Influence of low energy oxygen ions on some mechanical properties of polyethylene and polystyrene

M. D. Migahed, A. H. Oraby, M. Hammam*, K. A. El-Farahety and M. A. Abul-Ez
Department of Physics, Faculty of Science, Mansoura University, Mansoura, A.R. Egypt

and A. M. Ghander
Damietta Faculty of Science, Mansoura University, Mansoura, A. R. Egypt
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The creep and stress and strain relaxation behaviours of two different types of polymer have been investigated; polyethylene in strip form and polystyrene in fibre form. All measurements have been carried out before and after exposure to an oxygen ion beam of current densities 100 and 200 μA cm^{-2} at an energy of 0.5 keV for 1.8×10^3 and 0.9×10^3 s, respectively. Young's modulus has been measured as a function of temperature. The activation energies have been calculated from stress and strain relaxation measurements. The results obtained made it possible to determine a complete set of mechanical parameters, e.g. relaxation time τ, critical strength σ_c and structural sensitive parameter γ, for both before and after ion exposure. The mechanical properties of the polymers investigated were found to be improved after exposure to oxygen ions due to structural changes.

(Keywords: oxygen ions; mechanical properties; polyethylene; polystyrene)

INTRODUCTION

The application of a constant stress to a polymeric material causes a gradual change in its size due to creep. Clearly the material cannot continue to increase in size indefinitely and will eventually fracture. The time taken for the material to fracture will depend on the stress level, the ambient temperature, the type of environment, the component geometry, the molecular structure and the method of preparation[1].

Most plastic materials are produced and used because of their desirable mechanical properties. For this reason, these properties are considered to be the most important physical properties of polymers, and improvements to mechanical properties are often sought. Recently, the ion implantation technique has been used to modify the surface mechanical and electrochemical properties of iron or iron-based alloys[2] and ceramic materials[3]. Several effects which occur as a result of high-energy ion beam irradiation of polymers have been reported by Bello *et al.*[4]. Ion beam irradiation by inert gas ions appears to create pressure due to occluded gas, a condition inside the polymer which can lead to serious structural changes and unexpected electrical behaviour of the implanted polymer. A significant modification of the surface properties of organic films by irradiation with ion beams has been reported by Davenas *et al.*[5].

This paper deals with the influence of low energy oxygen ions on some mechanical properties of polyethylene (PE) strips and polystyrene (PS) fibres.

EXPERIMENTAL

The PE strips were Marlex 6006 produced by the Phillips Chemical Company. It is a linear polymer with a weight-average molecular mass $M_w = 1.3 \times 10^4$ and a number-average molecular mass $M_n = 1.06 \times 10^4$; the values for PS were $M_w = 1.65 \times 10^4$ and $M_n = 1.3 \times 10^4$. Samples of PS were made into tensile fibres (radius 1.27 mm). The PE samples were in the form of strips (4 mm thick, 28 mm wide). The distance between the grips was 40 mm. All tensile experiments were conducted on a locally manufactured testing machine (*Figure 1*). The testing machine is similar to that reported by Ogata *et al.*[6]. Elongation was measured manually with a travelling microscope with a sensitivity of $\pm 2 \times 10^{-2}$ mm. The temperature stability of the furnace was within ±0.5°C.

The samples were exposed to an oxygen ion beam produced by a coaxial electrode[7]. The samples were exposed to the continuous ion beam current at an energy of 0.5 keV for two different time intervals (0.9×10^3 and 1.8×10^3 s). Ion current densities of 100 and 200 μA cm^{-2} at a reduced pressure of oxygen gas of 4.1×10^{-2} Pa were used. Many samples were tested for each set of conditions to ensure reproducibility of the data.

