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Kinetics of chlorosulfonation and OsO_4 attack in the interlamellar regions of low and high density polyethylene studied by microhardness

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The microhardness of low density polyethylene (LDPE) fractions and of high density polyethylene (HDPE) samples has been studied as a function of molecular weight in the range of about 2×10^4 up to 4×10^6. Details of the lamellar structure were determined by transmission electron microscopy (TEM). The observed decrease of hardness with increasing molecular weight is mainly due to the increase in thickness of the interlamellar layers (i.e. a decrease of crystallinity). After chemical treatment with chlorosulfonic acid and with OsO_4 the samples show a drastic hardness increase. The kinetics of OsO_4 treatment as revealed by microhardness has been examined. The hardness increase is explained in terms of the large reduction in molecular mobility of the amorphous, interlamellar layers. The strongest hardening effects arise in consequence of the preferred reaction of these defect layers with increasing molecular weight. © 1997 Elsevier Science Ltd.

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INTRODUCTION

It is now established that microindentation hardness (H) is a property sensitive to morphological and structural changes in semicrystalline polymers[1–3]. Baltá Calleja and Kilian[4] developed an approach, based on a heterogeneous deformation model involving the heat dissipated by plastically deformed polymer crystals, to calculate the dependence of the crystal hardness H_c on the average thickness l_c of the crystalline lamellae. According to this approach

$$H_c = \frac{H_c^0}{(1 + b/l_c)} \quad (1)$$

where H_c^0 is the hardness of an infinitely thick crystal and $b = 2\sigma/\Delta h_f$ is a parameter which is proportional to the surface free energy σ of the crystal. For PE crystals $H_c^0 \simeq 170\,\text{MPa}$[4].

In the present study, the influence of the nature and size of the amorphous, interlamellar regions on the total hardness value has been examined. It is well known that polymer samples treated with chlorosulfonic acid and osmium tetroxide show a preferred reaction and incorporation of osmium atoms in the amorphous layers between the lamellae, yielding a remarkable hardening effect. Such a treatment is usual for fixation and selective staining of polyethylenes for electron microscopic investigations[5,6]. The observed preferred reaction of the amorphous material between lamellae and, in particular, of the surface layers of the lamellae increases the density of these regions, yielding dark-stained amorphous zones and bright crystalline lamellae in the electron micrographs.

Figure 1 shows typical lamellae in high magnification together with a scheme of the parameters, which can be determined directly. The non-crystalline regions between lamellae (l_a) consist of the sum of the amorphous interlamellar part (a) and the boundary layers (surface layers) of lamellae (g), i.e.

$$l_a = a + 2g \quad (2)$$

and the long period

$$L = l_c + l_a = l_c + a + 2g \quad (3)$$

To investigate the influence of staining on the mechanical properties, materials with a wide range of l_a thicknesses (fractions of low density polyethylene (LDPE)) have been used. Previous electron microscopy investigations of PE fractions with a broad molecular weight range reveal the strong influence of molecular weight on morphology[7–10]. From electron microscopic investigations of PE fractions[6–9] (molecular weights in the range of about 10^4 up to $\sim 10^6$ with narrow distribution) it is known that the increase of molecular weight affects more drastically the long period and the thickness of the amorphous layers than the thickness of the lamellae. This is illustrated in *Figure 2*,

