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Microhardness studies of chain-extended PE: II. Creep behaviour and temperature dependence

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The variation of hardness with indentation time has been investigated for chain-extended polyethylene (PE), other PE samples crystallised under different conditions and paraffins. Hardness is shown to decrease with indentation time for all the samples investigated according to a power-law. Chain-extended PE, produced by high pressure crystallization or annealing, flows at the lowest rate under the indenter of all the PE samples considered. On the other hand, paraffins creep at the highest rate. Creep behaviour depends markedly on the crystal thickness of the material. The mechanical properties at long indentation times seem to be determined primarily by the deformation modes of the crystals. The temperature dependence of hardness and that of the creep behaviour has also been investigated. In chain-extended PE, the softening of the sample and the higher rate of creep with increasing temperature are discussed in terms of the thermal expansion of the unit cell. © *2000 Kluwer Academic Publishers*

1. Introduction

Recent years have seen the microindentation hardness technique gaining increasing application in the characterisation of the structure and morphology of polymers [1–5]. The method uses a sharp indenter that penetrates the surface of the specimen upon application of a given load at a known rate. Pyramidal indenters are best suited for indentation tests. Here the hardness, in principle, does not depend on the size of the indentation and the elastic recovery is minimised in comparison to other indenters. During an indentation test the response of a polymeric material is initially elastic. When the stresses exceed the elastic limit, plastic flow occurs and a permanent deformation arises. At this stage, the plastic yield stress and the elastic modulus govern the elasto-plastic response to indentation [6]. When the load is removed, the indentation depth recovers elastically while the diagonal of the impression remains nearly unaltered [7]. The complicating effects of viscoelastic relaxation are usually minimised by measuring the indentation diagonal immediately after load release [8]. The size of the permanent area of impression has been shown to depend on the arrangement and structure of the microcrystals and the specific morphology of the polymeric material [8, 9]. From a mechanical point of view, the polymer may be regarded as a composite consisting of alternating crystalline and disordered elements [8]. An earlier study of the hardness dependence on the density, ρ, of melt crystallized polyethylene (PE), revealed that for crystallinities larger than 50%, the plastic strain is dominated by the deformation modes of the crystals [9].

The time dependent part of the plastic deformation during loading (creep) also plays an important role [9]. Hardness values reported in the literature usually refer to short indentation times of a few seconds so as to minimize creep. Several microindentation studies on polymeric materials show that hardness decreases with indentation time, following a function of the form [9]:

$$H = H_1 t^{-k} \tag{1}$$

where H_1 is the hardness at a given reference time $t = 1$ and k is the so-called creep constant. The creep behaviour of extruded PE fibres has also been investigated [10, 11]. In that case k was shown to be an anisotropic magnitude, with values in the range 5×10^{-2}–8×10^{-2} depending on indentation direction and extrusion temperature [11]. A decrease of hardness with increasing indentation time was also found for cold-drawn chain-folded and chain-extended PE [12]. The question as to how the creep behaviour of a polymeric material is affected by morphological or structural changes, however, still remains open.

The present paper is the second of a series concerning the study of the microhardness of chain-extended PE [13, 14] and describes the time dependence of microindentation hardness of chain-extended PE samples compared to their chain-folded counterparts. For the sake of comparison, data for the creep behaviour of a series of paraffins are also discussed. High pressure annealing or crystallization of PE is known to produce chain-extended lamellae [15, 16], in contrast to chain-folded

PE obtained from crystallization from the melt at atmospheric pressure. The different morphologies and microstructure developed for the same polymer in these systems provides a good opportunity to investigate the dependence of creep on morphology and microstructure for polymers of different molecular weight. The effect of measurement temperature on the hardness and creep behaviour of these systems is also investigated.

2. Experimental

2.1. Materials

PE moulded sheets of Rigidex 9 ($M_w = 155.000$ g/mol) and Hifax ($M_w > 2 \times 10^6$ g/mol) were treated at 130°C for different annealing times (see ref. [13] for more details). In addition, the original moulded sheets were crystallised or annealed at high pressure (~5 kbar) at different temperatures as described in the preceding paper [13]. In the present study, we also report data for Rigidex 9 and Hifax samples crystallised at 3 kbar and 4 kbar following a procedure analogous to that reported in ref. [13].

