Microhardness studies of chain-extended PE: I. Correlations to microstructure

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ABSTRACT

The hardness-microstructure correlation of various polyethylene (PE) samples crystallized at high pressure from the melt (chain-extended), with different molecular weights, has been investigated and compared to melt crystallized samples at atmospheric pressure (chain-folded). The hardness, H , of melt crystallized PE is confirmed to increase linearly with the logarithm of the annealing time, t_a , at a constant annealing temperature. The H increase with t_a is discussed in terms of the crystallinity and crystalline lamellar thickness variation. Unusually high hardness values are obtained for samples crystallized or annealed at high pressure as a consequence of the resulting high degree of crystallinity and large crystalline lamellar thickness values. However, it is shown that the high surface free energy value of the chain-extended crystals considerably lowers the hardness values from that of an ideal infinitely thick PE crystal. Analysis of the crystal hardness and the melting temperature data of different polymeric materials emphasizes the close existing relationship between both quantities.

Key Words: Microhardness, Chain-extended crystals, High pressure, Crystallization, Melting temperature.

INTRODUCTION

Since a model of local plastic deformation of lamellae stacks under a standard indenter was developed ¹, extensive research has provided experimental evidence of a close relationship between hardness and microstructure in polymeric materials ¹⁻³. According to the above studies, the microhardness of the lamellae crystallites, H_c , is related to the average lamellar thickness, l_c , through:

$$H_c = \frac{H_c^\infty}{1 + \frac{b}{l_c}} \quad (1)$$

where H_c^∞ is the hardness of an infinitely thick crystal and b is defined as $b=2\sigma_c/\Delta h$, where σ_c is the surface energy of the crystals and Δh is the energy required to plastically deform the crystalline lamellar stacks ¹.

Early microindentation studies on oriented chain-extended polyethylene (CEPE) already revealed the tendency of the hardness to increase with increasing average lamellar thickness ⁴. The crystal hardness of linear PE chain folded lamellae has also been shown to vary with l_c through equation (1), yielding for $H_c^\infty \sim 170$ MPa and b values in the range 10-30 nm ⁵⁻⁷. The microhardness of a series of melt crystallized polyethylene samples was investigated in a wide range of molecular weights ⁵⁻⁷. H_c , in this case, was shown to diminish with increasing molecular mass, M_w , up to $M_w \sim 2 \times 10^5$ g/mol in spite of the fact that l_c shows a parallel increase with M_w over the same molecular weight range ⁵⁻⁷. The dominant influence of b on the H_c values was then evidenced. The b -parameter increase with M_w was explained as a consequence of an increase in the number of entanglements and other defects at the crystal surface ⁵⁻⁷. For chain folded high molecular weight PE samples ($M_w > 2 \times 10^5$ g/mol), H_c , l_c and b appeared to be constant with increasing M_w ⁵⁻⁷. The b -values leveling-off at $M_w \sim 2 \times 10^5$

g/mol was interpreted in terms of a saturation of defects at the crystal surface. The crystallization conditions were also shown to influence the crystal hardness values ^{5,7}. H_c , l_c and the b-parameter values of quenched PE samples were shown to be lower than those corresponding to slowly cooled samples.

Although the hardness-microstructure correlation has been widely explored in melt crystallized PE at atmospheric pressure (chain folded lamellae), a study of the microhardness of melt isotropic high pressure crystallized (or annealed) PE is still missing. It is known that linear PE, after high pressure crystallization (~5 kbar), appears to have thicknesses in the micron range (chain-extended lamellae) in contrast to the material crystallized from the melt at atmospheric pressure composed of lamellae several tens of nm thick ^{8,9}.

The present paper is the first of a series of three concerning the study of the microhardness of chain-extended PE as compared to chain-folded PE. In part I, we report on the hardness-microstructure correlation of high pressure crystallized/annealed PE. In part II, the creep behaviour of chain-folded and chain-extended PE samples crystallized or annealed under various conditions is examined. The main concern in part III is the correlation of the microhardness of lamellar PE with other measured mechanical properties such as the yield stress and the elastic modulus.