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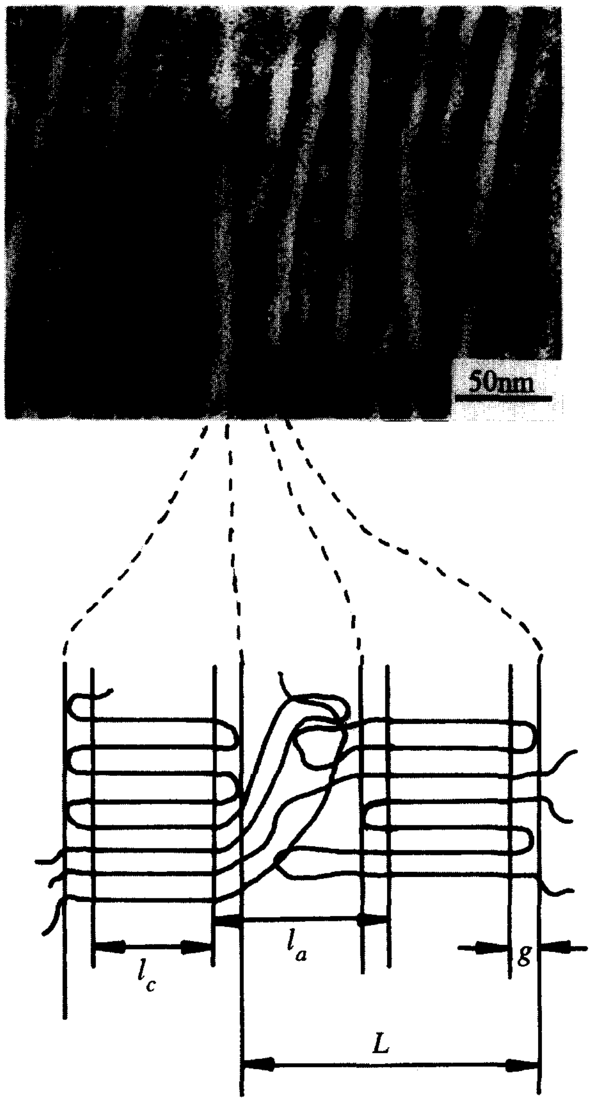

Figure 1 Details of the lamellar structure. Top: high magnification micrograph with unstained lamellae (bright), somewhat stained amorphous, interlamellar regions, and strongly stained surface layers of lamellae. Bottom: schematics of parameters determined directly on micrographs

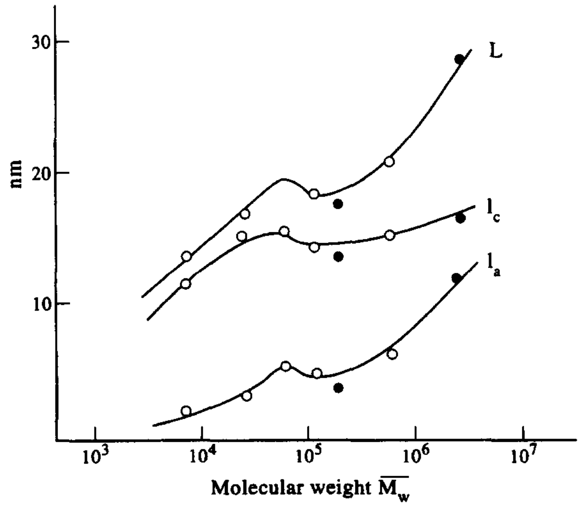

Figure 2 Variation of typical parameters from morphology in LDPE fractions with molecular weight. Thickness of crystalline lamellae (l_c), long period (L), and thickness of interlamellar regions (l_a) (refs 6–9)

which shows that l_a increases more rapidly with M_w than l_c does.

The investigation of these LDPE fractions could be very helpful in studying, principally, the influence of the thickness and chemical treatment of amorphous layers on the microhardness value.

To study the influence of chemically attacked amorphous layers on the microhardness the well known equation[3,4]

$$H = H_c(\alpha) + H_a(1 - \alpha) \qquad (4)$$

with a contribution of the amorphous zones to the hardness, H_a, different from zero must be applied. Here the value of H_c is given by equation (1) and α is the volume degree of crystallinity.

EXPERIMENTAL

Samples investigated

The samples investigated are fractions of commercial LDPE and HDPE. Two series of fractions of LDPE covering a wide molecular weight range and a very narrow molecular weight distribution, and three samples of HDPE with high and ultrahigh molecular weight, have been used (*Table 1*). The samples were subjected to the following treatments:

1. The LDPE fractions were chemically treated in two steps:
   (a) chlorosulfonic acid ($ClSO_3H$) treatment at room temperature for 24 h and at 45°C for 21 h;
   (b) chlorosulfonic acid treatment as above, with osmium tetroxide (OsO_4) at room temperature for 3 days.
3. Two of the LDPE fractions of LDPE: those with $M_w = 66\,400$ and $200\,000$, were first stained for 24 h with $ClSO_3H$ and then with OsO_4 at room temperature for different time periods: 0, 5, 7 and 12 days.
3. The HDPE samples were quenched from the melt and annealed for 2 h at 90 and 100°C.
4. The annealed HDPE samples were chemically treated:
   (a) with $ClSO_3H$ for 24 h; and
   (b) with $ClSO_3$ as in (a) and additionally with OsO_4 for 6 days.

