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Delayed elastic recovery of hardness indentations in polyethylene

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The depth of Vickers microindentations in high density, low density and linear low density polyethylenes has been studied by two wave interferometry. The evolution of the delayed depth recovery is explained in terms of the Burgers model of viscoelastic behaviour and the numerical parameters associated with the model are related to the crystallinity, elastic modulus and yield stress of the polyethylenes studied.

1. Introduction

The microindentation hardness test measures the resistance of materials to the plastic deformation produced by the impact of the indentor. As the polymeric materials show a complex viscoelastic behaviour, it was reasonable to suppose that the impressions produced by the Vickers indentor would not be constant in shape but they would recover with time. In a recent paper [1] we presented some first results confirming this supposition. Another demonstration of the viscoelastic response involved in the microindentation hardness, is the parallelism between the maximum loss modulus of polymers at the temperature of glass transition (measured by dynamic mechanical techniques) and the sharp maximum of the microhardness at that temperature [2].

This work reports the measurements of Vickers indentation recovery in polyethylene and relates this behaviour to the rheological models and the mechanical properties. Some macroscopic characteristics of the polymer structure (crystallinity, molecular weight) will be correlated with the values of the parameters which define the recovery of the impressions.

2. Experimental part

2.1. Materials

A series of commercial samples of polyethylene, including high density (HDPE), low density (LDPE) and linear low density (LLDPE) were studied. The commercial products, either pellets or powder, were placed between smooth polished copper plates, heated at five degrees above the melting point and hot pressd at 15 MPa for 10 min. The mouldings were cooled in two different ways: quenching in ice water and slow cooling at an approximate rate of $1^\circ C\,min^{-1}$. Different cooling rates allow different densities to be obtained and, therefore, various crystallinity values for the linear and branched polyethylenes. The moulded sheets were about 1 mm thick, which is large enough to cancel the perturbing influence of the substrate when the microhardness is measured.

2.2. Molecular weights and densities

The molecular weights of the polyethylene samples were measured by using a high temperature Ubbelohde viscometer, attached to a manostatic system of dry nitrogen. The viscosity-molecular weight relationships used (K values in $ml\,g^{-1}$) were

$$[\eta] = 67.7 \times 10^{-3} M^{0.67} \quad (1)$$

for HDPE and LLDPE dissolved in decalin at 135° C [3] and

$$[\eta] = 105 \times 10^{-3} M^{0.63} \quad (2)$$

for LDPE dissolved in p-xylene at 81° C [4]

The densities of the samples were determined at 23° C in an ethanol–water gradient column which had been calibrated with glass floats. The densities were converted to degrees of crystallinity by the relation given by Chiang and Flory [5].

2.2. Drawing procedures

The drawing of polyethylene sheets was carried out on an Instron dynamometer at 20° C. The width of the dumb-bell-shaped specimens was 0.4 cm and their gauge length was 2 cm. Although it is known the influence of the drawing rate on the deformation, at low elongation rates no significant changes are found, and, thus, a crosshead speed of $0.5\,cm\,min^{-1}$ was used. About six specimens of each sample were deformed and the values reported for the moduli and the yield stresses are the average of these samples. The moduli of elasticity (E) were calculated from the initial slope of the stress–strain curve.

2.3. Microindentation hardness measurements

The microhardness measurements were performed

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using a Vickers indentor attached to a Shimadzu Microhardness Tester model M. The microhardness values were calculated from the expression:

$$MH = 2 \sin 68° \, P/d^2 \text{ (MPa)} \quad (3)$$

where P is the contact load (N) and d is the length of the diagonal of the indentation surface (mm). A loading cycle of 10 sec and a load of 0.147 N were used for all the measurements, which were carried out at 25° C. These values were selected in order to ensure the complete reproducibility of the results [6] and to obtain indentations of sizes not exceeding the field of the interference objective used.

2.4. Indentation depth measurements by interferometry

Although attempts have been made to measure the indentation depth by scanning electron microscopy, or by shifting the focus plane in an optical microscope [7], two wave interferometry is expected to be successful for this kind of measurement, as it is considered simple, fast and accurate to study microstructures a few microns in size. As it is a non-contact method, no deformation is produced in the object during the measurements.

