MICROHARDNESS OF SEMICRYSTALLINE POLYMERS

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SYNOPSIS

A new approach to justify the dependence of microhardness of semicrystalline polymers, specially polyethylene, upon average crystal thickness is given. A basic model of deformation under local compression is proposed in terms of the heat dissipated by the plastically deformed crystals and the volume of crystals destroyed under the indenter. The results indicate that the mechanism of deformation is dictated by the initial mosaic-block structure controlling the generation of a final system of shear planes. Though the analysis is approximate, acceptable parameters give satisfactory agreement with observation.

1. INTRODUCTION

In recent years there has been increasing recognition of the importance of the surface structure of polymers as means of developing materials with improved physical properties. Within this context the study of indentation microhardness (MH) has emerged as a potential useful technique which can yield information regarding the microstructure of semicrystalline polymers at various morphological levels^{1,2}. This is possible because microindentations respond to specific changes in microstructure. Specifically, microhardness-critical stress needed to plastically deform the surface of semicrystalline polymers-has been shown to depend on structural parameters such as intermolecular distances within the crystals, lattice perfection and crystal dimensions³. In semicrystalline polymers microhardness measurements may also throw light on the changes in the

overall chain orientation⁴⁻⁷. There are two important aspects concerning the hardness study in polymers. First, there is the question of a quantitative justification for the observed dependence of MH on lamellar thickness and the information which can be obtained, in principle, by the microhardness technique regarding the volume fraction of crystalline material. This leads directly to the problem of relating MH to microdeformational mechanisms as this may permit a comparatively limited information to be put to optimum use. Secondly, there is the relationship between microscopic (microhardness) and macroscopic (modulus, yield stress) mechanical properties, where microstructural information has been valuable in correlation both types of properties⁸. A previous review of this subject has been given recently⁹.

The main concern of this paper is the development of a description of microhardness of semicrystalline polymers, derived thermodynamically, in terms of the average crystal thickness. The relevance of the latter structural parameter is highlighted as describing accurately the surface plastic behaviour of polymers under local compression.

2. CONCEPT OF MICROINDENTATION HARDNESS: BACKGROUND

The method most commonly used in determining the microhardness of a polymer surface is the static indentation test¹⁰. It involves the formation of a permanent impression after loading the surface of the material with a sharp indenter of known geometry. The microhardness is calculated as the ratio of peak contact load, p , to the projected area of impression, A :

$$H = k^* p/A = k p \delta^{-2} \quad (1)$$

where $k^*=18.191 \times 10^5$, and δ is the penetration depth of the indenter within the surface (for a Vickers pyramid $\delta = \sqrt{A/7}$ ($|H| = \text{MNm}^{-2}$; $|p| = \text{N}$; $|\delta| = \mu\text{m}$). The hardness, so defined, is considered to be indicative of the irreversible deformation processes characterizing the polymer material. These include phase transformations and twin formation, at low strains, and chain tilt and slip, crack formation and chain unfolding at larger strains³. The indentation stresses, although highly concentrated in the plastic region surrounding the contact, may extend into the more distant elastic matrix. Thus the material under the indenter consists of a spherical zone of plastic deformation (~4-5 times the penetration distance, δ , of the indenter below the specimen surface) surrounded by a larger zone of elastic deformation. For conventional instruments using forces $p \sim 0.1 \text{ N}$, the penetration distance (residual impression) left by a sharp indenter is for most commercial polymers, of the order of a few μm . However with the new instruments

operating down to $10\mu\text{N}$, the penetration distance can be reduced to a few hundred Å¹¹. Impressions, in this case, should be observed with help of an electron-microscope. To differentiate between reversible and irreversible contributions contact deformation measurement of the elastic recovery after unloading is required¹⁰. However, pyramid indenters provide a contact pressure which is nearly independent of indent-size and are less affected by elastic release than other indenters. The time-dependent contribution to plastic deformation during loading can be described by a law of the form $H=Bt^{-k}$, where B is a coefficient depending on temperature and loading-stress and k furnishes a measure for the rate of creep of the material. In previous investigations we have mostly adopted a MH value at 0.1 min because it approaches Tabor's relation^{3,5,9}. After load release a long delayed recovery can, often, be detected⁹. The relaxation of the residual impression depth increases with the volume fraction of "amorphous" material.