Generally, after application of the longest treatment times used, the samples showed surface layers smooth enough for microindentation. After longer treatment times ($t > 12$ days) the surfaces were damaged (the roughness increased), and the microhardness tests were infeasible.

Electron microscopy studies

LDPE and HDPE samples were stained as indicated above with $ClSO_3H$ and OsO_4. Ultrathin sections were cut in a cryo-ultramicrotome, and the sections were investigated in a 90 kV and 100 kV transmission electron microscope (TEM). In particular, the thicknesses of lamellae and long periods were measured directly on electron micrographs or by microdensitometry of the negatives. The thickness of interlamellar amorphous regions was calculated as the difference between the long period and the lamellar thickness.

Microhardness measurements

Microhardness (H) was measured at room temperature using a Vickers tester. The test uses a square

Table 1 Crystal thickness (l_c), long period (L), thickness of amorphous layer (l_a), linear crystallinity (α) and microhardness (H_{exp}) for two series of LDPE fractions and HDPE samples with different molecular weights

Sample	M_w	M_n	l_c (nm)	L (nm)	l_a (nm)	α (l_c/L)	H_{exp} (MPa)
HDPE	490 000	51 578	15	19	4	0.76	48
HDPE	1 600 000	257 648	14	21	7	0.67	46
HDPE	4 400 000	611 961	16	26	10	0.62	42
LDPE	16 300	9055	7.9	15.7	7.8	0.50	26
(A)	66 400	35 698	7.5	18.3	10.8	0.41	23
	200 000	104 166	7.6	18.8	11.2	0.40	19
LDPE	23 200	12 677	6.5	12.2	5.7	0.53	30
(B)	94 300	49 631	6.6	12.9	6.3	0.51	23
	840 000	426 395	6.9	14.0	7.1	0.49	20

Table 2 Microhardness values (MPa) of chlorosulfonated LDPE at various reaction temperatures (T_R) as a function of OsO$_4$ treatment time (t_t)

(a) $\bar{M}_w = 66\,400$, $H = 23$ MPa

	t_t (days)			
T_R (°C)	0	5	7	12
22 (24 h)	40	–	125	137
45 (21 h) + RT (4 h)	76	163	198	201
60 (7 h)	75	–	141	–

(b) $\bar{M}_w = 200\,000$, $H = 19$ MPa

	t_t (days)			
T_R (°C)	0	5	7	12
22 (24 h)	39	–	104	113
45 (21 h) + RT (4 h)	66	145	183	182
60 (7 h)	73	–	132	–

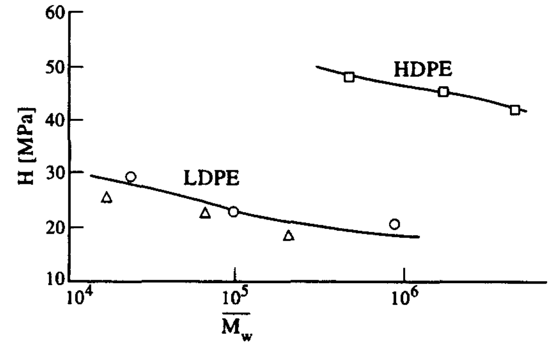

Figure 3 Influence of molecular weight of HDPE samples and LDPE fractions (series A (Δ); series B (O)) on microhardness

pyramidal diamond with included angles $\tau = 136°$ between the non-adjacent faces of the pyramid. The H value was derived from the residual projected area of indentation according to the expression $H = 2\sin(\tau/2)P/d^2 = 1.854P/d^2$, where d is the diagonal length of the impression in metres and P the force applied in N. The force is applied at a controlled rate, held for 0.1 min and removed. The length of the impression is measured to $\pm 1\,\mu$m with a microscope equipped with a filar eyepiece. A loading cycle of 0.1 min and loads of 0.5 and 1 N were used.