The basis of the method is the association of a small Michelson interferometer with an optical microscope in the observation of the samples with reflected light. The sample acts as the secondary mirror of the interferometer, and the illuminating plane wave reflected on it interferes with the plane wave reflected on the primary mirror of the interferometer, which operates as a reference mirror. The interference pattern produced by the recombination of the two waves is focused by the objective lens giving rise to an image containing sets of interference fringes in the areas in which the object varies in thickness. A pair of consecutive fringes corresponds to a variation of $\lambda/2$ in the sample thickness. Therefore, the illuminating λ being known, the count of fringes allows the depth of the corresponding indentation to be obtained immediately.

For indentations a few microns in depth this experimental method describes accurately the morphology of the indentation as topographic contour lines formed by the interference fringes, because the optical path difference is constant for lines of equal thickness. In the case of indentations having a depth greater than a limit of about 4 to 5 μm, the interpretation and even the observation of the fringes become very difficult [8], and other methods of measurement must be used.

In our experimental equipment a 20 × Ealing interference objective lens (focal length 8 mm) incorporating a Michelson interferometer, attached to a Zetopan Reichert microscope, was used. The sample was illuminated with the green line (λ = 547 nm) of a mecury spectral lamp, so the thickness variation corresponding to a pair of consecutive fringes is 0.27 μm. The depth of the samples was periodically measured between 15 min and 170 h after releasing the indentor.

3. Results and discussion

Difficulties in measuring the recovery of the indentation depth in polymers explain the absence of experimental results in the literature until very recently [1]. A previous review [9] suggested that data for polymers could be similar to those obtained for metals and ceramic materials.

The instantaneous recovery cannot be monitored by optical methods because the time elapsed between the release of the indentor and the measurement of the diagonal is too long, in practice not less than 15 sec. On the contrary, when evaluating the delayed recovery, it is observed that the length of the diagonal remains constant (we have checked it for times ranging from 15 sec to 170 h) and this constancy is in agreement with all the microhardness results on polymers [10, 11]. As we have reported previously [1], the complete set of polyethylenes which have been investigated, listed in Table I, show a large recovery of the impression depth, making it increasingly difficult to observe the indentation. In our experimental conditions, the depth measured 2 h after releasing the indentor ranged from 3.25 to 1.90 μm, depending on the sample, whereas after 170 h the measured depth ranged from 3.00 to 1.60 μm. Fig. 1 shows the interferometric patterns of two indentations of different depth. It can be seen that the residual impression is a pyramid of square section with smoothly curved edges.

It is obvious that the recovery of the indentation dimensions is due to the viscoelastic behaviour of the polymers. In view of this, we have tried to relate the results of this work to some of the rheological models. The Burgers model has been chosen as it is simple and adequately adjusted to other viscoelastic properties, for instance the dynamic mechanical ones.

The Burgers model describes the strain recovery under zero stress by means of the expression [12]

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \exp(-t/\tau) \quad (4)$$

TABLE I Microhardness values (MH), crystallinities $(1 - \lambda)_d$ and parameters of depth recovery (defined in Equations 5, 7 and 8 of the text) for various polyethylene samples of different molecular weights

Type	$M_w \times 10^{-5}$	$(1 - \lambda)_d$	MH (MPa)	τ (h)	γ	δ
HDPE	2.85	0.82	81	82	0.61	0.64
HDPE	2.85	0.65	48	75	0.73	0.77
HDPE	1.25	0.78	66	54	0.62	0.67
HDPE	1.25	0.67	47	51	0.70	0.76
LLDPE	1.30	0.52	23	68	0.85	0.86
LDPE	0.63	0.50	19	185	0.86	0.87
LDPE	0.63	0.48	15	186	0.90	0.93