THEORETICAL

The stress and strain properties of rubbery polymers can be represented by a simple power function[8]:

$$\sigma_t = b\varepsilon_t^x \qquad (1)$$

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* Present address: Department of Physics, University of Bahrain, PO Box 32038, State of Bahrain

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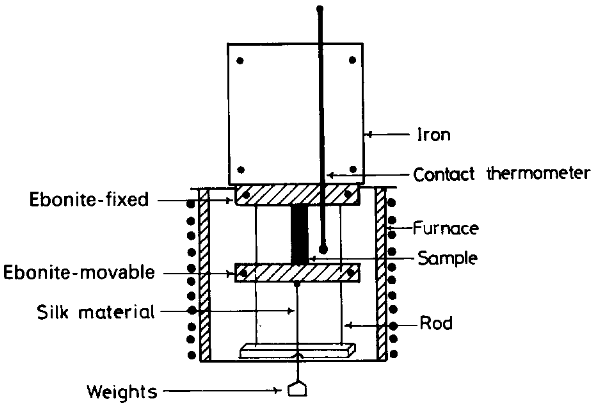

Figure 1 Schematic diagram of the testing machine

where σ_t is the stress for a given time interval, ε_t is the strain at the same interval, and b and x are constants for the material.

For rubbery polymers, the stress does not remain constant but gradually declines from an initial value σ_0 to a certain equilibrium value σ_∞, theoretically reached in a time $t \rightarrow \infty$. The quantitative description of stress relief is given by[9]:

$$(\sigma - \sigma_\infty) = (\sigma_0 - \sigma_\infty)\exp(-t/\tau) \qquad (2)$$

where σ is the stress left on the specimen after a time t and τ is the relaxation time.

Strain relaxation can be quantitatively defined to a first approximation by the following relation:

$$\varepsilon = \varepsilon_\infty[1 - \exp(-t/\tau)] \qquad (3)$$

where ε_∞ is the equilibrium strain.

The time dependence of strength in uniaxial extension at constant stress for various oriented polymeric materials is described by the following formula[9]:

$$\tau = A\exp(-\alpha\sigma) \qquad (4)$$

where σ is the specific tensile stress and α and A are constants which depend on the nature of the material and temperature. The temperature dependence of the relaxation time is given by:

$$\tau = \tau_0\exp(U_a/kT) \qquad (5)$$

where τ_0 is a constant equal to the period of thermal oscillation of atoms (10^{-13} s for all polymers), U_a is the activation energy for conformational transformation of molecules, k is Boltzmann's constant and T is absolute temperature. With the assumption that U_a drops linearly with increasing σ:

$$U_a = U_0 - \gamma\sigma \qquad (6)$$

where U_0 is the activation barrier for the polymer in the unstressed state and γ is a proportionality factor. Therefore, equation (5) can be written in the form:

$$\tau = \tau_0\exp[(U_0 - \gamma\sigma)/kT] \qquad (7)$$

Equation (7) shows that a decrease in the activation barrier causes a sharp decrease in the relaxation time.

RESULTS AND DISCUSSION

Figure 2 shows the stress–strain measurements of PS fibre at three different temperatures before and after exposing the samples to oxygen ions at an ion beam current density of 200 μA cm^{-2} for 0.9×10^3 s with an ion beam energy of 0.5 keV. Initially the stress σ is proportional to the strain ε according to Hooke's law, $\sigma = Y\varepsilon$, where Y is Young's modulus. The Young's modulus of a material is a function of the time of loading in a static experiment. The time of loading is constant in our experiments. A deviation from Hooke's law is seen as temperature increases. After oxygen ion exposure, the strain is decreased compared with the values before exposure at the same temperature. This implies an increase in the Young's modulus of the material after exposure. It seems that the material after exposure becomes stiffer as indicated by the stress–strain curve at 100°C. Similar results were obtained for PE strips before and after oxygen ion exposure (*Figure 3*).

Figure 4 shows the effect of temperature on the tensile strength and Young's modulus for PE strips before and after oxygen ion exposure at a dose of 200 mA cm^{-2} for 0.9×10^3 s and an ion energy of 0.5 keV. The results show that the tensile strength and Young's modulus decrease with increasing temperature. Also, the tensile strength was slightly increased after oxygen ion exposure.

Table 1 shows the temperature dependence of Young's modulus for PE strips and PS fibres before and after oxygen ion exposure at an ion beam current density of 200 μA cm^{-2} for 0.9×10^3 s. The values of Young's moduli obtained in the present work for non-exposed samples are in good agreement with the values reported in the literature[10,11].

