NOTE**ON THE RELATIONSHIP BETWEEN MICROHARDNESS AND
CRYSTAL PERFECTION OF CHAIN-EXTENDED
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Hardness, H , is a relevant mechanical packing-density sensitive property that implies resistance to local surface deformation against indentation [1]. From the common dependence of glass transition temperature, T_g , as well as of H on cohesion energy, an experimentally derived relationship between microhardness H and T_g of a number of amorphous polymers was recently found [2]:

$$H = 1,97 T_g - 571 \quad (H \text{ in MPa, } T_g \text{ in K}) \quad (1)$$

The importance of this equation is at least two-fold: (i) it allows the estimation of H values of any amorphous polymer, characterized by dominating single bonds in the main chain, with known T_g , and (ii) it makes possible the evaluation of the T_g of a polymer which is not commonly accessible in amorphous state and whose microhardness value can be obtained through extrapolation of a sample series to zero crystallinity [3, 4].

It looks challenging to check whether the same approach could be applied to crystalline polymers, i. e. accounting for the packing density of the crystallites to derive a similar simple relationship as Eq. 1. Crystal perfection can be described satisfactorily by the paracrystalline lattice distortion parameter $g_{(hkl)}$ formulated by Hosemann [5-7]. The g parameter describes the paracrystalline standard deviation of the lattice spacing d , $g = \Delta d/d$, where Δd , is the mean statistical fluctuation between the lattice planes. One may derive this parameter from the broadening of the reflections in the wide-angle X-ray scattering (WAXS) patterns.

In previous work
 ✓ Polyethylene (PE) with different degrees of branching was crystallized from the melt using two undercoolings ($\Delta T = T_m - T_c = 10^\circ\text{C}$ and 68°C) [8,9]. In this way samples with a systematic variation in the crystalline structure were obtained [8,9] as verified by the observation that the commonly reported equilibrium melting temperature T_m° of PE was obtained via extrapolation to infinitely large crystals [10]. The strong effect of crystallinity and crystal size on H has been highlighted [9-13]. In ref. 10 it was emphasized that the crystal size effect reflects

rather the influence of crystal perfection, i.e. packing density, because the extrapolation of the experimental data of H_c as function of $g_{(110)}$ referring to the two crystallization conditions results in the crystal hardness values for the “defect free” crystals, H_c^∞ , of 142 MPa. A similar extrapolation to “infinite” large crystals from lamellae thickness, l_c , derived from small angle X-ray scattering (SAXS) and from coherent crystal sizes, D_{200} , (WAXS) data yield in H_c^∞ of 133 and 141 MPa, respectively. These values are, however, much lower than those previously derived from thermodynamic predictions using the plot H_c vs. $1/l_c$ [9].

If the samples with highest degree of branching (more than 4 branches per 100 C atoms) are omitted, a linear variation of H vs. g_{110} can be observed [10]. Extrapolation for $g_{110} = 0$ yields $H_c^\infty = 124.4$ MPa value which is slightly lower as compared with the above cited H_c^∞ value. In addition, from the linear plot H or H_c vs. $g_{(110)}$ a simple equation for the calculation of H from the paracrystalline lattice distortions parameter $g_{(110)}$ was derived [10]:

$$H_c = H_c^\infty - k g_{(110)} \quad (2)$$

The aim of this note is to verify whether the relationship between H_c and $g_{(110)}$ (Eq. 2) may hold for PE samples characterized by other morphology, for example chain-extended crystal samples crystallized or annealed at high pressure. This may permit to fill up the gap in the linear relationship (Eq.2) by PE crystals characterized by high perfection.

Previously prepared commercial PE samples were used in this study [14,15] Rigidex 9 (B. P. Chemicals Ltd.- Grengemouth, UK) and Hifax 1900 (Hercules Powder Co. Inc. Wilmington, DE), supplemented by a fraction of PE extracted from Rigidex polyethylene by solvent treatment [16]. Hifax has a molecular weight in excess of two million, whereas $M_n = 11\,700$ g/mol and $M_w = 155\,000$ g/mol for Rigidex.

