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# Correlation of hardness and microstructure in unoriented lamellar polyethylene

## Part 2 *Study of elastic modulus*

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The stress–strain diagrams of a series of melt-crystallized polyethylene samples with a varying number of chain defects have been investigated. The elastic modulus, *E*, and the surface hardness, *MH*, markedly decrease with increasing number of defects. The mechanical behaviour of the lamellar structure of PE modulated by a major exclusion of chain defects from the crystals is discussed in the light of Takayanagi's two-phase model. The data suggest that *E* is very sensitive to the fraction of tight crystalline bridges between lamellae. The correlation found between *E* and *MH* emphasizes, in addition, the different and complementary role played by the amorphous layer in each mechanical test. In the former case one measures the elastic deformation of the layer reinforced by tie molecules. In the latter test the plastic deformation under compression of the lamellae sandwiched between noncrystalline layers is contemplated. In both cases the influence of the number of defects drastically affects the nature of the crystalline lamellae and surface layer and consequently substantially modifies both types of properties.

## 1. Introduction

In a previous study [1] the local deformation of the lamellar structure of melt-crystallized polyethylene was investigated using micro-indentation hardness. The surface hardness of the material was discussed on the basis of a composite structure consisting of "hard" lamellae separated by "weak" amorphous layers. It was shown that the critical stress needed to deform plastically the lamellar structure was dependent on the dimensions of the unit cell, degree of lattice perfection and lamellar thickness. The materials having thinner and less perfect crystals were found to be more readily indented. Furthermore, microhardness was shown to depend conspicuously on the macroscopic density of the material. In order to cover a wide range of structural parameters [2], samples with varying concentrations of chain defects (branches, unsaturations) were analysed.

The purpose of the present paper is to extend the earlier studies [1] to the investigation of the elastic modulus of the samples as a function of their microstructure and to explore whether there is any correlation between this property (reversible elastic deformation of lamellar microstructure at very small strains) and the value of microhardness (irreversible plastic deformation of the structure at larger strains, above the yield point).

## 2. Materials and methods

We have investigated a series of commercial polyethylene samples with a varying range of chain defects and of molecular weights (Table I). The samples for the mechanical test were 0.7 mm thick plates which were formed by melting for 3 min at 60° C, under a pressure of 10 MN $m^{-2}$ to remove air bubbles. The samples were then cooled down at a rate of 1° C $min^{-1}$ to room temperature. In order to investigate the texture by means of optical microscopy, samples of 50 to 100 $\mu m$ thickness were crystallized under the same conditions. For the measurement of the elastic modulus the samples were cut in the usual dumb-bell form. The width of the sample in the

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TABLE I Molecular weight defect concentration, elastic modulus, microhardness, density, crystallinity and spherulite radii of the samples investigated

| Sample | $M_n$ (X $10^3$) | $M_w$ (X $10^3$) | $\epsilon$ (%) | $E$ (MN m$^{-2}$) | $HV$ (MN m$^{-2}$) | $\rho$ (g cm$^{-3}$) | $\alpha$ | $R$ ($\mu$m) |
|---|---|---|---|---|---|---|---|---|
| Sclair 2907* | 9.3 | 53.6 | 0 | 2400 | 85 ± 4 | 0.968 ± 0.001 | 0.80 | 30 ± 3 |
| Sclair 2407 | 9.3 | 53.6 | 0 | 1480 | 77 ± 4 | 0.068 ± 0.001 | 0.73 | 30 ± 3 |
| Lupolen 5011 | – | 120.00 | 0.70 | 450 | 53 ± 3 | 0.953 ± 0.001 | 0.60 | 10 ± 4 |
| Hostalen GF | – | – | – | 1045 | 63 ± 3 | 0.952 ± 0.001 | 0.68 | 20 ± 4 |
| Epolene N12 | 2.10 | 11.55 | 2.63 | 600 | 40 ± 2 | 0.935 ± 0.001 | 0.50 | 20 ± 5 |
| Lupolen 1810 | – | 54.00 | 3.04 | 255 | 19 ± 1 | 0.910 ± 0.001 | 0.42 | 5 ± 2 |
| Epolene C13 | 11.30 | 284.50 | 3.61 | 84 | 18 ± 0.5 | 0.905 ± 0.001 | 0.37 | 23 ± 7 |
| Epolene C10 | 6.50 | 20.95 | 4.77 | 50 | 17 ± 1 | 0.898 ± 0.001 | 0.29 | 24 ± 6 |
| Epolene C101 | 4.35 | 18.30 | 5.34 | 120 | 17.5 ± 1.0 | 0.904 ± 0.001 | 0.37 | 38 ± 8 |
| Epolene C12 | 4.00 | 11.00 | 6.90 | 20 | 6.5 ± 0.5 | 0.887 ± 0.001 | 0.20 | 18 ± 5 |