EXPERIMENTAL

Materials

Work was concentrated upon commercial PE samples: Rigidex 9 (B. P. Chemicals Ltd.) and Hifax 1900 (Hercules Powder Co. Inc.), supplemented by a fraction of PE extracted

from Rigidex polyethylenes by solvent treatment ¹⁰. Hifax has a molecular weight in excess of two million while $M_n=11.700$ g/mol and $M_w=155.000$ g/mol for Rigidex.

Initially, both the standard and the high molecular weight materials were prepared as a 1 mm thick molded sheets at atmospheric pressure by slow cooling from the melt. These samples have not only been studied themselves but also subjected to various further treatments. Portions of such sheets were wrapped in aluminum foil, immersed in a glycerin bath at 130 °C for various periods of time and subsequently quenched in ice water.

High pressure annealing was performed at 5.35 kbar for 15 minutes and various temperatures according to the procedure of Bassett and Carder ¹¹.

High pressure crystallization consisted of cooling from the melt at 260°C and 4.95 kbar at a rate of ~ 1 Kmin⁻¹.

Techniques

Samples have been characterized with respect to density, lamellar thickness and melting behaviour.

Density values to ± 0.004 g/cm³ were obtained at 23.0°C with a column of mixed toluene and carbon tetrachloride. The volume degree of crystallinity, α , was derived from density measurements following:

$$\alpha = \frac{\rho - \rho_a}{\rho_c - \rho_a} \quad (2)$$

where ρ is the macroscopic density, ρ_c is the density of the crystalline phase and ρ_a is the density of the amorphous phase ($\rho_a=0.860$ g/cm³). The density of the crystalline phase has been shown to decrease with increasing molecular mass ⁶. Hence, we take $\rho_c = 0.999$ g/cm³ and $\rho_c = 0.998$ g/cm³ for the standard and the high molecular weight material respectively.

Portions of all specimens were immersed in 95% nitric acid at 60°C for 3 days and then measured for molecular length by gel permeation chromatography (GPC) ¹². GPC has been shown to give a reliable measure of crystal thickness for chain-extended polyethylenes. Small angle X-ray scattering (SAXS) experiments using a Rigaku Denki camera and a sealed 1kW tube were carried out on chain-folded Rigidex 9 samples. CuK_α radiation with a Ni filter was used. The long period, L, is derived from the first order Bragg maximum. The crystalline lamellar thickness, l_c , is obtained using:

$$l_c = \alpha L \quad (3)$$

where α is at least 0.70.

The melting temperatures, T_m , for all samples investigated correspond to the peaks of the traces taken at 8Kmin⁻¹ with a Perkin Elmer DSC 1B calibrated against indium.

Hardness, H, was measured from the residual impression left behind by the indenter after a six seconds indentation time. A Vickers diamond was utilized and loads of 147, 245, 490 and 981 mN were used to correct for the instant elastic recovery. Vickers hardness is defined as ¹³:

$$H = k \frac{P}{d^2} \quad (4)$$

where P is the applied load, d is the diagonal of the indentation and k is a geometric factor equal to 1.854. At least ten imprints were made under each load. The H-value was determined within $\Delta H/H \approx 0.05$.

The crystal hardness is calculated assuming that plastic deformation takes place only in the crystalline regions ¹³:

$$H = H_c \alpha \quad (5)$$

RESULTS

Chain folded PE: hardness variation with annealing time

Table 1 collects the values of the density, crystallinity, long period, crystalline lamellar thickness as derived using equation (3), Vickers hardness, crystal hardness (derived using equation (5)) and melting temperatures for the PE samples annealed at $T_a=130^\circ\text{C}$ for different annealing times, t_a . Figures in brackets refer to the proportion of material melting at each T_m . Figures 1a and b illustrate the typical morphology of chain folded PE crystallized from the melt at atmospheric pressure. Fig. 1a shows the surface morphology of high molecular weight material crystallized at 128°C for 65 hours. In the sample of Fig.1b standard molecular weight material was cooled from the melt at 8 Kmin^{-1} . The interior is here full of immature banded spherulites in which about three bands have developed.