3. HARDNESS RELATING TO MICROSTRUCTURE: A THERMODYNAMICAL APPROACH

Semicrystalline polymeric solids show a distinct morphology of stacks of crystalline lamellae intercalated by "amorphous" disordered regions. The lamellae themselves possess a mosaic-block superstructure with liquid-like lattice distortions (paracrystallites) and a high concentration of lattice defects at the grain boundaries reducing the lateral cohesion of stacked lamellae in the solid. From a mechanical viewpoint the material may be regarded as a composite consisting of alternative hard (crystalline) and soft-compliant (amorphous) layers. The hardness of such a system can be approximated to:

$$H = w_c H_c + (1-w_c) H_a \quad (2)$$

where H_c and H_a are the intrinsic hardness values of the lamellar crystals and amorphous layers respectively. The additivity law expressed by eq. 2 has been verified for mixtures of two polyethylenes with well differentiated values¹².

Since $H_c \gg H_a$ ($H_a \sim 0.5 \text{ MN/m}^2$)

the heat dissipated by the plastically deformed crystals can be written as:

$$\Delta\phi_{cd} = \Delta\phi / V_{cd} \quad (3)$$

where $\Delta\phi$ is the ~~total enthalpy~~ ^{work performed during indentation} and V_{cd} is the volume of crystals destroyed under the stress field of the indenter. If we assume that the volume of destroyed crystals is proportional to the volume of material physically displaced under the indenter:

$$V_{cd} \approx \alpha A \delta \quad (4)$$

The mechanical work performed during indentation must be equal to:

$$W = p \delta = \Delta\phi \quad (5)$$

By combination of eqs. 1-5 one is led to the simple relationship:

$$H_c = H_0 \Delta\phi_{cd} ; H_0 = k/\alpha \quad (p=\text{const}) \quad (6)$$

Since the indentation of the polymer surface involves a yielding process one expects a substantial destruction and/or severe modification of a volume fraction of lamellae localized at the surface. For $p \sim 0.1\text{N}$ values of $V_{cd} \sim 10^3 \mu\text{m}^3$ have been derived for melt crystallized polyethylene³. It is interesting to express V_{cd} in terms of the modified microstructural units left after deformation. Let us assume that the destruction of lamellae is heterogenous and involves a generation of a more or less dense system of shear-planes, wherein the energy of deformation is grossly dissipated (fig. 1). Assuming the original crystal blocks to be cubic in shape the relative fraction of "shear planes" will be, in a first approximation:

$$\text{surface/volume} \approx \ell_c^{-1} \quad (7)$$

Hence the volume of destroyed crystalline material can be approximated to:

$$V_{cd} = V_0 (1 + b_1 \ell_c^{-1}) \quad (8)$$

One can then express eq. 6

$$H_c = H_0 \frac{\Delta\phi}{V_{cd}} = \frac{H_0 \Delta\phi^*}{(1 + b_1 \ell_c^{-1})} ; \quad (\Delta\phi^* = \frac{\Delta\phi}{V_0}) \quad (9)$$

This expression is of great interest because it correlates the "crystal hardness" of a polymeric material to the thickness ℓ_c of its building mosaic-block units. It is noteworthy that for $\ell \rightarrow \infty$, H_c approaches to $H_0 \Delta\phi^*$, which is the maximum possible value of dissipated energy through plastic deformation. For polyethylene⁹ $H_0 \Delta\phi^* \approx 170 \text{ MNm}^{-2}$. Eq. 9 offers a quantitative measure for intrinsic plastic deformation of semicrystalline polymers, predicting a clear dependence of H_c with the size of the constituent units.

4. COMPARISON OF CALCULATED AND EXPERIMENTAL DATA

Fig. 2 illustrates the plot of H_c as a function of ℓ_c^{-1} for different lamellar structures crystallized from the melt. The experimental data^{3,8} show a good agreement with the calculated (solid) curve according to eq. 9 using $b_1 = 20 \text{ nm}$.

