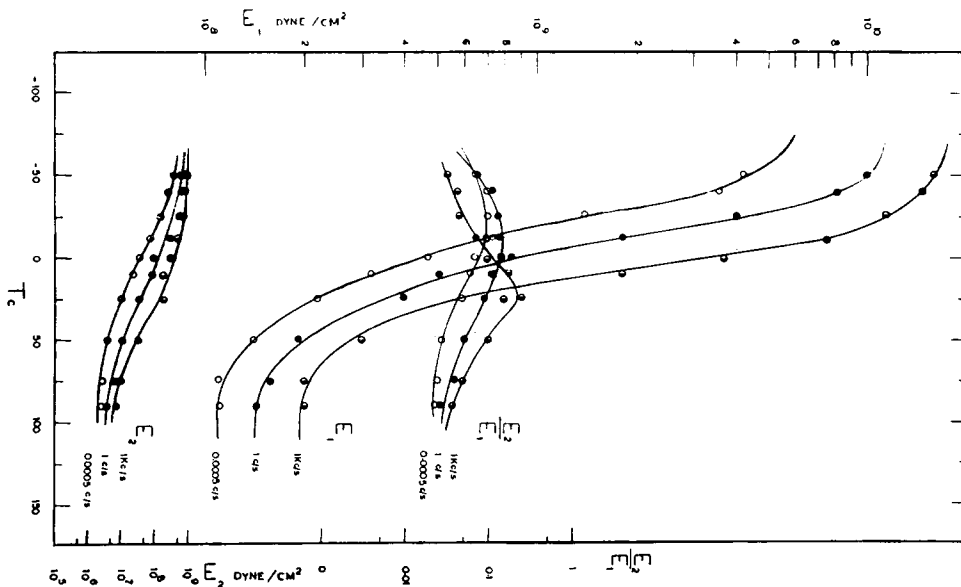

Fig. 2. The real part of Young's modulus (E_1), the imaginary part (E_2), and the internal friction (E_2/E_1) plotted vs. temperature for three different frequencies. Dose, 8 units.
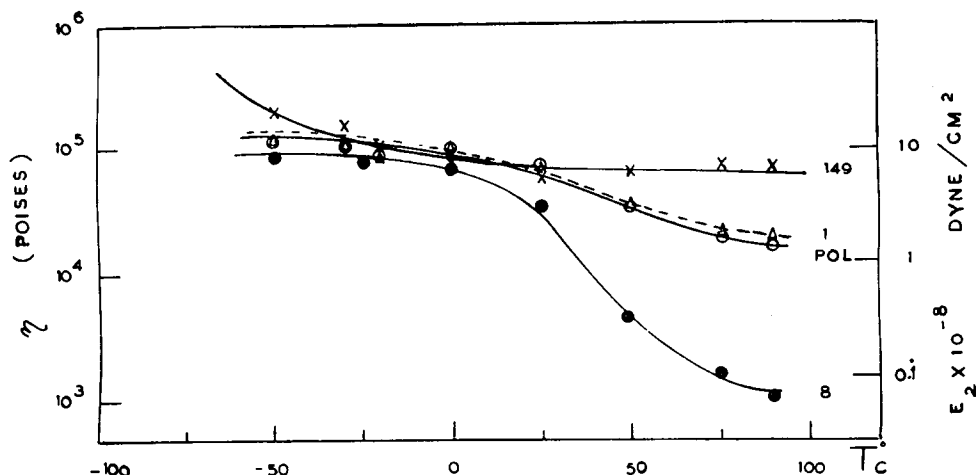
Fig. 3. Real part of dynamic viscosity and imaginary part of Young's modulus vs. temperature (1 kilocycle/sec.) for four typical specimens. The curve for 8 units (rubbery polyethylene) is the lowest in the figure.