centre was 2.5 mm and the gauge length 10 mm. The samples were tested in an Instron machine at a rate of 0.1 mm min$^{-1}$ at room temperature. The elastic modulus was determined at a strain of 1%.

The microhardness was measured using a Vickers microhardness tester with a Vickers square pyramidal diamond. A loading time of 0.1 min and a load of 20 g were used. Non-elastic recovery was detected (for further details see previous references) [1]. The samples had a spherulitic texture which was recognized by using a polarizing microscope. The average radius of the spherulites was measured by light scattering using a laser source of $\lambda = 632.8$ nm in combination with crossed polarizers [3]. The volume fraction of crystalline material was derived from the enthalpy of fusion measured with a Perkin-Elmer DSC II taking a value of $\Delta H = 2.8 \times 10^8$ J m$^{-3}$ for the crystalline phase. The macroscopic density was measured using a density gradient column containing 57% toluene ($\rho = 864$ kg m$^{-3}$ and 43% dioxane ($\rho = 1030$ kg m$^{-3}$)).

## 3. Results

The elastic modulus, the microhardness, the density and the crystallinity of the investigated samples are collected together in Table I. Fig. 1 illustrates the true stress as a function of the strain for different chain defect contents ($\epsilon$). One can see that the elastic modulus dramatically decreases with increasing number of defects. For $\epsilon < 3\%$ the macroscopic deformation proceeds through neck formation whereas for $\epsilon > 3\%$ the macroscopic deformation occurs homogeneously when the yield point is reached. Fig. 2 shows the existence of a clear correlation between elastic modulus and microhardness. It is noteworthy that for very low values of $E$ ($< 300$ MN m$^{-2}$) hardness represents a more sensitive and readily obtainable quantity. Fig. 3 confirms the previously obtained relationship between microhardness and density. However, the character of the present curve is quadratic and it does not show the sigmoidal variation previously inferred [1]. This may be due to the fact that the present samples were crystallized in air and the former ones were crystallized in silicone oil. We suspect

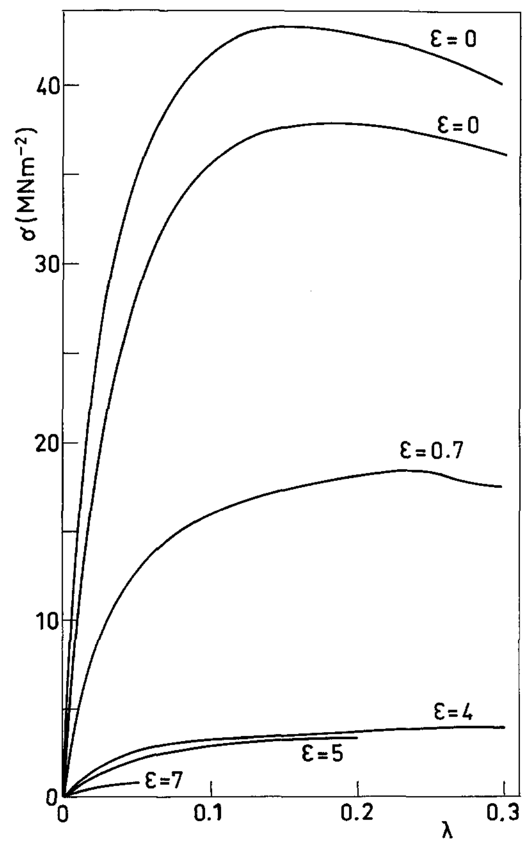


*Figure 1* True stress–strain curves for various LDPE samples with differing number of defects.