Table 1 shows that hardness values for the standard molecular weight samples are higher than those for high molecular weight material. H is known to vary with α following equation (5). The higher H values for the PE samples of lower molecular mass is mainly due to the higher degree of crystallinity observed. In addition, the standard molecular weight samples reveal higher H_c values than the Hifax samples, especially at prolonged annealing treatment. As mentioned in the introduction, previous studies on linear PE slowly crystallized from the melt had shown that the b-parameter value increases with increasing molecular weight up to a critical molecular weight around $2 \times 10^5\text{ g/mol}^{5-7}$. Hence, the higher H_c values determined for the Rigidex samples can be related to a lower value of the b-parameter (see equation (1)).

Table 1 also reveals a hardness increase with increasing annealing time for the two molecular weights investigated. A parallel α and l_c increase with t_a is also observed.

The crystal thickening as t_a is increased can also be inferred from the melting temperatures collected in table 1. Upon annealing, the DSC traces show two endothermic peaks. The peak at higher temperatures ($T_m > T_a$) is due to a fraction of the molten material recrystallizing during annealing into thicker lamellae. The peak at lower temperatures ($T_m < T_a$) is due to the remaining material recrystallizing during cooling leading to thinner lamellae. The high temperature melting peak is displaced to higher temperatures (thicker lamellae) with increasing t_a and, at the same time, the amount of transformed material yielding thicker lamellae increases.

Chain extended PE: hardness-microstructure correlation

Table 2 collects the density, crystallinity, crystalline lamellar thickness values as measured from GPC (denoted l_{GPC}), hardness, crystal hardness and melting temperatures for the Rigidex and Hifax samples annealed or crystallized at high pressure. Figures in brackets following l_{GPC} or T_m data refer to the proportion of material associated to each l_{GPC} or T_m value. The phase structure of similar pressure-crystallized polyethylenes is known from NMR measurements ¹⁴. Figures 1c and d show electron-micrographs of CEPE crystallized at 4.95 kbar from the melt at 260°C (see table 2). Fig. 1c illustrates the morphology of a standard molecular weight sample. Here the spaces between large lamellae are filled with smaller lamellae composed of lower molecular weight material⁹. On the other hand, in Fig. 1d, corresponding to a high molecular weight sample, the hierarchy of lamellae is not believed to be accompanied by molecular fractionation⁹.

The first finding is the high hardness values obtained when high-pressure crystallization or annealing is applied to the samples. The unusually high H values found in the high pressure crystallized or annealed samples are a consequence of both: i)

the high α values observed ($\alpha > 0.90$ except for Hifax crystallized at 5 kbar) and ii) the extremely large crystalline lamellar thickness values detected (see table 2). The lower α -value obtained for the high molecular weight material crystallized at 5 kbar, as compared to the same sample annealed at 5 kbar, is in accordance with general experience^{8,9} which suggests that annealing produces higher α -values than crystallization because the process of partial melting followed by recrystallization is able to use pre-existing nuclei.

At first sight, it is surprising that the hardness values of the chain-extended lamellae samples with very high degrees of crystallinity, are markedly lower than the crystal hardness of infinitely thick crystals, which is commonly accepted to be of $H_c^\infty \sim 170 \text{ MPa}$ ^{1,5-7}. The plot of H_c^{-1} vs. l_c^{-1} for chain-folded and chain-extended polyethylenes may clarify this aspect (see Figure 2). The error in the l_c^{-1} values represented in Figure 2 lie within the symbol limits. The value $H_c^\infty = 170 \text{ MPa}$ for $l_c^{-1} = 0$ has been also included in this plot. We may write equation (1) as

$$\frac{1}{H_c} = \frac{1}{H_c^\infty} \left(1 + b \frac{1}{l_c} \right) \quad (6)$$

