

# Annealing effects in lamellar linear polyethylene as revealed by microhardness

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The changes in surface microhardness of lamellar polyethylene, as a consequence of annealing treatment, have been investigated. The variations in hardness are interpreted in terms of morphological changes primarily related to the lamellar thickness. In the low temperature range, hardening is related to elimination of crystal defects. In the intermediate annealing range the rapid hardness increase can be associated with a well-defined stacking of lamellae which thicken with increasing temperature. Nearer the melting point the regular good lamellar stacking is destroyed through partial melting and recrystallization, yielding a larger proportion of new thin lamellae which contribute to the drastic hardness depression observed.

## 1. Introduction

In recent years the understanding and controlling of the surface mechanical behaviour of polymers, especially polyethylene (PE), has been the object of intensive activity in this laboratory [1–7]. A correlation of microhardness (MH) with various elements of polymer characterization – chain structure, chain packing, coherently diffracting lattice-volume, macroscopic density – has been established [2]. Nonetheless, the most revealing fact is that, irrespective of a given texture, hardness is a property which is directly related to the thickness of the crystalline lamellae densely stacking within the solid [8]. The detailed molecular and supermolecular mechanisms, involving a local irreversible deformation of the polymer microstructure at strains above the yield point, have been discussed elsewhere [2, 6]. Thus thicker lamellar crystals having larger equilibrium cohesion energies oppose a greater resistance to plastic compression under the indenter than thinner ones. The latest studies [9, 10] show, in addition, that the penetration of electron-dense groups within the amorphous interphase of the composite lamellar structure in PE, modify the stability of the crystallites, reinforcing the mechanical behaviour of the material and yielding hardness values in the vicinity of some metals. It is useful at this point to examine the effect of annealing on the

microhardness behaviour of PE. It is known that annealing is a convenient method of increasing the polymer strength [11]. This method is frequently applied in the manufacture of fibres and films. However, despite the numerous studies on annealing in the past 25 years [12] there remains a lack of agreement concerning the underlying molecular mechanisms responsible for the annealing effects observed.

The purpose of this investigation is to explore how the hardening of PE proceeds as a function of annealing temperature, in the light of changes in the lamellar structure, as revealed by electron microscopy (EM), small-angle X-ray diffraction (SAXS), and differential scanning calorimetry (DSC). Specifically, the sudden decrease in hardness near the melting point is discussed in terms of the melting of a fraction of lamellae followed by recrystallization, with a consequent change in the lamellar properties.

## 2. Experimental details

In this study we have used linear polyethylene Rigidex 9 (BP chemical Ltd) ( $M_n = 11\,700$ ,  $M_w = 169\,000$ ). The sample was prepared as 1 mm thick moulded sheet at atmospheric pressure by cooling from the melt at  $1\text{ K min}^{-1}$ . Sheets of this polymer were annealed at temperatures between 85 and 130°C, wrapped in aluminium foil and

immersed in a Wood's metal bath. Following their removal after 1 h they were quenched in ice-water. The hardness values were measured using a microhardness tester with a square-pyramidal indenter of 100  $\mu\text{m}$  height. The material hardness was obtained by computing the ratio of peak contact-load to the projected area of the impression:  $\text{MH} = kP/d^2(\text{Pa})$ ; where  $d$  is the length of the impression diagonal,  $P$  is the load applied (1N) and  $k$  a constant equal to 1854.4. A loading cycle of 0.1 min was used.

The SAXS patterns of the samples were obtained at room temperature using point collimation pairs of 0.3 to 0.2 mm and a rotating anode X-ray generator operating at 40 kV/200 mA. The diffraction patterns were recorded on to films though a position linear sensitive counter was also employed for preliminary checks. The long periods were calculated according to Bragg's law from the maxima of the scattering observed after background subtraction. The position of the maxima can be estimated to within  $\Delta L/L \sim 4 \times 10^{-2}$ . As the condition of large lateral coherence dimensions is not met in these crystals, the maxima were not corrected with the  $\theta^2$  Lorentz factor [13].

The DSC curves were recorded using a Perkin Elmer IB calorimeter at a scanning speed of 16 K  $\text{min}^{-1}$  in the sensitivity range of 4  $\text{mcal sec}^{-1}$ . The melting temperatures recorded are the peaks of traces calibrated against indium. A density gradient column was employed using a mixture  $\text{CCl}_4/p$ -xylene (17 vol%  $\text{CCl}_4$ ) to determine the densities of the samples investigated.