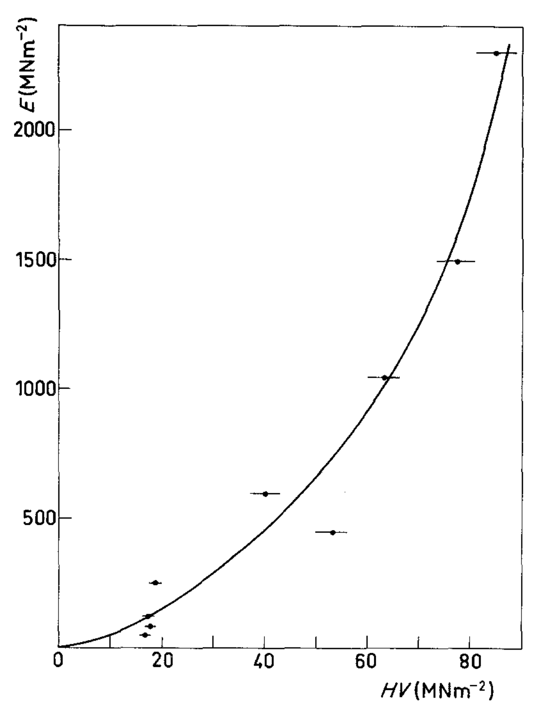


*Figure 2* Elastic modulus as a function of microhardness for different samples of LDPE.

that penetration of silicone oil at high temperature may have contributed to the softening of the material in the previous work.

Fig. 4 shows the typical spherulitic texture for three polyethylene samples with increasing defect concentration. As can be observed, the spherulitic size is similar in the three cases. This is confirmed by the light scattering patterns of the samples showing radii of ~20 to 30 μm. We admit that segregation of low molecular weight material towards the edge of the spherulites may have occurred [4]; however, in this mode of crystallization such segregation could not be seen.

## 4. Discussion

The unoriented crystalline polymer solid is a two component system with the lamellae separated by amorphous layers containing chain folds, free chain ends and tie molecules. The stacks of parallel lamellae are included in the spherulites [5] as ribbons emerging radially from the centre. Shearing motions and normal deformation leading to lamellar separation are the expected deformation modes of the amorphous regions at small strains. These modes are impeded by the presence of tie molecules. Since the crystalline regions are very much stiffer than the amorphous regions, the local strain in the amorphous component should, on average be higher and in the crystalline component smaller than the macroscopic strain. In such a composite structure the lamellae will act as force transmitters and the amorphous layers reinforced by tie molecules become the main contributors to the strain. In addition, the complicated spherulitic morphology of the solid makes the stress and strain fields extremely inhomogeneous [6]. A simplified approach at this level is to assume that these stress–strain fields are, on a macroscopic scale at least, similar in samples with similar spherulitic sizes. This size is mainly controlled by the presence of heterogeneities [7]. Thus in this work we have chosen samples with similar concentrations of nucleation density giving rise to a comparatively uniform spherulitic size.