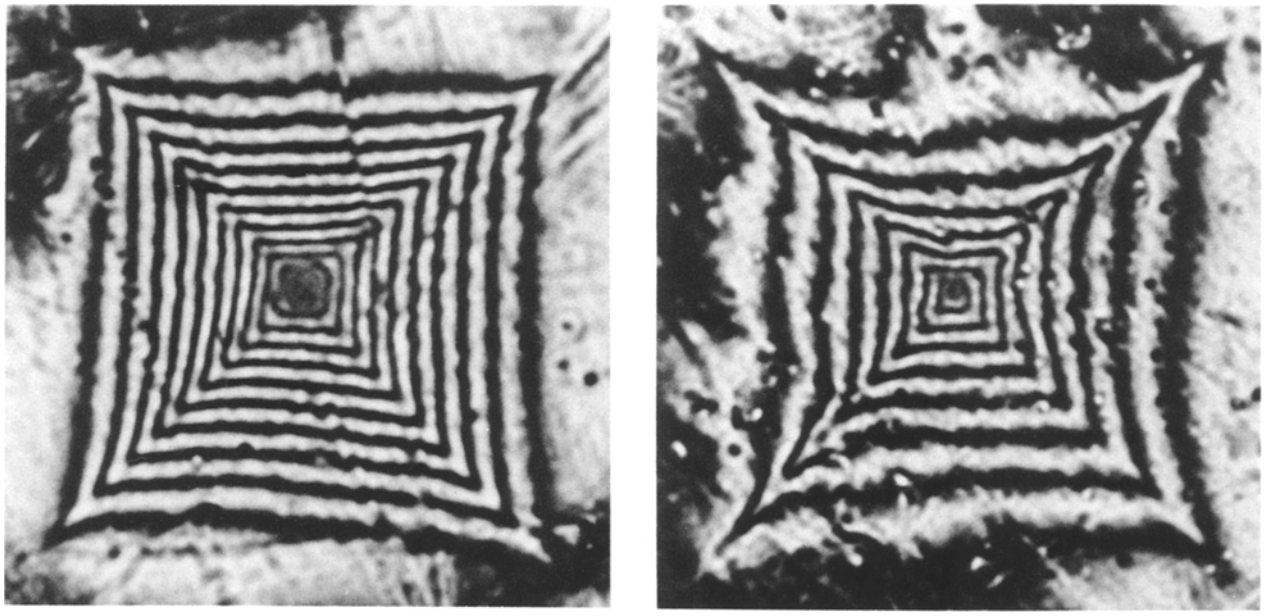

Figure 1 Micrographs of two Vickers indentations in HDPE (left) and LLDPE (right). The diagonal lengths are 75 and 109.5 μm, respectively.

This case is the one taking place in microhardness measurements after releasing the indentor. The depth (h) recovery derived from Equation 4 can be expressed by

$$100h(t)/d = \alpha + \beta \exp(-t/\tau) \quad (5)$$

where $\alpha + \beta$ and α are related to the instantaneous and delayed recoveries respectively and τ is the retardation time. The experimental results fit the proposed model well, as illustrated in Fig. 2.

Due to the Vickers indentor geometry, the value under load of the adimensional parameter $100h/d$ is constant ($= 14.29$) and independent of the impression size and of the microhardness of the material. Thus, the fractional recovery can be given by

$$(14.29 - 100h(t)/d)/14.29. \quad (6)$$

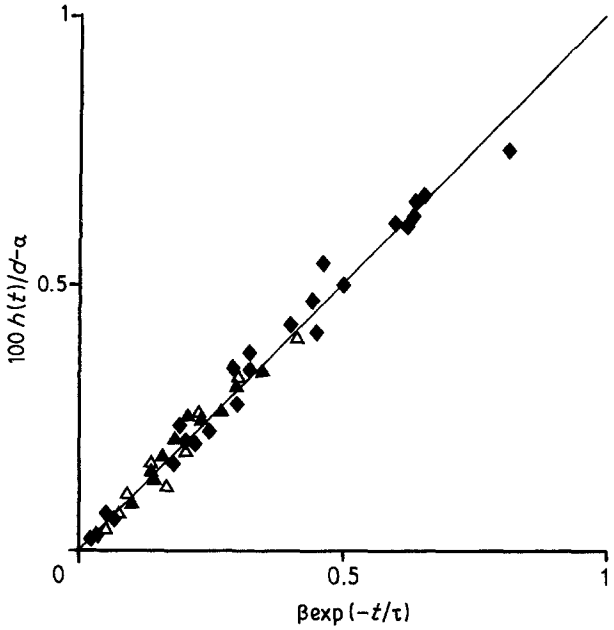

Figure 2 Evolution of depth, according to Equation 4 in the text, for high density (◆), low density (▲) and linear low density (△) polyethylenes.

By combining Equations 5 and 6, the instantaneous and final depth recoveries (γ and δ, respectively) can be expressed for times 0 and ∞, in the form

$$\gamma = [14.29 - (\alpha + \beta)]/14.29 \quad (7)$$

$$\delta = (14.29 - \alpha)/14.29 \quad (8)$$

Table I lists the values of these parameters of the samples studied.