The thickness of the lamellae for all chain-extended PE samples has been measured by gel permeation chromatography following treatment with fuming nitric acid as described in part I [13]. The average crystalline lamellar thickness for chain-folded samples was determined from small angle x-ray experiments [13].

A series of even paraffins was also investigated. The number average of carbon atoms ranges from 20 to 40. The samples were quenched from the melt at 0°C. The C_{20} paraffin presents the lowest melting temperature from the series of paraffins investigated ($T_m = 309.9$ K). The temperature dependence of microhardness for this series of paraffins was the object of an earlier study [17].

2.2. Techniques

Microhardness measurements on all samples were carried out at room temperature except when stated employing a Vickers pyramid diamond. The microhardness value, H, was derived from:

$$H = 1.854\frac{P}{d^2} \qquad (2)$$

P is here the applied load and d the diagonal of the residual impression. The permanent deformation was measured immediately after load release to avoid long delayed recovery. Loads of 147, 245, 490 and 981 mN were used, for an indentation time of 0.1 min, in order to correct for the instant elastic recovery. This correction was then applied to derive the H values using indentation times in the range 0.1–21 min and a load of 147 mN.

A hot plate, capable of being controlled between 25 and 140 °C was used for hardness measurements at higher temperatures. The hot stage temperature was calibrated against various polycrystalline standards. In order to improve the optical contrast of the impressions at high temperatures a 100 Å thick aluminium film was evaporated on the polymer surface.

The dependence of hardness on indentation time for the series of even paraffins was also investigated for comparison with the creep behaviour of PE. Microhardness measurements for C_{20} were performed at room temperature. Microindentation experiments on other paraffins investigated were carried out at a temperature T_e determined from:

$$\frac{T_{C20} - T_r}{T_{C20}} = \frac{T_{Cn} - T_e}{T_{Cn}} \qquad (3)$$

where T_{C20} is the melting point of the C_{20} paraffin, T_r is room temperature and T_{Cn} is the melting temperature of the paraffin with n carbon atoms. This procedure was considered to provide equivalent testing conditions for all the paraffin systems under study.

3. Results

3.1. Hardness variation with indentation time

Fig. 1 illustrates a double logarithmic plot of H as a function of indentation time, according to Equation 1, for the various isotropic PE samples ($M_w = 155.000$ g/mol) prepared under different conditions. Data near $t = 0.1$ min are usually adopted as the hardness value for polymers [8, 9]. The high degree of crystallinity and large crystalline lamellar thickness values observed on chain-extended PE samples give rise to unprecedentedly high H values [13] (see Fig. 1). In addition, the hardness of chain-folded PE was shown to increase on annealing (see Fig. 1) according to the crystal thickness increase. A detailed discussion of the hardness variation with the processing conditions and a description of the morphology of chain-folded and chain-extended samples is given in part I [13]. In all cases H follows a power-law decreasing function with indentation time. According to Equation 1, the slope of each straight line

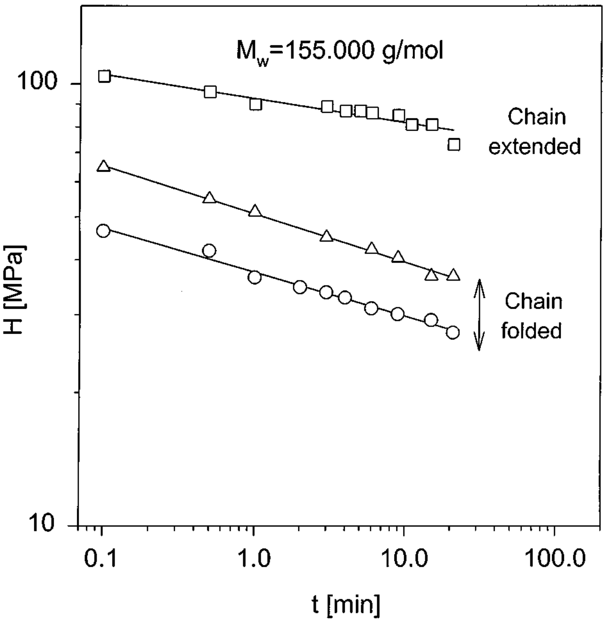

Figure 1 Double logarithmic plot of hardness vs. indentation time for standard molecular weight PE samples: ○ , original moulded film; △, annealed at 130°C for 1 h; □, annealed at 235°C and 5 kbar.