In previous work !

Initially, the high molecular weight materials were compression molded at atmospheric pressure by slow cooling from the melt. The high pressure annealing was performed at 5.35 kbar for 15 min, and various temperatures (235, 245°C) following the procedure of Bassett and Carder [17]. High-pressure crystallization consisted of cooling from the melt at 260°C and 4.95 kbar at a rate of ~ 1 K/min [14].

For the purpose of the present study the chain extended PE samples were analyzed by means of WAXS to derive the paracrystalline lattice distortion parameter $g_{(110)}$. It is important to note that the samples under investigation are characterized by chain extended crystals (lamellae thicknesses between 1000 and 3000 Å [14,15]).

Fig. 1 shows the WAXS diffractogram of one of the samples as function of the reciprocal vector s ($s = 1/d_{hkl}$). The Miller indices for some reflections are given. The upper trace with the intensity multiplied by 10 shows the second order reflection 220 well resolved. A standard of Si was used to correct the instrumental broadening of the reflections. The observed shape of the reflections from both Si and PE was Lorentzian type. Both 110 and 220 reflections were used to calculate the paracrystalline lattice distortion $g_{(110)}$ and crystal coherent size $D_{(110)}$ using the corrected integral breadth of the reflections $\delta\beta_{hko}$ as described in ref. [7]. Thus, from a plot of $\delta\beta_{hko}$ (in Å⁻¹) vs. $s^2_{(hko)}$ the ordinate intercept is equal to $1/D_{(110)}$ and the slope is $\pi g_{(110)}$. Values of $D_{(110)}$ and $g_{(110)}$ for the extended chain crystal PE samples are collected in Table 1 together with other properties of the samples including the microhardness values reported previously [14,15].

The data for the chain-extended samples (Table 1) are plotted together with those of the formerly studied chain-folded samples of branched PE in Fig. 2. The latter materials are characterized by relatively high values of $g_{(110)}$ (up to 4.0 %) because of the rather imperfect chain structure. As a matter of fact, this is the reason why the interval of the lowest values of $g_{(110)}$ (below 1.0 %) remained till now uncovered.

Since chain-extended PE samples are characterized by high crystallinity values of about 95% [14], (Table 1) we expected to be able to cover the original gap [10] in Fig. 2. The H_c data from Table 1 for the chain-extended PE samples fit rather well to the H_c values of branched PE samples covering the existing $g_{(110)}$ interval for the crystals with high perfection (see Fig. 2).

The fact that the present measurements on chain-extended PE samples widens significantly the interval of $g_{(110)}$ values may offer, in principle, the possibility to derive more reliable values for the constants H_c^∞ and k in Eq. 2. From the straight line in Fig. 2 one obtains $H_c^\infty = 128.0$ MPa and $k = -28.30$ ($r^2 = 0.94$). It is to be noted that the plot of measured H values vs. $g_{(110)}$ also gives a linear relationship with $H_c^\infty = 116.0$ MPa and $k = -31.89$ ($r^2 = 0.97$).

It is astonishing that the extrapolated value from Fig. 2 $H_c^\infty = 128.0$ MPa is much lower than the reported one ($H_c^\infty = 170$ MPa) derived from the dependence H_c vs. $1/l_c$ for PE samples with chain-folded crystals [11]. The observed difference may originate from the different chemical structure of the PE used. In the present case the majority of data are restricted to highly branched PE [10], while in the former study [11] H_c^∞ is extrapolated from H_c values corresponding to a large number of samples including linear PE and low molecular paraffins. While in this case the data fit to a curve describing a basic model of deformation, theoretically derived by Baltá Calleja and Kilian [11] in terms of the heat dissipated by the plastically deformed crystals, the data of Fig 2 solely reflect the empirical relationship between H and g . For this reason it is hardly reasonable to perform any extrapolation in Fig. 2 to $g = 0$. In the same time, the theoretically derived equation relating H_c and $1/l_c$ [11] contains parameters (as enthalpy of plastic deformation), which are not easily accessible for experimental evaluation. Eq. 2 offers, in contrast, the opportunity of a direct H evaluation for crystalline polymers with known g values.