A study of the effect of temperature on the stress relaxation of PE strips and PS fibres was performed before and after oxygen ion exposure at a dose of 100 μA cm^{-2} for 1.8×10^3 s and an ion energy of

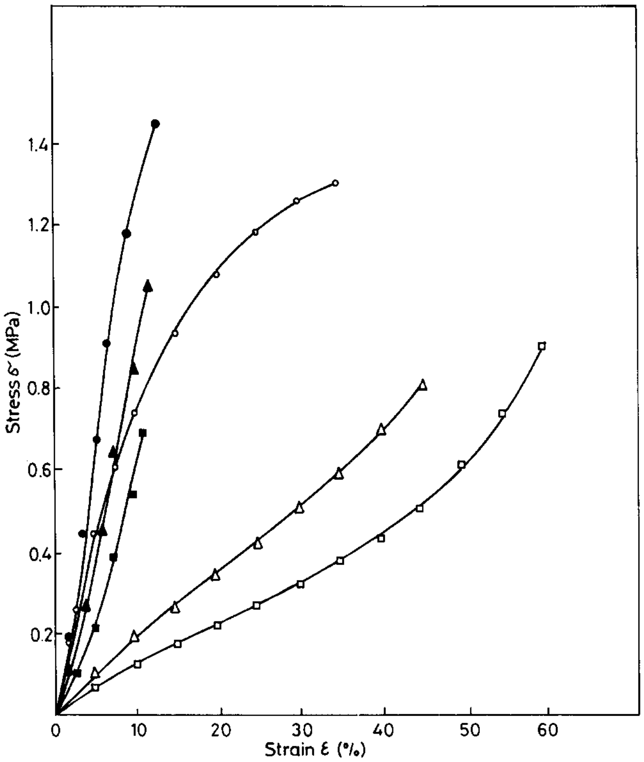

Figure 2 Stress–strain relationships at different temperatures for PS fibres before and after oxygen ion exposure: (○) PS at 20°C; (△) PS at 60°C; (□) PS at 100°C; (●) PS and oxygen ion exposure at 20°C; (▲) PS and oxygen ion exposure at 60°C; (■) PS and oxygen ion exposure at 100°C

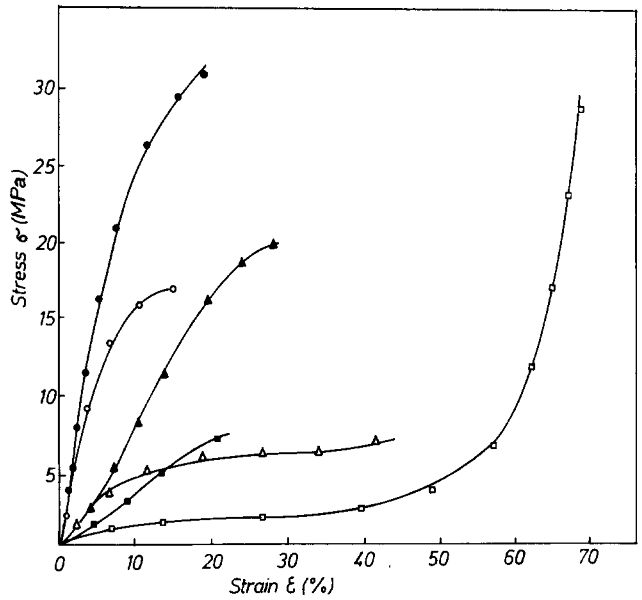

Figure 3 Stress–strain relationships at different temperatures for PE strips before and after oxygen ion exposure: (○) PE at 20°C; (△) PE at 80°C; (□) PE at 120°C; (●) PE and oxygen ion exposure at 20°C; (▲) PE and oxygen ion exposure at 80°C; (■) PE and oxygen ion exposure at 120°C