Eq. 9 offers, in fact, a direct description of the hardness of a large stack of crystal lamellae in terms of their average crystal thickness, including the defective surface boundary (non-homogeneous microphase)^{13,14}. Paraffins can, likewise, be described by means of eq. 9, simply by using the chain length parameter. The value of $b_1 = 200 \text{ \AA}$ applies for samples melt crystallized at atmospheric pressure. We have shown elsewhere that b_1 is a decreasing function of crystallization pressure¹⁵. For PE samples crystallized, for instance, at $p = 150 \text{ MN/m}^2$ a fitting constant $b_1 = 10 \text{ nm}$ is required¹⁵.

Since $H_c \ll H_a$ the overall hardness of the polymeric material will be:

$$H = H_c w_c = H_0 \Delta\phi^* w_c / (1 + b_1 \ell_c^{-1}) \quad (10)$$

where w_c is the molar fraction of crystalline material. Eq. 10 offers a convenient model relating the plastic behaviour of the material with its microstructural parameters. Structural changes affecting ℓ_c and w_c can thus, be adequately interpreted by using eq. 10. For instance, annealing of PE in range II produces a substantial lamellar thickening ℓ_c and only a minor increase¹⁶ in w_c . The independent contribution of these two parameters in the hardness of annealed PE can thus be followed accurately through eq. 10.

5. MECHANISM OF PLASTIC DEFORMATION

Let us finally discuss the local micromechanism of plastic deformation from the initial existing mosaic-block structure into the final modified one. The dissipated heat per unit volume V_0 under the indenter can be defined as:

$$\Delta\phi_{cd}^* = \Delta\phi / V_0 = p \delta / V_{cd} \quad (11)$$

We further assume that plastic deformation of crystals mainly proceeds by a multitude of shearing planes. Therefore, on the basis of a cubic symmetry for the cross-section of a crystal block we are led to

$$\Delta\phi_{cd}^* = \Delta\phi / V_0 = \frac{\Delta h}{V_0} \left(\frac{4a_0}{\ell_p} \right) \quad (12)$$

where a_0 is the average lateral intermolecular distance within the crystals and ℓ_p describes the average lateral dimension of the final "crystal block", with invariant thickness ℓ_c , after plastic deformation. From eqs. 11 and 12:

$$\ell_p = \frac{4\Delta h}{V_0} \frac{V_{cd}}{p \delta} a_0 \quad (13)$$

Furthermore, by using eqs. 8 and 13 we obtain:

$$\ell_p = K(1+b_1\ell_c^{-1}) a_0/\delta \quad ; \quad \text{where } K = \frac{12\Delta h}{V_0 p} \quad k = 4V_0\Delta h/p \quad (14)$$

This equation relates the average lateral dimension of the newly created blocks, ℓ_p , to the original mosaic-block dimensions before plastic deformation (fig. 1). Table I collects the ℓ_p and ℓ_c values for a series of polyethylene samples with varying chain-defect concentration X_{nc} , together with the average value of the lateral coherent dimensions of the system D_c prior to deformation¹⁷. The ratio $n_a = D_c/\ell_p$ is proportional to the number of surface defects (boundaries) produced after plastic deformation.

These data show first, that the final dimension ℓ_p is practically independent from the initial mosaic-block length; secondly, that ℓ_p corresponds to 4-5 intermolecular distances yielding elementary "crystal rods" constituted by 16 to 25 stems. The ratio n_a decreases substantially with decreasing size of the original crystal block dimensions. Fig. 3 illustrates the correlation found between n_a and the molar degree of crystallinity. These results support the concept that the maximum number of shearing planes increases progressively with rising degree of crystallinity. Thus for a fully crystalline lamellar system with a thickness ℓ_c , the number of shearing planes below the indenter tends to become infinite despite of having a constant final limiting size ℓ_p . On the other hand, for low crystallinities the original mosaic blocks are so small that they are nearly unmodified after plastic deformation. The present results characterize the mechanism of local plastic deformation of semicrystalline systems as exclusively governed by the primary mosaic-block structure regulating the intrinsic "solid state" deformation mechanism.

Fig. 4 illustrates the large increase of dissipated energy with rising molar mass-fraction of crystalline material. The solid line was computed according to (Table I):

$$W_{diss}^{C*} = 4\ell_c\ell_p W_p \quad (15)$$

The contribution of the dissipated energy from the smallest crystals to the overall deformation energy of the total system is negligible. The solid state deformation process occurs predominantly for very large crystal sizes entailing large crystallinity values.