TABLE I Processing conditions and creep constant for the PE samples investigated.

Sample	Processing conditions	$k \times 10^2$
Chain-folded $M_w = 1.55 \times 10^5$ g/mol (Rigidex)	Compression moulded	10.4
	$T_a = 130°C$ $t_a = 0.1$ h	11.9
	$T_a = 130°C$ $t_a = 1$ h	11.0
	$T_a = 130°C$ $t_a = 3$ h	11.7
	$T_a = 130°C$ $t_a = 24$ h	11.2
	$T_a = 130°C$ $t_a = 70$ h	12.3
Chain-extended $M_w = 1.55 \times 10^5$ g/mol (Rigidex)	Annealed at 235°C (5.3 kbar)	5.8
	Annealed at 245°C (5.3 kbar)	6.8
	Crystallised at 225°C (3 kbar)	5.2
	Crystallised at 240°C (4 kbar)	5.4
	Crystallised at 260°C (5 kbar)	6.3
H020 (fraction of Rigidex)	Crystallised at 260°C (5 kbar)	7.0
Chain-folded $M_w > 2 \times 10^6$ g/mol (Hifax)	Compression moulded	9.5
	$T_a = 130°C$ $t_a = 0.1$ h	8.4
	$T_a = 130°C$ $t_a = 1$ h	9.4
	$T_a = 130°C$ $t_a = 3$ h	11.6
	$T_a = 130°C$ $t_a = 24$ h	7.8
	$T_a = 130°C$ $t_a = 70$ h	11.9
Chain-extended $M_w > 2 \times 10^6$ g/mol (Hifax)	Annealed 235°C (5.3 kbar)	7.0
	Annealed 245°C (5.3 kbar)	7.9
	Crystallised at 225°C (3 kbar)	3.9
	Crystallised at 240°C (4 kbar)	3.6
	Crystallised at 260°C (5 kbar)	4.7

shown in Fig. 1 offers a measure of the rate at which the material is displaced under the indenter (creep constant). Results show that k is lowest for chain-extended PE samples. The values of the creep constants for all the samples investigated are given in Table I. The data collected in this table confirm that medium molecular weight chain-extended PE samples creep less under the indenter, with k values in the range 0.05–0.07, than the atmospherically-crystallized samples, which show k values in the range 0.10–0.12. Fig. 2 presents a double logarithmic plot of H vs. t for chain-folded and chain-extended high molecular weight samples; again the dependence of log H on log t_a is linear. The k values for all the high molecular weight samples investigated are included in Table I. For them also the rate of creep is higher for the atmospherically-crystallized samples ($k \sim 0.08$–0.12) than for the pressure-crystallized material ($k \sim 0.04$–0.08). Finally, no significant variation of k with M_w is observed.

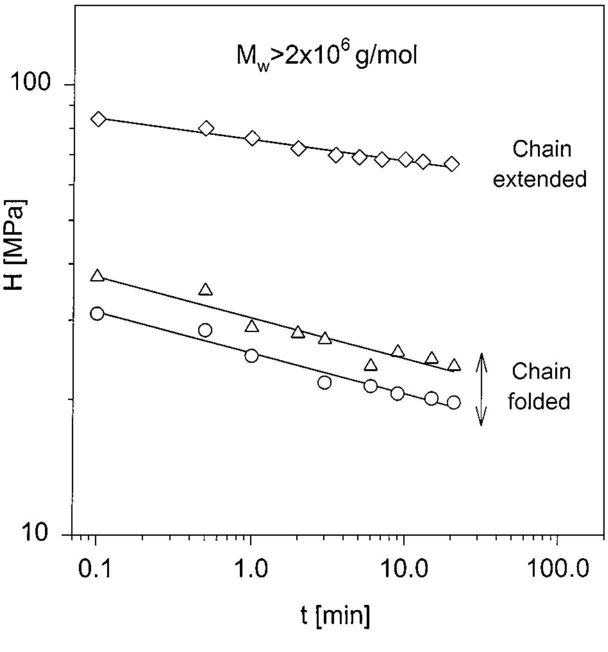

Figure 2 Plot of log H vs. log t for high molecular weight PE samples: ○, original moulded films; △, annealed at 130°C for 1 h; ◇, crystallised at 260°C and 5 kbar.