According to equation (6), H_c^{-1} linearly increases with l_c^{-1} at constant b -value. The ordinate-intercept of a H_c^{-1} vs. l_c^{-1} plot gives $1/H_c^\infty$, and the slope is proportional to the b -parameter value. Figure 2 shows that the data for chain-folded Rigidex samples can be fitted to a straight line yielding $b=21 \text{ nm}$ (the intercept agrees with $1/170 \text{ MPa}^{-1}$)^{1,5-7}. The b value obtained is consistent with other b -values reported on slowly crystallized PE samples of similar molecular mass⁵⁻⁷. Data for CEPE are also presented in Figure 2. Here the l_c values correspond to the weighed average of the l_{GPC} values collected in table 2. A fit to the data of the high pressure crystallized (or annealed) samples (assuming an ordinate-intercept of $1/170 \text{ MPa}^{-1}$) yields a b -value of $\sim 85 \text{ nm}$.

DISCUSSION

Chain folded PE: hardness variation with annealing time

Figure 3 illustrates the variation of H and H_c for all the chain-folded PE samples investigated as a function of $\log t_a$. Figure 4 shows the parallel variation of α and l_c values for the standard and the high molecular weight materials as a function of t_a in a semi-logarithmic scale. The linear increase of hardness and crystal hardness with $\log t_a$ is a consequence of the same type of annealing time dependence for α and l_c (see equations 1 and 5). Similar results have been reported on oriented dried PE gels annealed at different annealing times ¹⁵.

Chain extended PE: hardness-microstructure correlation

The data of Figure 2 clearly show that the b -values for CEPE crystals are notably larger than for chain folded lamellae. What can be the reason for this difference? Let us recall first that, according to equation 6, for a given average lamellar thickness, l_c , the b -parameter determines the microhardness of the lamellae crystallites, H_c , and second that b , is, in addition, directly proportional to the basal surface free energy ¹. Previous investigations on CEPE and chain-folded crystals showed a common reduced plot of the fractional change in crystal thickness against supercooling ¹⁶. Consequently, the basal surface free energy of chain-extended and chain-folded crystals is similar in both. This suggests that the higher b -value observed for chain-extended lamellae with respect to chain-folded is presumably due to a lower Δh value (see Figure 2). The interlamellar regions in oriented CEPE have been shown to exhibit a higher mass deficit per unit area than in chain-folded polymer ¹¹. This fact, together with a reduction of the entanglements' density in the amorphous regions within CEPE lamellae, could explain

the lower energy required for plastic deformation of the CEPE lamellae with respect to the chain-folded material.

In a previous paper, the existing analogy between equation (1) and Thomson-Gibbs equation

$$T_m = T_m^o \left(1 - \frac{b^*}{l_c} \right) \quad (7)$$

where T_m^o is the equilibrium melting point and $b^*=2\sigma_e/\Delta h_f$ (Δh_f being the melting enthalpy), was highlighted. While the crystal hardness depression due to the finite thickness of the lamellae is given by the ratio b , the melting point depression is characterized by an equivalent ratio b^* which is related to the equilibrium properties of the crystals. By combination of equations (7) and (1) we obtain:

$$\frac{1}{H_c} = -\frac{b}{b^* H_c^\infty T_m^o} T_m + \frac{1}{H_c^\infty} \left(1 + \frac{b}{b^*} \right) \quad (8)$$