It can be easily shown[1] that the maxima of E_2, the imaginary part of Young's modulus, and E_2/E_1, the internal friction, lie for a fixed frequency ω at two different positions, each describing a different retardation time, t, given by the two following equations:

$$\omega_{t_1} = 1 \qquad (1)$$

$$\omega_{t_2} = \sqrt{\frac{c_1 + c_2}{c_2}} \simeq \sqrt{\frac{c_1}{c_2}} \qquad (2)$$

and

$$\log \frac{t_2}{t_1} = \frac{1}{2} \log \frac{c_1}{c_2} \qquad (3)$$

On the other hand, since $t \propto e^{\Delta Ha/RT}$,

$$\log \frac{t_2}{t_1} = \frac{\Delta Ha}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (4)$$

where T_1 and T_2 are the absolute temperatures at which the maxima of E_2 and E_2/E_1 against T occurred.

Choosing the fixed frequency of 1 kilocycles/sec., say, we can substitute the values in eqs. (3) and (4) for comparison. The values of c_1 and c_2 can be taken as $2 \times 10^{10.5}$ and $1 \times 10^{7.5}$, respectively, denoting the glassy and the rubbery moduli given by the curve of Figure 2. The value of the activation energy can be taken as 15 kcal./mole (the average below 0°C. from unpublished work[6] by the author). T_1 can be taken from Figure 2 as −23°C., the temperature where the E_2 curve begins to level (it can be shown that this relaxation peak is not fully pronounced due to the free volume) and T_2 as 27°C. When these values are substituted

in eqs. (3) and (4), the values of $\log t_2/t_1$ from these two equations are estimated as 1.65 and 2, respectively, which proves the internal consistency of the material.

(c) The Second-Order Transition Temperature

The temperature about which the real part of Young's modulus increases enormously and the polymer is transformed into a glasslike material has been called the second-order transition temperature or the glass temperature. It is also described as the brittle temperature since the polymer is changed from a highly viscous liquid or rubbery solid to a brittle material that will break if a sudden sharp bend is applied. Also it can be described as the lowest temperature at which an observable value of viscous flow can take place under the effect of the thermal agitation forces acting on the molecules and within the time limits of the experiment.

Eyring[4] described the transition temperature as the temperature at which the segments of the long polymer chains begin to move farther apart, resulting in the appearance of new holes which enable the side groups attached to the polymer chain, or whole segments of the chain, to undergo free rotation to more or less any degree along the axis of the polymer chain. Uberreiter[7] described it as an internal melting point above which the polymer behaves as a liquid of constant volume capable of undergoing plastic and elastic deformations of a high order with a Poisson's ratio 0.5 while at the same time preserving the external fixed shape of a solid. The second-order transition temperature is known to be not an equilibrium transition in the thermo-

dynamic sense and is not associated with a latent heat. Boyer[2] specified the physical properties in which the second-order transition manifestations may occur: (a) the volume-temperature curve, (b) heat capacity, (c) compressibility, (d) thermal conduction, (e) elasticity modulus, (f) refractive index, (g) dielectric properties, and (h) x-ray pattern. He also stated that the value of this temperature is a function of the speed of the test used to observe it, being higher the faster the speed of the test. For this reason it may be referred to as the apparent second-order transition.

This fact is shown in Figure 2, where the transition occurred at about $-30°$, $-3°$, and $27°$C. for the frequencies 0.0005, 0.01, and 1000 cycles/sec., respectively. From the specific volume-temperature curve of this specimen as given by the author in an unpublished work, it was shown that there is also a transition in the curve at about $20°$, confirming its change from rubbery to glasslike material.

References

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Synopsis

Polyethylene irradiated in the B.E.P.O. pile at Harwell has been found to acquire new mechanical properties. At a certain dose, polyethylene was found to behave like rubber.

Résumé

Le polyéthylenè acquiert des propriétés mécaniques nouvelles par irradiation à la pile B.E.P.O. à Harwell. Pour une dose déterminée, il se comporte comme un caoutchouc.

Zusammenfassung

Es wurde gefunden, dass Polyäthylen, das in der B.E.P.O. Pile in Harwell bestrahlt wurde, neuartige mechanische Eigenschaften annimmt. Bei einer gewissen Dosis zeigte Polyäthylen das Verhalten von Kautschuk.