3.2. Temperature dependence of hardness

Fig. 3 shows the hardness variation with temperature for a chain-extended high molecular weight sample crystallized at 260°C and 5 kbar. Hardness is known to vary with temperature according to [9, 17, 18]:

$$H = H_0\,e^{-\beta T} \tag{4}$$

where H_0 is the hardness at 0 K, β is the coefficient of thermal expansion and T is the absolute temperature of measurement. The data in Fig. 3 give a β value of 5.31×10^{-3} K^{-1} within the temperature range 20°C < T < 100°C. Near $T = 100°C$ there is an inflexion in the hardness vs. temperature plot, leading to much higher β values for $T > 100°C$ ($\beta \approx 2.2 \times 10^{-2}$ K^{-1}). From indentation experiments on other semicrystalline polymers [18], β values in the range of $\sim 10^{-2}$ K^{-1} are reported. These values are larger than those found for chain-extended PE below 100°C. Fig. 3 also includes the variation of the cross sectional area per molecule in the unit cell, A ($A = a \times b/2$), vs. T for an infinitely thick PE crystal, as taken from reference 19. The gradual variation of A vs. T for $T > 60°C$ (dashed line) has been drawn by extrapolation of the low temperature data. One sees that the increase in the cross-sectional area of PE with temperature parallels the H decrease observed with increasing temperature.

Fig. 4 shows the variation of log H with log t for the chain-extended PE sample of Fig. 3 measured at two different temperatures. The rate of creep under the indenter clearly increases when the temperature

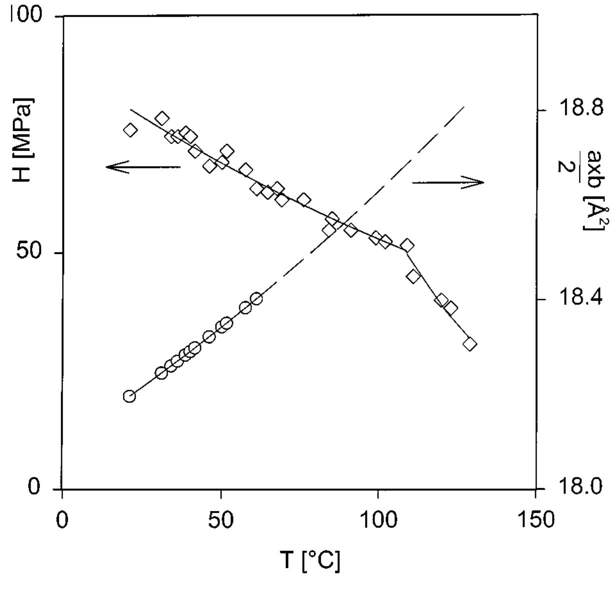

Figure 3 Temperature dependence of hardness for $t = 1$ min (◇) and the cross sectional area per molecule of the unit cell (○) for the high molecular weight sample crystallised at 260°C under 5 kbar.