RESULTS AND DISCUSSION

Influence of molecular weight on microhardness

The microhardness values of the two series of LDPE fractions and HDPE samples are given in *Table 1* together with results of the quantitative determination of the morphological parameters. *Figure 3* shows the plot of microhardness as a function of molecular weight. It is clear that with increasing molecular weight the microhardness decreases for both LDPE fractions and HDPE samples. The higher values of the HDPE samples are due to the much larger l_c and α values (higher crystallinity). In preceding studies we showed that the b-parameter of equation (1) and σ from d.s.c. experiments increase with molecular weight M_w, leading to the view that defects and molecular entanglements are increasingly segregated into the defective surface boundary[11–13].

According to the results shown in *Figure 2*, the LDPE fraction with the highest molecular weight (840 000) should possess a slightly larger long period and thickness of the amorphous layers than those given in *Table 1*. This discrepancy arises as a result of the large variety of morphologies arising in this material. In addition to the spherulite-like structures with radially arranged and densely packed lamellae, giving rise to the small long periods L, other regions with irregularly arranged lamellae and larger long periods also exist. Since the ordered regions were measured in more detail than the unordered ones, the true average should give larger values of long period and amorphous thickness and a somewhat smaller crystallinity.

Kinetics of OsO$_4$ treatment for chlorosulfonated LDPE

Table 2 gives the variation of microhardness for the two LDPE fractions with $\bar{M}_w$ equal to 66 400 and 200 000, respectively, as a function of both the chlorosulfonation reaction temperature T_R and the treatment time with OsO$_4$ t_t. The ClSO$_3$H treatment causes a very noticeable and similar hardening in both samples. The hardening increases remarkably with the temperature of treatment. The H values presented are in agreement with previous data reported earlier[12].

Figure 4 shows the variation of H as a function of treatment time with OsO$_4$ for chlorosulfonated LDPE samples. After 7 days of OsO$_4$ treatment, the hardness increases dramatically (by about 3 times the original value), reaching, in some cases, values of the order of those found for crystalline PET (~200 MPa)[14]. The

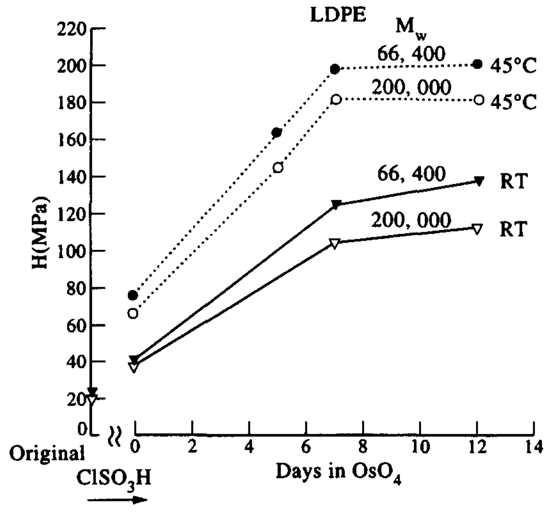

Figure 4 Influence of treatment time with OsO_4 on microhardness of two fractions of chlorosulfonated LDPE with lower (66 400) and higher (200 000) molecular weights