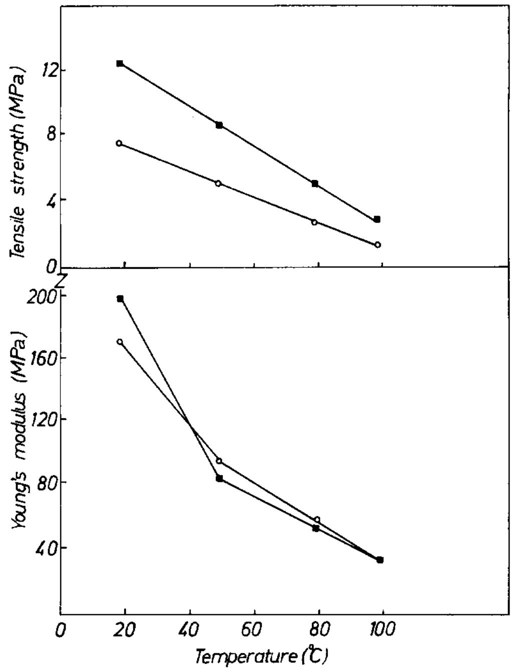

Figure 4 Dependence of Young's modulus and tensile strength on the temperature for PE strips before (○) and after (■) oxygen ion exposure

Table 1 Dependence of Young's modulus on temperature for PE and PS before and after oxygen ion exposure

	Young's modulus (MPa)				
	PE strips			PS fibres	
T (°C)	Before exposure	After exposure	T (°C)	Before exposure	After exposure
20	170	196	20	8.2	12
50	94	83	40	3	9.5
80	57	53	69	2	7.5
100	33	33	100	1.4	5.3

0.5 keV. The results are shown in *Figure 5*. From this figure, τ values for each sample were obtained at the corresponding temperatures. A plot of $\ln \tau$ *versus* $1/T$ at different stresses, before and after oxygen ion exposure for PE strips, is shown in *Figure 6*. Extrapolation of the

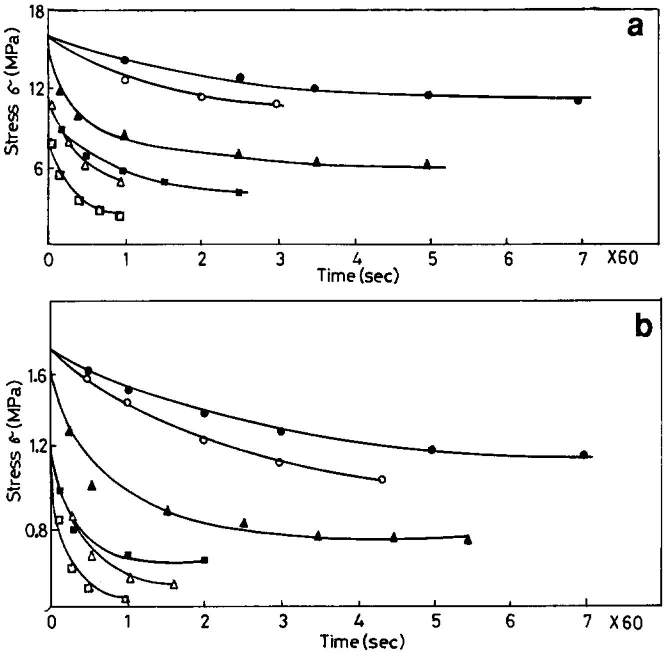

Figure 5 Stress–time relationships at different temperatures before and after oxygen ion exposure. (a) PE strips: (○) PE at 20°C; (△) PE at 60°C; (□) PE at 80°C; (●) PE and oxygen ion exposure at 20°C; (▲) PE and oxygen ion exposure at 60°C; (■) PE and oxygen ion exposure at 30°C. (b) PS fibres: (○) PE at 20°C; (△) PS at 60°C; (□) PS at 80°C; (●) PS and oxygen ion exposure at 20°C; (▲) PS and oxygen ion exposure at 60°C; (■) PS and oxygen ion exposure at 80°C