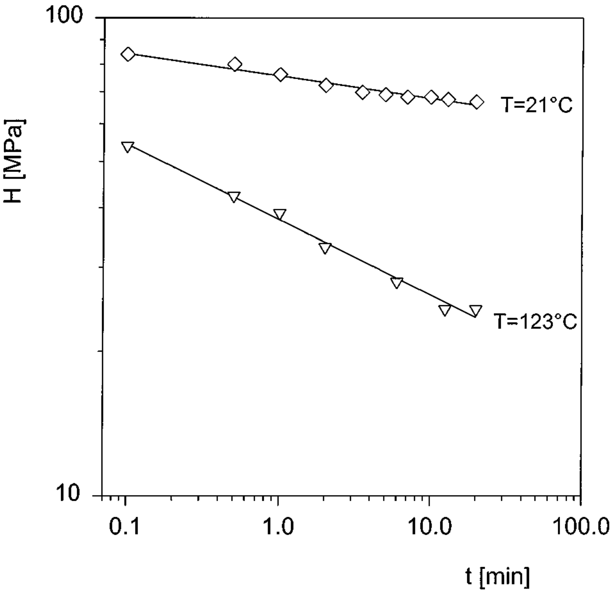

Figure 4 Plot of log H vs. log t at two different temperatures for the high molecular weight sample crystallised at 260°C under a pressure of 5 kbar.

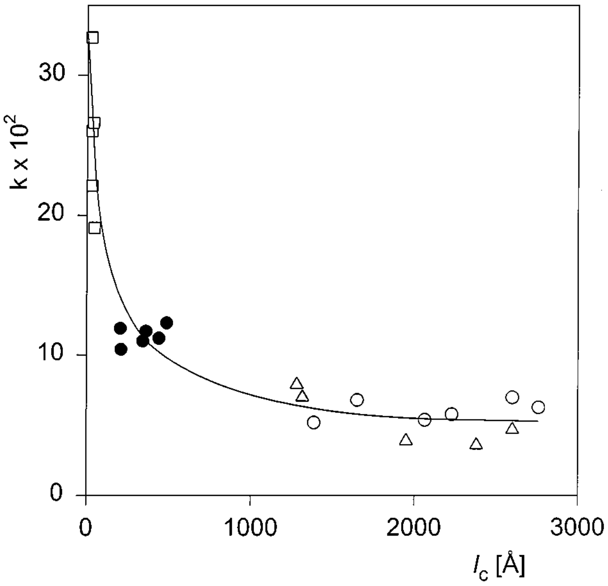

Figure 5 Plot of k vs. l_c for the various materials: □, paraffins; ●, chain-folded PE (Rigidex); ○, chain extended PE (Rigidex); △, chain-extended high molecular weight PE.

is raised from room temperature ($k = 0.05$) to 123°C ($k = 0.16$).

4. Discussion

4.1. Creep-microstructure correlation

The results compiled in Table I show that the k values of all chain-folded PE samples lie in the range 0.08–0.12, apparently independent of the molecular mass of the sample. The chain-folded high molecular weight material exhibits crystallinity values, α, in the range 0.5–0.6, while values for the lower molecular mass PE samples are as high as 0.84 after long annealing treatments [13]. Hence, the creep behaviour of the samples varies little with the level of crystallinity. On the other hand, chain-extended PE presents a higher resistance to plastic flow under the indenter ($k = 0.04$–0.08) than chain-folded PE ($k = 0.08$–0.12). A possible reason for the different creep behaviour found for PE samples crystallised at high and atmospheric pressure follows from Fig. 5. Here, the plot of k as a function of the crystalline lamellar thickness, l_c, for all PE and paraffin samples, shows that there is a close relationship between the creep constant and the crystal thickness. At small l_c values, k decreases steeply with increasing crystal thickness. However, the rate of decrease is substantially reduced when l_c approaches values for chain-folded PE. At large l_c values, k remains approximately constant.

In accordance with previous studies on melt crystallised PE samples [9], we suggest the following deformation modes of the material during an indentation test: on the initial, quasi-elastic stages of indentation, the amorphous layers are deformed under the applied compressive force and crystallites remain more or less intact. However, at larger indentation times, with the disordered regions highly compressed, the mechanical properties are primarily governed by the plastic deformation of the crystals. The above proposed model of deformation accounts for the creep behaviour of the investigated samples being largely independent of crystallinity while depending strongly on the thickness of the crystals.

4.2. Temperature dependence of hardness

The softening of chain-extended PE with increasing temperature is directly related to the thermal expansion of the crystalline phase, which induces a decrease in the cohesion energy of the molecules. The cross sectional area data in Fig. 3 do not show an inflexion point at $T \sim 100$°C as these data have been calculated from the extrapolation of the A values at low temperatures [19]. In addition, the thermal expansion of the amorphous regions, which represents 24% of the material [13], could also contribute to the H decrease with increasing temperature.