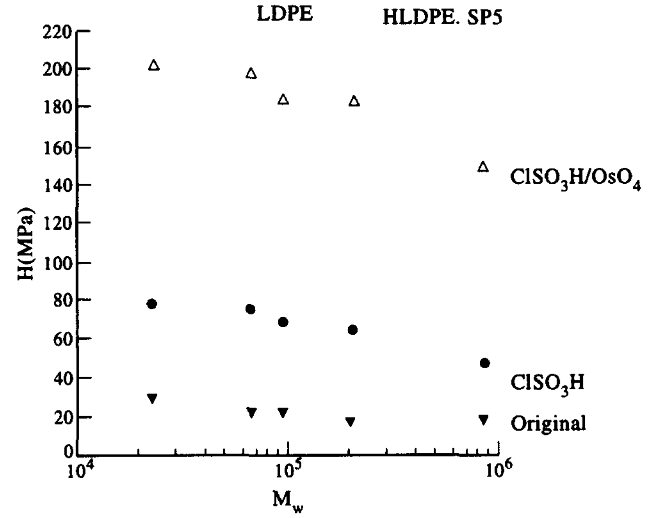

Figure 5 Change of the microhardness of LDPE fractions as a function of molecular weight for the original untreated samples (▼) and after chemical treatment with $ClSO_3H$ (4–24 h at RT; then 21 h at 45°C) (●) and with $ClSO_3H/OsO_4$ (as before) (7–10 days) (△)

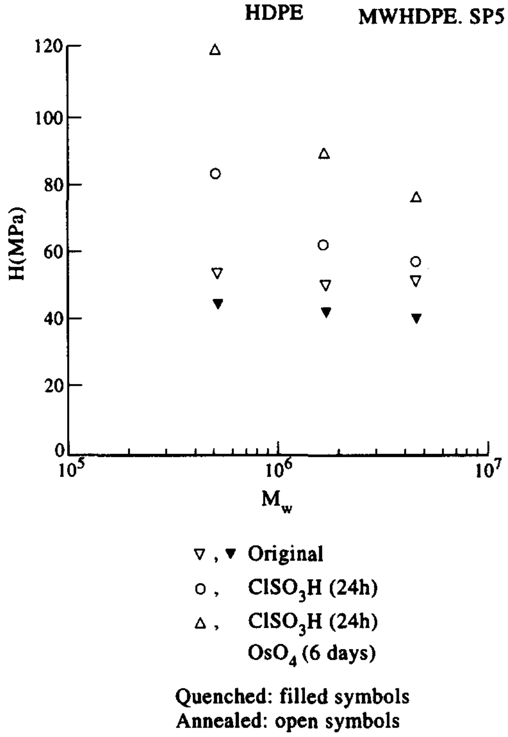

Figure 6 Change of microhardness of HDPE as a function of molecular weight for the original samples with different thermal history: quenched (▼), annealed (2 h at 130°C) (▽) and after chemical treatment: $ClSO_3H$ (24 h) (○); $ClSO_3H$ 24 h/OsO_4 6 days (△)

chlorosulfonated PE samples at 45°C show H values that are nearly twice those of the corresponding chlorosulfonated samples at room temperature. For longer times than 7 days in OsO_4 a levelling off of the H values is observed.

These results can be explained as follows. $ClSO_3H$ penetrates the amorphous phase and is randomly fixed at molecular segments of this phase, thus offering a higher mechanical resistance to the plastic deformation of the lamellar stacks under the applied compressive stress field of the microindenter. It is known that reaction at higher temperatures activates the reaction with SO_3H groups[15,16], thus providing an additional element of mechanical stability. Hence the H values of PE samples chlorosulfonated at 45°C are higher than those of samples treated at room temperature.

OsO_4 also penetrates the amorphous phase and is fixed at molecular segments of the interlamellar phase and, in particular, at the surface layers of the lamellae. This reaction rapidly increases the mechanical resistance to plastic deformation. Increasing the treatment time enhances the penetration of OsO_4 molecules between the crystalline lamellae. After a treatment of 7 days at 45°C, saturation seems to be reached and no additional OsO_4 penetrates into the material. If the samples are treated at room temperature, the penetration of OsO_4 into the amorphous regions occurs at a much slower rate, i.e. for longer times. Extrapolation of the curves in *Figure 4* up to the saturation value, reached at 45°C, seems possible.

The contribution of the amorphous layers to the microhardness of the material can be described by means of equation (4). Since H_c remains constant during the etching treatment, it turns out that after an OsO_4 treatment time of 12 days at 45°C, H_a increases from 0 up to values of 300 MPa. This means that the hardening of the amorphous layers reaches values which are typical for metals such as Ag or Pt reinforcing the micromechanical properties of the treated polymer.