Sections of the samples at various stages of annealing were obtained for electron microscope observations using Kanig's chlorosulphonation method [14]. The conditions for the acid treatment were selected according to previous studies [15]. The sections were collected on to carbon-coated grids and observed in the TEM under very low beam intensity to minimize shrinkage effects. [16].

### 3. Results and discussion

It is known that most of the annealing changes occurring in polymers with a lamellar morphology can be described in terms of three temperature ranges (I, II and III) [12]. However, these three temperature regions, when measuring properties such as crystallinity or lamellar periodicity, are not so well defined for melt-crystallized samples. Our aim is to show that the variation of MH, and

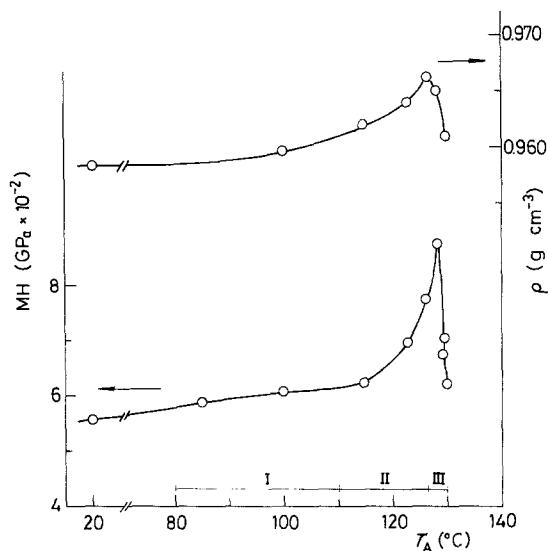


Figure 1 Variation of microhardness and density of lamellar linear PE (Rigidex 9) upon heating to temperature ranges I, II and III.

macroscopic density ( $\rho$ ) as a function of annealing temperature ( $T_A$ ), yields three well-differentiated regions of behaviour (Fig. 1). While in region I, MH and  $\rho$  just show a slight increase with  $T_A$ , the value of  $L$  given in Fig. 2 remains nearly constant. In region II the three quantities show a more conspicuous and rapid increase with  $T_A$ . Finally, in region III, MH reaches its highest value of 0.088 GPa at 128 $^\circ$  C, falling thereafter, approximately to the value for the untreated material ( $\sim 0.06$  GPa). It is noteworthy that the maximum

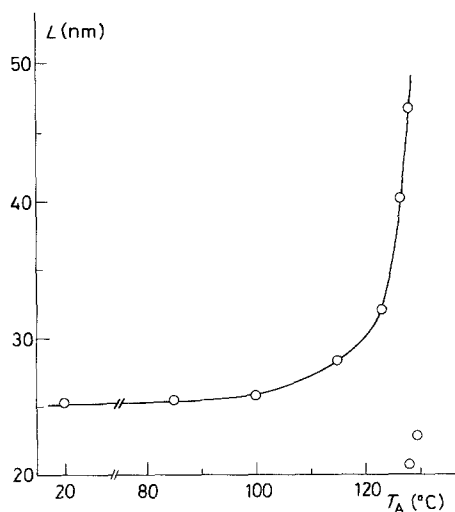


Figure 2 Long periods of the melt-crystallized PE investigated after annealing at  $T_A$ .

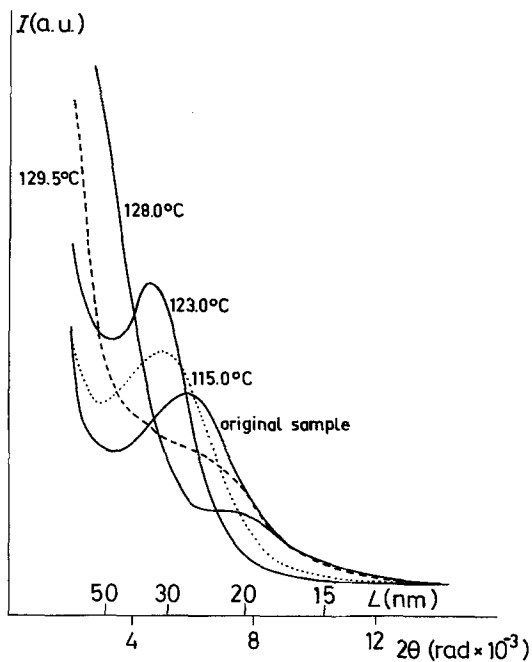


Figure 3 Microdensitometer of scattering intensity plotted against  $\theta = \lambda/L$  for annealed PE samples at various temperatures. The curves were taken at room temperature.