The retardation times τ, also listed in Table I, are roughly constant for each polyethylene type, suggesting that τ is a parameter dependent only on molecular weight and type of branching. In fact, the retardation times in the branched polyethylenes are much higher than for linear polyethylenes which show values of the parameters γ and δ slightly lower than those of branched polyethylenes. With respect to the influence of the molecular weight, the linear polyethylenes show a small decrease of the parameters of the depth recovery and a corresponding increase in the retardation time as the molecular weight increases. However, the slight increase of τ when crystallinity increases does not occur in all the samples and seems to be less important than the increase of the retardation times for branched polyethylenes. This result shows that the studies of the retardation times of the depth recovery of Vickers impressions in polyethylene allows a distinction to be made between its different types even for different crystallinity level. This last parameter, on the contrary, markedly affects the plain microhardness value.

The crystallinity of the polyethylene samples has been also related to the parameters of the depth recovery. Fig. 3 shows that both instantaneous and final recoveries diminish as crystallinity increases. The decrease of crystallinity, determined from density measurements, reveals the larger extent of the non-ordered regions (interfacial and amorphous) which are responsible of the delayed elastic recovery. The results shown in Fig. 3 can be adjusted to straight lines of correlation coefficients 0.995 and 0.990 for the

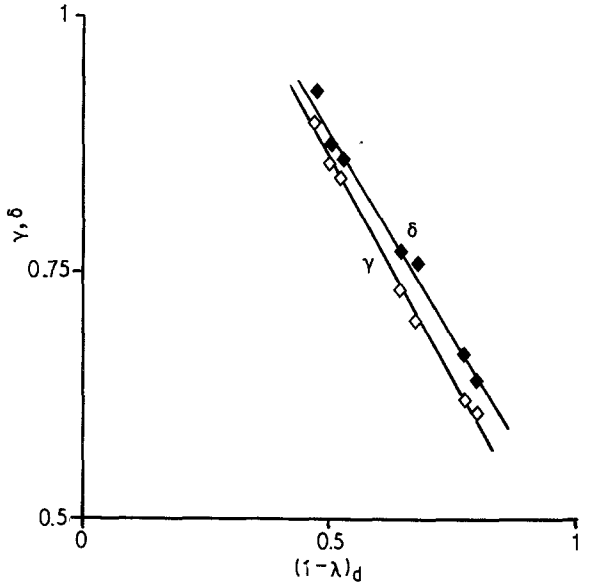

Figure 3 Instantaneous (γ) and final (δ) fractional recoveries as a function of polyethylene crystallinity.

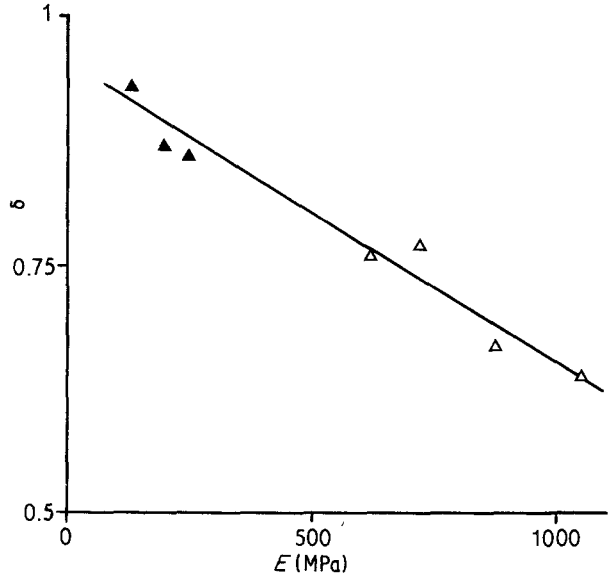

Figure 5 Correlation between final fractional recovery, δ, and Young modulus for high density (△) and low density (linear and branched) (▲) polyethylenes.

instantaneous and final recoveries, respectively. The close similarity of both lines allows us to use only the final recovery, δ, in the following.

The important contribution of the disordered regions to the dimensions of microhardness indentations can also be reasserted by means of considerations about the energy involved in the indentations. We have checked that successive indentations do not change the dimensions of the impression. Thus, the deformations produced by indentations later than the first one are considered to be essentially elastic and the associated energy can be estimated from the potential energy variation when the indentor lowers from the position of the residual impression to the one determined by the geometry of the indentor. These positions have been precisely determined [1] by drawing the geometrical profiles of two cross-sections of a residual indentation. The associated elastic energy is written in the form

$$W_{el} = P\gamma d/7 = \gamma W_t \quad (9)$$

where W_t is the total energy involved in the first measurement. As the γ values for polyolefins range from 0.61 to 0.90 (see Table I), they will be the fractions of energy used for the elastic deformation. In other words, the elastic energy employed in the deformation of non-ordered regions cannot be neglected with respect to the plastic one spent in breaking the crystallites.