The next question arises: How does the presence

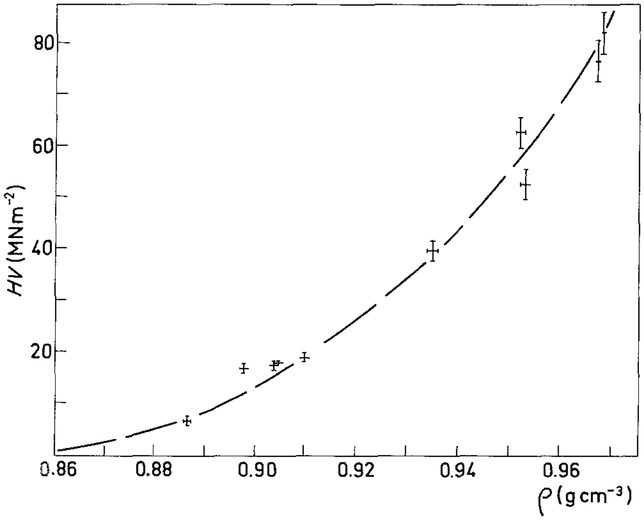
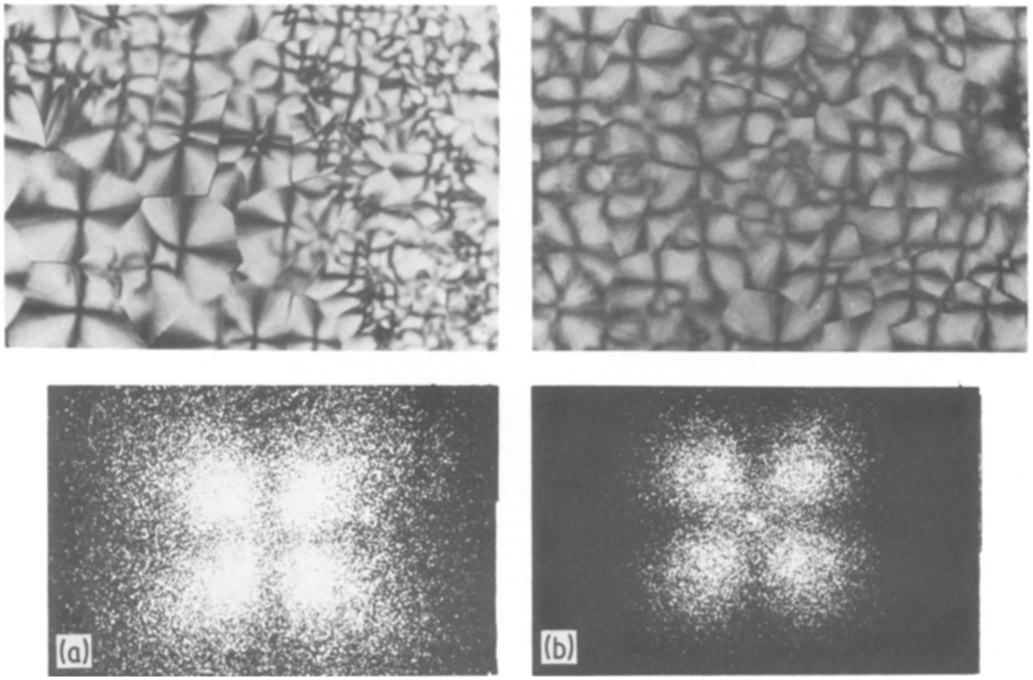


*Figure 3* Dependence of microhardness on macroscopic density.



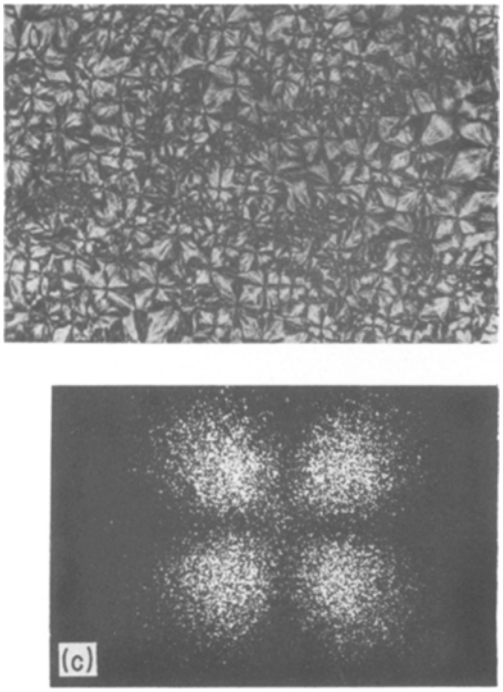


*Figure 4* Spherulitic morphology and SALS of LDPE with different chain defect concentrations. (a) Linear; (b) $\epsilon = 4.8\%$; (c) $\epsilon = 6.9\%$. Scale: 2.8 mm ≡ 10 μm.