Equation (8) shows that the reciprocal value of the crystal hardness is related to the melting temperature of the crystals. Figure 5 shows the plot of H_c^{-1} vs. T_m for chain folded and chain-extended PE samples investigated in this paper (T_m was taken as the weighed average of the melting temperatures collected in tables 1 and 2). The data for chain-folded material fit into a straight line. From this linear fit, one can derive a value for T_m^o , provided the H_c^∞ value is known. Assuming $H_c^\infty=170$ MPa, a T_m^o value of 413 K is obtained. In addition, from the slope of this linear regression ($T_m^o = 413$ K, $H_c^\infty=170$ MPa) a b/b^* value of 44 is inferred. Previous investigations on melt crystallized PE in a wide range of M_w revealed a parallel b and b^* increase with increasing M_w in a way that the b/b^* ratio remains constant ($\sim 30-40$)⁶. The reported H_c^{-1} and T_m values in the mentioned paper have been included in Figure 5 and they agree with the linear fit to the H_c^{-1} - T_m plot presented in this paper. On the other hand, H_c^{-1} - T_m data for the chain-

extended morphology slightly deviate from the linear fit corresponding to the chain-folded morphology. This deviation can be interpreted in terms of a different b/b^* value for CEPE. As we have seen that Δh for CEPE is four times lower than Δh for the chain-folded material, then the ratio $b/b^* = \Delta h_f^0 / \Delta h$ must be lower for the latter material. Indeed, the CEPE data fit into a straight line with a slope 4 times larger than that found for the chain-folded polymer (see dotted line in Figure 5).

According to equation (8), the H_c^{-1} - T_m plot for different polymeric materials will fit into a straight line provided the b/b^* ratio is constant. Figure 5 includes data from our laboratory for high pressure crystallized poly(ethylene terephthalate) (PET) and atmospheric pressure crystallized poly(ethylene oxide) (PEO) samples^{17, 18}. From the linear regression fit for the H_c^{-1} - T_m data of PET and PEO (Figure 5), values of $H_c^\infty = 392$ MPa for PET and 150 MPa for PEO are obtained (assuming $T_m^0 = 558$ K and 341.9 K for PET and PEO are respectively^{17, 18}) in agreement with previous results¹⁷⁻¹⁹. The b/b^* ratio derived from the slope of the plots is around 2 for PET and 95 for PEO. This result suggests that for flexible polymers the energy required for plastic deformation of the crystals is much lower than the melting enthalpy. As the chain stiffness increases, the b/b^* ratio seems to decrease as a consequence of a higher energy required for crystal deformation.

CONCLUSIONS

- The hardness of isotropic PE samples with chain-folded morphology is confirmed to linearly increase with $\log t_a$ due to a parallel linear increase of α and l_c with the logarithm of the annealing time.

- Unusually high H values are obtained when PE samples are crystallized or annealed under high pressure as a consequence of the high degree of crystallinity and crystalline lamellar thickness values developed ($\alpha > 0.90$ and $l_c \sim 150-300$ nm).
- The b -value (mechanical) of chain-extended PE crystals is shown to be ~ 4 times higher than the b -value for chain-folded crystals. This fact considerably lowers the H value of CEPE crystals with respect to H_c^∞ .
- The b/b^* ratio is four times larger for chain-extended than for chain-folded lamellae. This result could be a consequence of the lower energy required for plastic deformation of the chain-extended lamellae.
- The plot of H_c^{-1} versus T_m allows T_m° to be derived provided H_c^∞ is known and viceversa.

We are thankful to Dr. R. H. Olley, Dr. D. Patel and Dr. A. M. Hodge for the elaboration and supply of the PE electron-micrographs of Figure 1. Thanks are also due to DGICYT (Grant PB94-0049), Spain, for the support of this investigation. One of us (A.F.) thanks the 'Comunidad Autónoma de Madrid' for the award of a postdoctoral grant.