In summary, the discussed results justify the obtained correlation between crystal hardness and lamellar thickness in semicrystalline polymers (polyethylene). Microhardness, thus, depends mainly on the plastic deformation of the lamellar crystals which are viewed as non-homogeneous solid microphases.

Table 1:

Average crystal dimensions before (ℓ_c , D_c) and after (ℓ_p) plastic deformation and number of shearing planes (n_a)^p and dissipated energy (W_{diss}) after crystal destruction for different polyethylene samples with varying number of chain defects (x_{nc}) and molar degree of crystallinity (w_c). The quantity w_p is the molar crystallinity including the crystal surface defective parts. Parameters are defined in ref. 14.

x_{nc}	ℓ_c /nm	$\langle D_c \rangle$ /nm	w_p /mol%	w_c /mol%	ℓ_p /nm	n_a	W_{diss}^{C*}
0.0019	26.0	171	0.997	0.922	1.95	8.8	3957
0.007	27.0	148.5	0.979	0.849	1.78	8.3	2980
0.0176	12.0	109	0.908	0.708	1.95	5.6	1182
0.0263	10.8	98.5	0.829	0.605	2.30	4.3	1068
0.0304	10.0	80.5	0.789	0.56	1.60	5.0	674
0.0361	9.0	64.5	0.731	0.502	1.58	4.1	526
0.048	7.0	75.5	0.612	0.396	1.63	4.6	353
0.0534	5.8	98	0.561	0.355	2.12	4.6	452
0.069	5.0	50	0.425	0.254	1.57	3.2	180

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REFERENCES

1. Baltá Calleja, F.J. Colloid & Polymer Sci., 254, 258-266, 1976.
2. Bowmann, J. and Bevis, M. Colloid & Polymer Sci., 255, 954-966, 1977.
3. Baltá Calleja, F.J., Martinez-Salazar, J., Cacković, H. and Loboda-Cacković, J. J. Materials Sci., 16, 739-751, 1981.
4. Baltá Calleja, F.J. and Bassett, D.C. J. Polymer Sci., 58C, 157-167, 1977.
5. Baltá Calleja, F.J., Rueda, D.R., Porter, R.S. and Mead, W.T. J. Materials Sci., 15, 765-772, 1980.
6. Rueda, D.R., Baltá Calleja, F.J. and van Hutten, P.F. J. Materials Sci. Lett., 1, 496-498, 1982.
7. Rueda, D.R., Baltá Calleja, F.J., Garcia, J., Ward, I.M. and Richardson, A. 19, 2615-2621, 1984.
8. Martinez-Salazar, J. and Baltá Calleja, F.J. J. Materials Sci., 18, 1077-1082, 1983.
9. Baltá Calleja, F.J. "Advances in Polymer Science", 66, 117-148, 1985
10. Lawn, B.R. and Howes, V.R. J. Materials Sci., 16, 2745-2752, 1981.
11. Bangert, H., Wagendrizted, A. and Aschinger, H. Philips Electron Optics Bull., 119, 17- , 1983.
12. Martinez-Salazar, J. and Baltá Calleja, F.J. J. Materials Sci. Lett. (in press)
13. Holl, B., Heise, B. and Kilian, H.G., Colloid & Polymer Sci., 261, 978-992, 1983.
14. Kilian, H.G., Colloid & Polymer Sci., 261, 374-380, 1984.
15. Baltá Calleja, F.J., Rueda, D.R., Garcia, J., Wolf, F.P., Karl, V.H. J. Materials Sci. (in press)
16. Rueda, D.R., Martinez-Salazar, J. and Baltá Calleja, F.J. J. Materials Sci. (in press)
17. Martinez-Salazar, J. and Baltá Calleja, F.J., J. Crystal Growth, 48, 283-294, 1980.

Fig. 1. Model of lamellae deformation beneath the stress-field of the indenter

Fig. 2. H_c against reciprocal crystal thickness including defective boundaries (eq. 9)

Fig. 3. Plot of reciprocal number of shearing planes after crystal destruction vs. molar degree of crystallinity.

Fig. 4. Increase of dissipated energy during crystal destruction as a function of molar fraction of crystalline material

CORRECTION

H_c
 MNm^{-2}

Fig 5

plastic deformation

plastic deformation