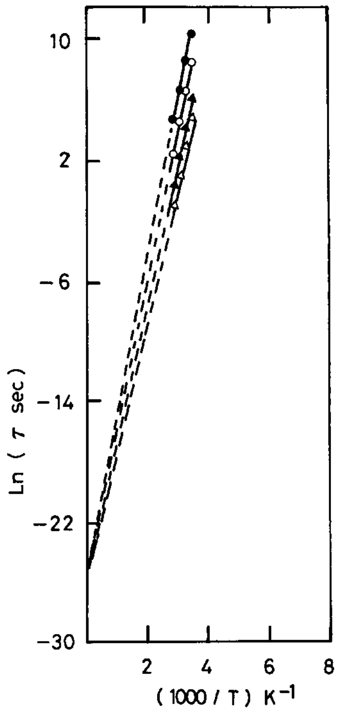

Figure 6 Ln τ *versus* $1/T$ plot for PE strip at different stresses before and after oxygen ion exposure: (○) before exposure, $\sigma = 6$ MPa; (△) before exposure, $\sigma = 12$ MPa; (●) after exposure, $\sigma = 6$ MPa; (▲) after exposure, $\sigma = 12$ MPa

Table 2 Mechanical parameters for PE and PS before and after oxygen ion exposure

	PE strip		PS fibre	
Parameter	Before	After	Before	After
U_0 (kJ mol^{-1})	86	95	92	110
γ	1.3×10^{-6}	2.1×10^{-6}	1×10^{-5}	2.5×10^{-5}
A	3×10^{4}	34×10^{4}	5.1×10^{4}	86×10^{4}
α	5.8×10^{-7}	5.5×10^{-7}	5.8×10^{-6}	7.1×10^{-6}
τ_0 (s)	5.1×10^{-12}	9.3×10^{-12}	1.5×10^{-13}	6.9×10^{-13}
σ_c (MPa)	69	61	6.8	5.8

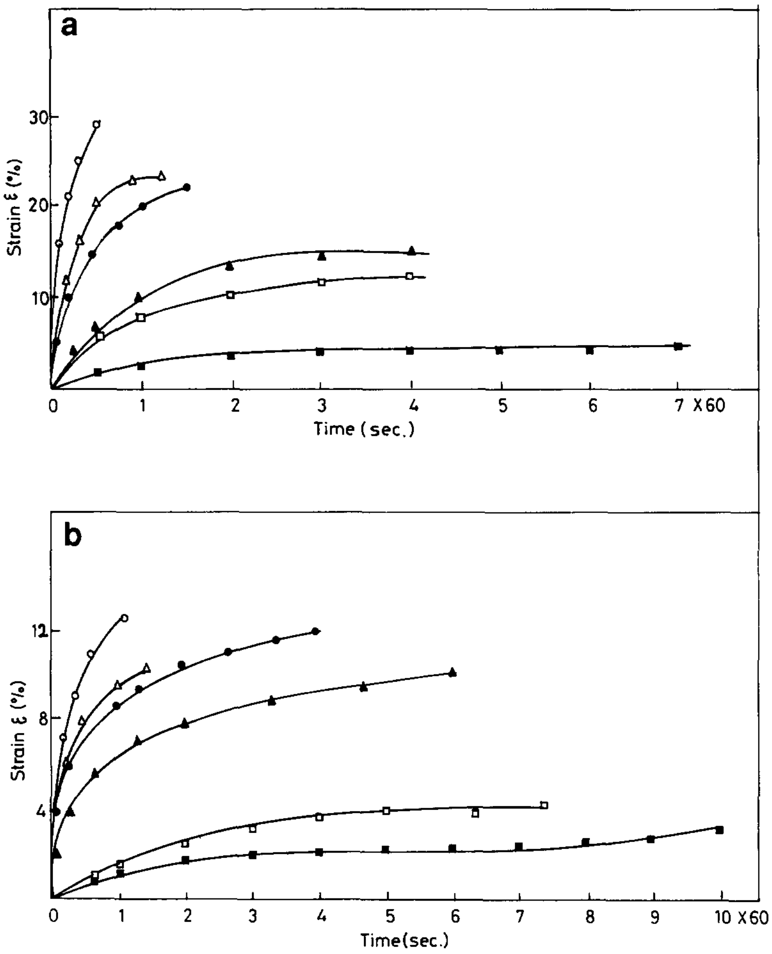

Figure 7 Strain–time relationships at different temperatures before and after oxygen ion exposure. (a) PE strips: (○) PE at 20°C; (△) PE at 60°C; (□) PE at 80°C; (●) PE and oxygen ion exposure at 20°C; (▲) PE and oxygen ion exposure at 60°C; (■) PE and oxygen ion exposure at 80°C. (b) PS fibres: (○) PS at 20°C; (△) PS at 60°C; (□) PS at 80°C; (●) PS and oxygen ion exposure at 20°C; (▲) PS and oxygen ion exposure at 60°C; (■) PS and oxygen ion exposure at 80°C