hardness value obtained is comparable to the level of surface hardening occurring after exposure to sulphuric acid for a few hours [10]. The dramatic decrease in MH is followed by a concurrent decrease in density. Simultaneously, at 128°C, in addition to the maximum value of  $L$  at 48 nm, a second periodicity of 20 nm emerges (Fig. 2).

Annealing in region I heals crystalline defects [17], probably through a solid diffusion mechanism of defects towards the surface layer [18]. This mechanism improves the packing of the chains within the crystals and gives rise to the observed increase in X-ray scattering intensity and microhardness in region I. The dependence of MH on the packing density of the macromolecules within the crystals has been shown previously [2]. At intermediate temperatures (region II) the rate of the lamellar-periodicity increase is equal to the rate of hardening. In this region the lamellar thickness consequently increases without the melting of crystals contributing to the overall rise in hardness. Evidence for this is shown independently from the gradual shift of the endothermic peak towards higher temperatures (Fig. 4). Nevertheless at  $T_A \sim 128^\circ\text{C}$  an incipient peak at a lower temperature suggests the start of the melting and recrystallization of a few lamellae within the mat-

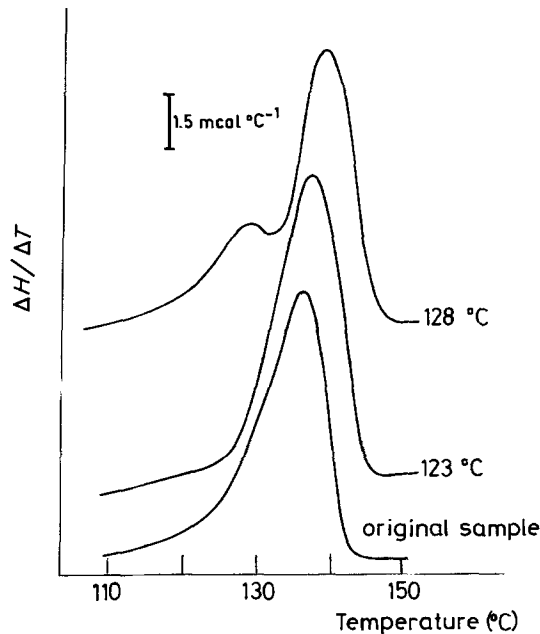
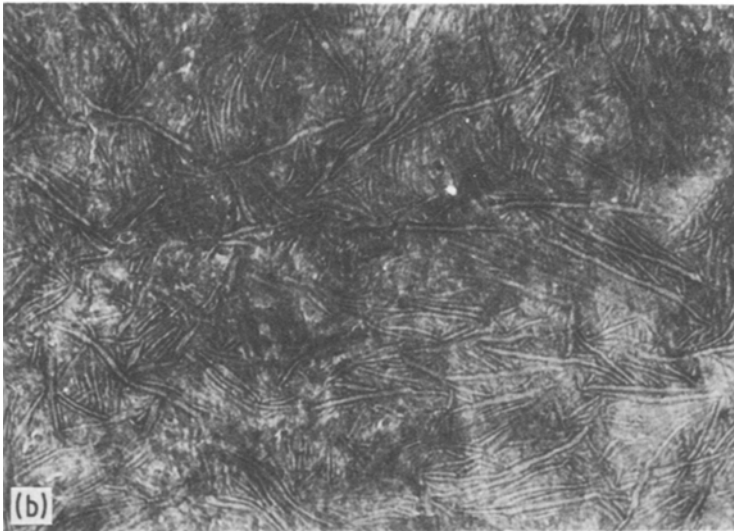
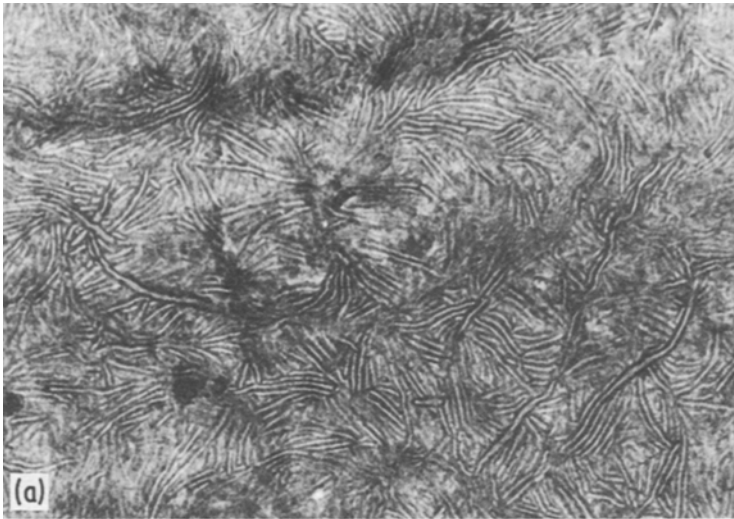
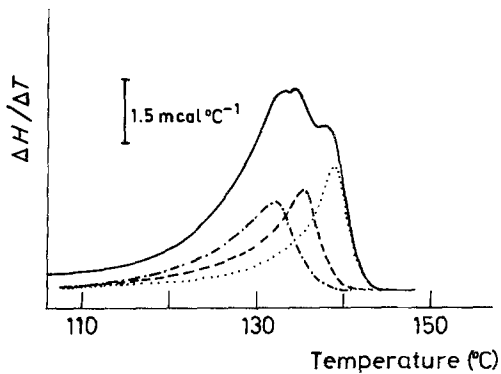