of chain defects affect the value of the modulus? In a previous study [2] we showed that the majority of chain defects tend to be rejected from the lattice. As a result the crystalline lamellae are thinner and the amorphous layers thicker with increasing numbers of chain defects. Consequently one may expect that, for a given stress, the strain will increase and the modulus will consequently decrease with the thickness of the amorphous layer, i.e. with increasing defect concentration. This expectation is substantiated by the data of Table I and Fig. 1.

We can describe the reversible mechanical response of the lamellar structure of PE with chain defects in the light of the oversimplified, though useful, model suggested by Takayanagi [8]. This model takes into account the one-dimensional lamellar structure with alternation of crystalline and amorphous layers. Nearly all the crystalline component, $\alpha$, is located in the crystalline layers with a small fraction, $\psi$, bridging the amorphous layer (see Fig. 5). Hence one has the largest part of the crystalline material occupying a volume fraction, $\phi$, of the sample in series with a two-component layer having a parallel arrangement of amorphous and crystalline material occupying a fraction $1 - \psi$ and $\psi$ of the layer, respectively. The crystalline bridges can be taut-tie molecules connecting the lamellae – the presence of crystalline bridges connecting lamellae has been recognized in the past [9] – and evidence

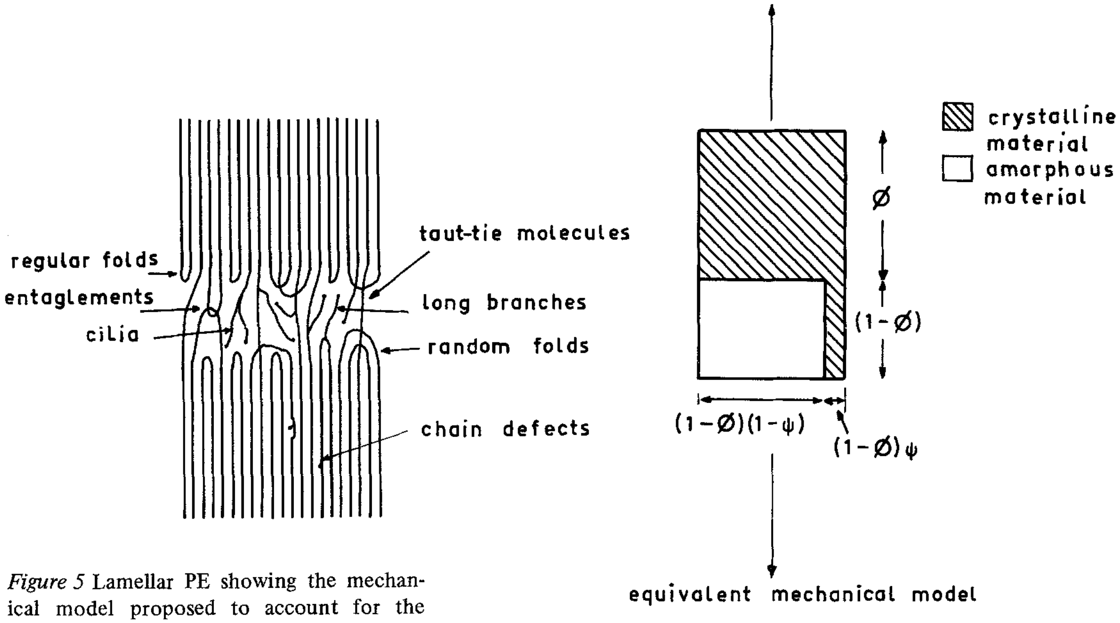


*Figure 5* Lamellar PE showing the mechanical model proposed to account for the variation of PE against $\alpha$.