The H values of the sample with the lower molecular weight (66 400) are slightly larger than those of the sample with the higher molecular weight (200 000); this difference increases with increasing time of OsO_4 treatment. The reasons can be twofold: (1) the smaller long period of the sample with $M_w = 66\,400$ gives a higher crystallinity (see *Table 1*) and, therefore, a somewhat larger microhardness; (2) the longer lamellae in the sample with $M_w = 66\,400^7$ act as longer and better diffusion paths for the chemical agents, giving rise to a more effective hardening.

Influence of M_w *and chemical treatment on microhardness*

Figures 5 and *6* show the dependence of H as a function of M_w for LDPE and HDPE samples before and after $ClSO_3H$ and $ClSO_3H/OsO_4$ treatment, respectively. The original, untreated samples show a decreasing tendency of H values with increasing M_w (see *Figure 3*), in agreement with other data observed previously[13].

After $ClSO_3H$ treatment the hardness of the original LDPE fractions noticeably increases, also showing a decreasing tendency with increasing M_w. For the samples treated with OsO_4 a very large additional increase of hardness is observed. In this case the rate of decrease of hardness with increasing M_w is even larger than for the only chlorosulfonated samples (see *Figure 5*). The increase of H after chemical treatment is based on the same hardening effect, explained in connection with *Figure 4* (i.e., hardening of the amorphous interlamellar layers). More interesting is the effect that the rate of decrease of hardness with increasing M_w is larger for the $ClSO_3H/OsO_4$ treatment than for the $ClSO_3H$ treatment alone. If the chemical fixation and hardening of the total amorphous phase were responsible for the increase of H, then the samples with higher M_w and therefore thicker amorphous layers (see *Table 1*) would show higher microhardness values than the samples with lower M_w. Therefore, another explanation is given, based on the electron microscopy observation that not all the amorphous parts between lamellae are stained to the same degree, but preferentially the surface layers of the lamellae. This means that, out of the amorphous layers with total thickness l_a, only the part of the boundary layers g is effective in increasing the hardness (see equation (2)). The thickness of these boundary layers is about 1.5–2 nm and relatively constant without variation with molecular weight[7–10]. Since the thickness of lamellae changes much less than the long period, the number of lamellae per unit volume decreases with increasing M_w. Analogously, the number of lamellar surface layers serving as the main diffusion and reaction paths decreases. In addition, the length of lamellae decreases with molecular weight. Both the smaller number of surface layers and their shorter length reduce the diffusion and absorption of chemical agents and therefore reduce the attainable hardness value. The result is the observed effect, shown in *Figure 5*.

The initial H values for the HDPE samples are larger than those for the LDPE samples (*Figure 6*) because of the higher crystallinity and crystal thickness values of HDPE (see *Table 1*). A difference in H between the quenched and the annealed samples is observed. The annealed samples show higher initial H values than the quenched ones, due to the thickening of the crystals, which contributes to the hardening as is easily explained by considering equation (1)[3,4]. Chemical treatment of annealed samples yields a strong increase of microhardness. The reason is, as in the case of LDPE, a hindering of molecular mobility after $ClSO_3H$ and an additional hardening by OsO_4 treatment. The decrease of H with molecular weight is also based on the same morphological features as in the case of LDPE: a larger increase of long period and thickness of amorphous layers, compared with a smaller increase of the thickness of lamellae, gives rise to a reduced number of lamellae. A smaller number of lamellae and of surface layers of lamellae reduces the penetration paths for chemical agents and, therefore, induces a reduction of the hardening effect.

CONCLUSIONS

In conclusion, it is shown that the morphology and, specifically, the size of the interlamellar regions determines the microhardness values of the initial PE samples. Chlorosulfonation produces an initial mechanical hardening of the amorphous phase, in which reaction time and temperature play an important role. Finally, the osmium tetroxide reaction induces an additional intense hardening, which is time-dependent and reflects additional details of the morphology of PE such as the decisive role of the lamellar surface layers. Values for H_a as high as 300 MPa are found for chlorosulfonated samples treated with OsO_4 for 7–12 days.

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