It seems attractive to attempt to modify Eq. 2 in such a way that it also would account for the contribution of the surface energy and eventually for the enthalpy

of plastic deformation to the H_c values as the reported hardness equation [11] does, in analogy with the classical Gibbs-Thomson equation relating melting temperature and crystal sizes [18].

There is a further striking observation related to the H values of chain-extended samples. Their H values are surprisingly low if one takes into account their density (and respective crystallinity) as well as their extremely low $g_{(110)}$ values (Table 1). What could be the reason for these low H values typical for highly imperfect crystals?

In order to answer this question we have to remind an earlier thorough study of Bassett et al. [19] on the effect of lamellae thickness on the elastic modulus E of PE samples with chain-extended crystals. It was found that E increases strongly with l_c up to values of 1500 Å and thereafter falls down [19]. Quite similar behavior has been reported by Baltá Calleja et al. [20] studying the dependence of H on l_c for oriented chain-extended PE. A leveling of H is found when l_c reaches values of about 1500 Å and above.

Obviously, these observations [19,20] indicate that the positive effect of crystal size on the mechanical properties of chain-extended PE has some limit after which the effect is negative (E , [19]) or a leveling is observed (H , [20]). Taking into account the fact that the chain-extended samples of this study are characterized by dominating lamellae thickness values above 1500 Å [14], it becomes clear why the H values are that small and fit to the series of samples of highly branched PE with very imperfect chain-folded crystals.

In conclusion, the present results (Fig. 2) support the validity of Eq. 2. The latter can be applied (i) to linear and branched PE, and (ii) to PE with chain-folded or chain-extended crystals for evaluation of their microhardness without measuring it; one only needs to determine experimentally the paracrystal lattice distortion parameter $g_{(110)}$ using WAXS.

In accordance with our expectations and the previous findings [2,10], it should be stressed that, the microhardness depends primarily on the packing density. For amorphous polymers the packing density can be expressed by the T_g value [2]. For crystalline polymers (polyethylene) the paracrystalline lattice distortion parameter g offers a convenient description of the packing density [10]. In principle, both magnitudes allow one to calculate the microhardness by means of Eq. 1 or 2 without carrying out any microhardness measurements.

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Table 1. Degree of Crystallinity (α), Crystal Microhardness (H_c), Coherently Diffracting Domains (D_{110}), Paracrystalline Lattice Distortion Parameter (g_{110}), for PE samples with extended chain crystal morphology prepared under high pressure

Sample	Processing Conditions [14]	Pressure, kbar [14]	α [14]	H_c , MPa [14]	D_{110} , Å	g_{110} , %
Rigidex 9 ($M_w = 1.55 \times 10^5$ g/mol)	Annealed at 235°C	5.3	0.92	113	570	0.48
Rigidex 9 ($M_w = 1.55 \times 10^5$ g/mol)	Crystallized at 260°C	5.0	0.94	106	720	0.51
Hifax ($M_w > 2 \times 10^6$ g/mol)	Annealed at 245°C	5.3	0.96	112	711	0.31

FIGURE CAPTION

Figure 1: X-ray diffractogram for Rigidex 9 (5.3 kbar, annealed at 235°C). Indices of some reflections are indicated. The intensity of the upper trace of higher s -values was multiplied by a factor 10.

Figure 2: Dependence of crystal microhardness H_c on the paracrystalline lattice distortions parameter $g_{(110)}$ for samples of branched PE crystallized from the melt at ambient pressure $\Delta T = 10^\circ\text{C}$ ($\circ$) and $\Delta T = 68^\circ\text{C}$ ($\bullet$) characterized by chain-folded crystals [10], and PE samples ($\blacktriangle$) crystallized under pressure and characterized by chain-extended crystals (Table 1).

Figure 1

Figure 2