The crystallinity level of polymers is a structural factor which plays an important role in their mechanical properties. Thus, the yield stress, Y, and, to a lesser extent, the elastic modulus, E, are governed by the degree of crystallinity [13]. Therefore, a correlation between depth recovery and Y and E values can be expected. Figs 4 and 5 confirm this relation and the results fit straight lines of correlation coefficients 0.99

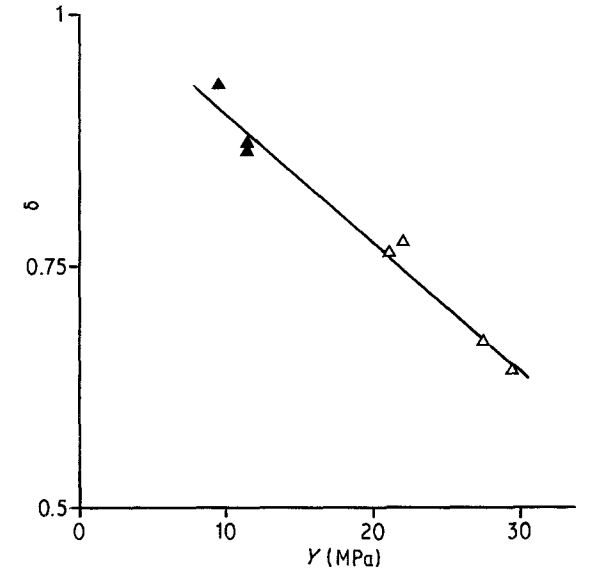

Figure 4 Final fractional recovery, δ, against yield stress for high density (△) and low density (linear and branched) (▲) polyethylenes.

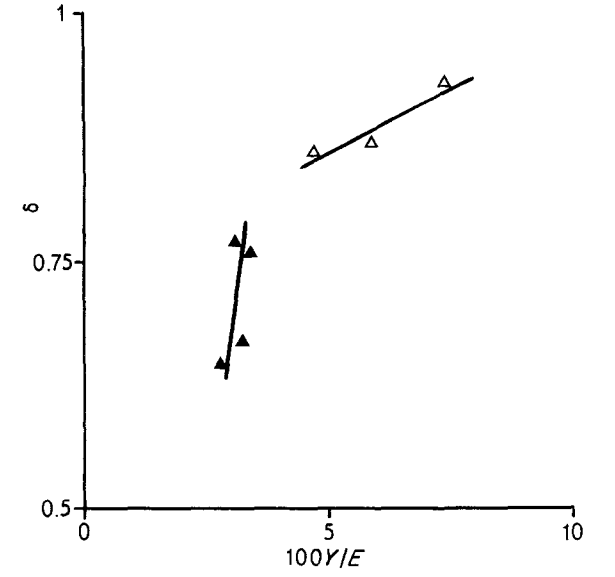

Figure 6 Variation of the final fractional recovery as a function of the yield stress/elastic modulus ratio, for low density (linear and branched) (△) and high density (▲) polyethylenes.

and 0.98 for Y and E respectively. Moreover, there is another linear relation (correlation coefficient 0.99) between the depth recovery and the microhardness values listed in Table I.

These linear relations contrast with the equation proposed by Lawn and Howes [7] for ceramics and steels, which is

$$(2h/d)^2 = k^2 \cot^2\psi - [2(1-\nu)^2 k^2 \cot\psi]\, MH/E \quad (10)$$

where k is a geometrical factor, $\psi = 74°$ and $\nu = 0.41$ is the Poisson ratio of polyethylene [14, 15]. Breval and MacMillan [16] have modified Equation 10 by adding to it the MH/E square term. Notwithstanding, the proposed correction is practically negligible for MH/E values ranging from 0.07 to 0.15. i.e., those of the polymers. We have reported previously [1] that the recovery of Vickers indentations in polymers does not obey Equation 10 and here we have shown that it is directly related to E, Y and MH, separately.

Finally, it is worthwhile to point out the relation between depth recovery and the ratio Y/E. It is clear from Fig. 6 that polyethylene samples lie along two different straight lines, according to their densities. This fact shows again the influence of the structure of polyolefins on the microhardness indentations. This influence is manifested on the depth recovery reported in this work and also on the dimensions of the indentation surface which is going to be published elsewhere [6].

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