Figure 4 Shift of the melting peaks for PE annealed in range II. The appearance of a second weak lower peak at  $T_A = 128^\circ\text{C}$  indicates a partial recrystallization of the material into thinner lamellar stacks.

erial. Fig. 5a illustrates the lamellar structure of the annealed sample near 123°C, showing a fairly regular stacking with only a few thicker lamellae. In the high temperature region (III), close to  $T_M$  (130.5°C), the appearance of a second periodicity (Fig. 2) indicates the coexistence of two distinct stackings of lamellae: (a) is due to a further thickening of the original lamellae, and (b) is caused by a melting and subsequent recrystallization of a fraction of thinner lamellae. However, since the thick lamellae predominate at 128°C (Fig. 4), they are the ones dictating the plastic deformation of the material which contributes to the highest MH value detected. At the final stage of annealing (129.5°C) the second periodicity appears clearly at 22 nm (Figs. 2 and 3) while the first maximum is just hardly detectable. The existence of the thickest crystals is, nevertheless, clearly assessed by the presence of a very high melting peak (137°C) (Fig. 6). The later stage of the annealing process is additionally supported by the electron micrograph of Fig. 5b), illustrating the presence of well-defined thick independent wide lamellae and a larger proportion of thinner ones. It is noteworthy that the regular good stacking of Fig. 5a (at 123°C) has been destroyed at 129.5°C (Fig. 5b), and the lamellar stacking is



*Figure 5* Electron micrographs of PE film taken at room temperature: (a) annealed for 1 h at 123°C (range II); (b) annealed for 1 h at 129.5°C (range III). The bright lines correspond to the crystals ( $\times 40\,000$ ).



*Figure 6* Melting endotherm with resolved peaks of PE annealed at 129.5°C (range III).

now more local and less perfect. This irregular structure of dominant thin lamellae alternated by a few thick ones contributes to the notorious depression of the overall hardness in region III.

In conclusion, the microhardness technique allows one to adequately distinguish between the three regions of annealing for lamellar melt-crystallized PE. In region I there is a smooth linear hardening of the material ( $\sim 1 \times 10^{-3} \text{ GPa deg}^{-1}$ ) with  $T_A$  associated with an improvement of crystal perfection, possibly due to the diffusion of kinks towards the surface layer. At the intermediate temperature region (II), a much faster hardening process ( $\sim 20 \times 10^{-3} \text{ GPa deg}^{-1}$ ) caused by a lamellar thickening mechanism is detected.

Finally region III is characterized by a sudden drop in MH due to a substantial recrystallization of locally molten crystals, into thinner lamellae, which are competing with a smaller fraction of the remnant thicker and wider isolated lamellae.

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