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Sample	t_a [hours]	ρ [g/cm ³]	α	L_{SAXS} [Å]	l_c [Å]	H [MPa]	H_c [MPa]	T_m [K]
Rigidex 9 ($M_w=1.55 \times 10^5$ g/mol)	0	0.9569	0.70	210	147	47	67	399.7
	0.1	0.9621	0.74	206	152	58	78	399.5(62%) 403.4(38%)
	1	0.9610	0.73	342	250	64	88	398.4(62%) 405.4(38%)
	3	0.9672	0.77	362	279	83	108	397.4(38%) 406.4(62%)
	24	0.9729	0.81	440	356	82	101	394.0(15%) 407.5(85%)
	70	0.9760	0.84	486	408	89	106	392.4(11%) 408.0(89%)
Hifax ($M_w>2 \times 10^6$ g/mol)	0	0.9241	0.47			31	66	401.4
	0.1	0.9315	0.52			39	75	399.2(53%) 403.7(47%)
	1	0.9325	0.53			38	72	397.7(45%) 406.7(55%)
	3	0.9373	0.56			45	80	398.0(53%) 406.7(47%)
	24	0.9395	0.58			49	85	396.0(28%) 407.5(72%)
	70	0.9450	0.62			51	82	408.5

Table 1. Density, degree of crystallinity, long period, lamellar thickness, Vickers hardness, crystal hardness and melting temperature for the polyethylene samples annealed for various times t_a at 130°C.

Sample	Processing conditions	Pressure (kbar)	ρ [g/cm ³]	α	l_{GPC} [Å]	H [MPa]	H _c [MPa]	T _m [K]
Rigidex 9 (M _w =1.55 × 10 ⁵ g/mol)	Annealed at 235°C	5.3	0.9881	0.92	125(3%) 300(10%) 1700(32%) 3000(55%)	104	113	396.7(5%) 403.7(9%) 413.5(86%)
Rigidex 9 (M _w =1.55 × 10 ⁵ g/mol)	Annealed at 245°C	5.3	0.9890	0.93	250(20%) 2000(80%)	126	136	396.5(5%) 403.0(3%) 407.0(7%) 411.4(85%)
Rigidex 9 (M _w =1.55 × 10 ⁵ g/mol)	Crystallized at 260°C	5.0	0.9905	0.94	316(12%) 3100(88%)	100	106	411.7
H020 (fraction of R9)	Crystallized at 260°C	5.0	0.9851	0.90	250(8%) 2800(92%)	110	122	412.4
Hifax (M _w >2×10 ⁶ g/mol)	Annealed at 245°C	5.3	0.9925	0.96	200(10%) 1400(90%)	107	112	415.7
Hifax (M _w >2×10 ⁶ g/mol)	Crystallized at 260°C	5.0	0.9649	0.76	224(15%) 3000(85%)	84	111	417.0

Table 2. Processing conditions, applied pressure during annealing/crystallization, density, degree of crystallinity, crystal thickness, Vickers hardness, crystal hardness and melting temperatures for the PE samples investigated.

LEGEND TO FIGURES

Figure 1. a) PE (Hifax) crystallized at atmospheric pressure from the melt at 128°C for 65 hours; b) PE (Rigidex 9) slowly cooled from the melt at atmospheric pressure; c) CEPE (Rigidex 9) crystallized at 4.95 kbar from the melt at 260°C (see table 2); d) CEPE (Hifax) crystallized at 4.95 kbar from the melt at 260°C (see table 2).

Figure 2. Plot of H_c^{-1} vs. l_c^{-1} for standard molecular weight chain-folded (●) and chain-extended PE (○) and high molecular weight CEPE (△). The open diamond represents the ideal hardness of an infinitely thick PE crystal^{1,5-7}.

Figure 3. H and H_c as a function of $\log t_a$ for chain folded PE: $M_w=1.55 \times 10^5$ g/mol (●, ○) and $M_w > 2 \times 10^6$ g/mol (▲, △).

Figure 4. Plot of α and l_c values as a function of $\log t_a$ for chain folded PE: $M_w=1.55 \times 10^5$ g/mol (●, ○) and $M_w > 2 \times 10^6$ g/mol (▲).

Figure 5. Variation of H_c^{-1} with T_m for different polymeric materials: standard molecular weight chain-folded (●) and chain-extended PE (○); high molecular weight chain-folded PE (▲); chain folded PE as taken from reference 6 (◆); PEO (▽)¹⁸; PET (□)¹⁷. The dotted line fits to the data for CEPE.

Fig. 2

Fig. 3

Fig. 4

Fig. 15