straight lines obtained yields a single point which corresponds to a constant which is close in value to the period of thermal oscillations of the atoms ($\tau_0 \approx 10^{-12}$–10^{-13} s for all polymers). Equation (7) was used to calculate several parameters before and after oxygen ion exposure. The values obtained are listed in *Table 2*. The magnitude of U_0 is close to the energy of chemical bonds for polymers[9], γ is a structure-sensitive parameter, A, α and τ_0 are constants of the material, and σ_c is the critical strength of the material.

Inspection of *Table 2* reveals that most of the mechanical parameters seem to increase with oxygen ion exposure. This indicates that a change in the structure of the materials and consequently an improvement in some mechanical properties are achieved. Similar qualitative results were obtained for PS fibres both before and after oxygen-ion exposure.

A study of the effect of temperature on the strain relaxation time of PE strips and PS fibres was also performed before and after oxygen ion exposure. *Figure 7* shows strain–relaxation time of PE strips and PS fibres at three different temperatures before and after oxygen ion irradiation at a dose of 100 μA cm^{-2} for 1.8×10^3 s and an ion energy of 0.5 keV. All the parameters listed

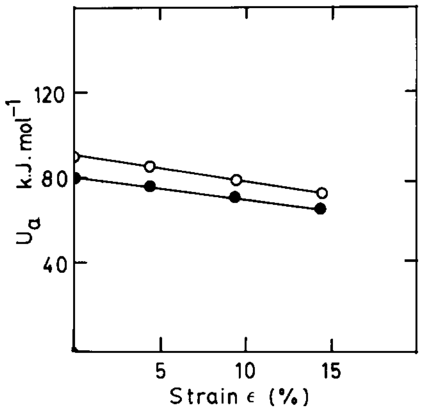

Figure 8 Activation energy for conformational transformation of molecules (U_a) *versus* strain before (●) and after (○) oxygen ion exposure of PE strips

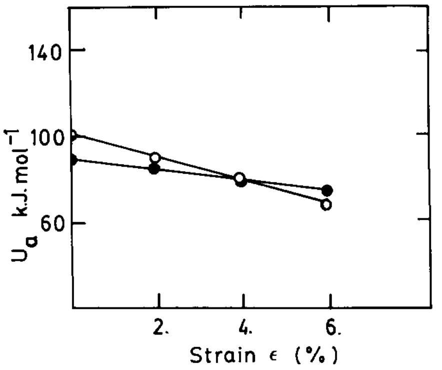

Figure 9 Activation energy for conformational transformation of molecules (U_a) *versus* strain before (●) and after (○) oxygen ion exposure of PS fibres

in *Table 2* have been recalculated from the strain measurements and were identical to those obtained in *Table 2*.

Figure 8 shows the relationship between the activation energy for conformational transformation of molecules of PE strips and strain before and after oxygen ion exposure. *Figure 9* shows the same relationship for PS fibres. The samples were exposed to oxygen ions at a dose of 100 μA cm^{-2} for 1.8×10^3 s and an ion energy of 0.5 keV. The results show a slight increase in the activation energy after irradiation. Also, the activation energy for conformational transformation of molecules generally decreases with increasing strain.

CONCLUSIONS

The mechanical measurements showed a pronounced change in the tensile strength of the investigated materials after oxygen ion exposure. The materials become stiffer as indicated by the stress–strain study. Further, parameters such as activation energy, critical strength and relaxation time, which determine the mechanical properties of the material, have been determined before and after oxygen ion exposure. The results obtained revealed that exposure improved some of the mechanical properties of the materials studied.

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