is shown in Fig. 6 for a sample of high molecular weight polyethylene fraction crystallized from the melt. The elastic modulus of this model is given by:

$$1/E = (1-\phi)/\{\psi E_c + (1-\psi)E_a\} + \phi/E_c \quad (1)$$

where $E_a$ and $E_c$ are the moduli of the amorphous and crystalline component, respectively. If one assumes a ratio $E_c/E_a \sim 500$ (for instance, $E_c \sim 5\,\mathrm{GN\,m^{-2}}$ and $E_a \sim 0.01\,\mathrm{GN\,m^{-2}}$, respectively [10]) then one expresses the ratio $E/E_a$ as a function of crystallinity, $\alpha$, and bridging parameter, $\psi$, in the following simplified form:

$$E/E_a \simeq (1 + 500\psi)/(1-\alpha) \quad (2)$$

In Fig. 7 we have plotted the ratio $E/E_a$ as a function of $\alpha$ according to Equation 2 for several values of $\psi$. The experimental data for the samples investigated are also plotted in Fig. 7. These results suggest that not only does the elastic modulus decrease with increasing volume fraction of non-crystalline content, but also that it is very sensitive

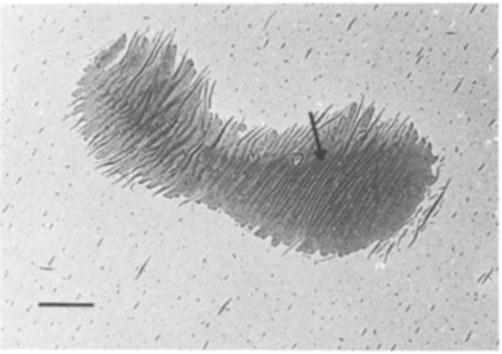


*Figure 6* Electronmicrographs of high molecular weight PE showing intercrystalline links. Scale bar = 50 nm.

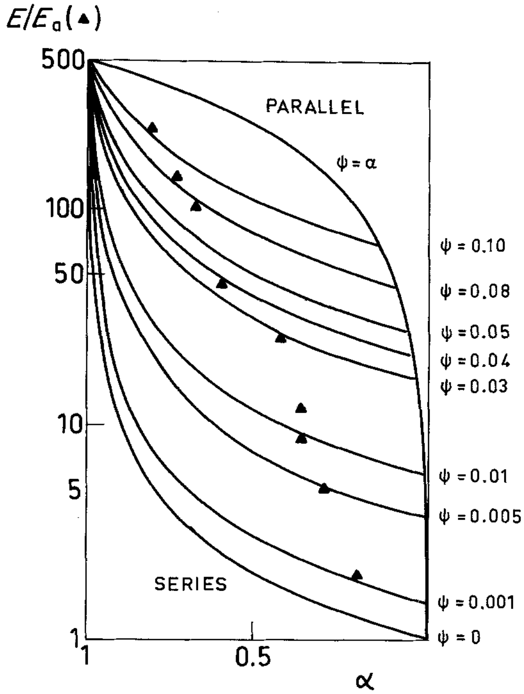


*Figure 7* Plot of $\log E$ against $\alpha$ for different values of $\psi$ according to Equation 2. The experimental data for the LDPE samples investigated are given.

to the bridging parameter (number of tie-taut molecules). The fraction of tight bridges calculated on the basis of this model decreases, in fact, from $\psi = 10\%$ for $\alpha = 0.8$ to $\psi = 0.01\%$ for $\alpha = 0.2$.

Finally, in comparing the correlation found between $E$ and $MH$ (Fig. 2) one should emphasize that while in the former case the major role is played by the amorphous layer reinforced by tie molecules, which is elastically deformed at small strains, in the latter case the plastic deformation of the lamellae at larger strains seems to depend markedly on crystal thickness and perfection. In addition, with the introduction of chain defects, while the crystal thickness and crystal perfection diminish the amorphous layer is simultaneously enhanced. This complementary influence of $\epsilon$ on the nature of crystalline lamellae and amorphous layers seems to contribute to the observed correlation between $E$ and $MH$.

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