The inflexion observed at 100°C when examining the behaviour of hardness with temperature, suggests two different mechanisms. On the lower temperature side, the deformation of crystals may be dominated by a chain slip mechanism. At $T = 100$°C, the higher rate of creep of the material may be connected with the onset of torsional motions of the chain segments around the chain axis, inducing partial disordering of the crystalline lattice [9] preparatory to melting of the thinnest/most deformed lamellae.

The data presented in Fig. 4 show that the rate of creep of the material is also temperature dependent. This means that the k-parameter increases as the cross sectional area per molecule in the unit cell of PE is expanded.

5. Conclusions

- — The hardness of chain-folded and chain-extended PE has been shown to decrease with indentation time following a power-law.
- — The creep behaviour of chain-folded PE shows little dependence on the molecular mass of the

sample (and hence, of the degree of crystallinity), within the range of M_w investigated.

- The k-parameter seems to primarily depend on the crystal thickness. Thus, chain-extended PE shows the lowest rates of creep of all morphologies and paraffins the highest ones. The yield behaviour at long indentation times is dominated by the deformation mode of the crystals.
- The softening of chain-extended PE with increasing temperature correlates with the thermal expansion of the cross sectional area per molecule in the unit cell.
- The creep constant increases with increasing temperature, i.e., with the cross sectional area of the unit cell.

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References

1. F. J. BALTÁ CALLEJA and S. FAKIROV, *Trends Polym. Sci.* **5** (1997) 246.
2. T. JAWHAI, J. C. MERINO, J. C. RODRIGUEZ-CABELLO and J. M. PASTOR, *Polymer*. **34** (1993) 1613.
3. S. OSAWA and R. S. PORTER, *ibid.* **37** (1996) 2095.
4. J. D. KIELY, R. Q. HWANG and J. E. HOUSTON, *Phys. Rev. Lett.* **81** (1998) 4424.
5. E. H. LEE, G. R. RAO and L. K. MANSUR, *Trends Polym. Sci.* **4** (1996) 229.
6. B. J. BRISCOE and K. S. SEBASTIAN, *Proc. R. Soc. Lond. A* **452** (1996) 439.
7. P. EYERER and G. LANG, *Kunststoffe*. **62** (1972) 222.
8. F. J. BALTÁ CALLEJA, *Trends Polym. Sci.* **2** (1994) 419.
9. *Idem. Adv. Polym. Sci.* **66** (1985) 117.
10. F. J. BALTÁ CALLEJA, W. T. MEAD and R. S. PORTER, *Polym. Engng. Sci.* **20** (1980) 393.
11. F. J. BALTÁ CALLEJA, D. R. RUEDA, R. S. PORTER and W. T. MEAD, *J. Mater. Sci.* **15** (1980) 765.
12. F. J. BALTÁ CALLEJA and D. C. BASSETT, *J. Polym. Sci.: Polym. Symp.* **58** (1977) 157.
13. A. FLORES, F. J. BALTÁ CALLEJA and D. C. BASSETT, *J. Polym. Sci., Polym. Phys.* (part I of this series), **37** (1999).
14. A. FLORES, F. J. BALTÁ CALLEJA, G. E. ATTENBURROW and D. C. BASSETT, *Polymer*. in press (part III of this series).
15. D. C. BASSETT, *ibid.* **17** (1976) 460.
16. D. C. BASSETT in “Principles of Polymer Morphology” (Cambridge University Press, Cambridge, 1981).
17. F. ANIA, H. G. KILIAN and F. J. BALTÁ CALLEJA, *J. Mater. Sci. Lett.* **5** (1986) 1183.
18. F. J. BALTÁ CALLEJA, C. SANTA CRUZ, A. GONZÁLEZ ARCHE and E. LÓPEZ CABARCOS, *J. Mater. Sci.* **27** (1992) 2124.
19. G. T. DAVIS, R. K. EBY and J. P. COLSON, *J. Appl. Phys.* **41** (1970) 4316.

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