Crystallinity in polyethylene-based membranes and fibres*

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The crystallinity in membranes and fibres prepared by sulphochlorination of low-density polyethylene was determined by an X-ray diffraction method. A considerable decrease in the crystallinity was detected as the sulphochlorination reaction proceeded. The rate of decomposition of crystalline phase was strongly influenced by the degree of perfection of the polyethylene crystals and was much greater that the less-perfect crystals in the cold-drawn fibres than for more perfect crystals in sheets.

Keywords Decomposition; kinetics; crystallinity; sulphochlorination; crystal perfection; polyethylene

INTRODUCTION

The transport of molecules through polymeric membranes has been shown to be influenced by the degree of crystallinity of the polymer[1-4]. The behaviour of ion-exchange membranes or fibres consisting of a polyethylene-based matrix may thus be influenced by changes in crystallinity which may take place during chemical modification of the matrix. A widely used group of membranes of this type are usually prepared by sulphochlorination of low-density polyethylene, followed by hydrolysis or aminolysis[5-7]. The reaction may take place in the liquid or the gaseous phase, with u.v. light or organic promotors for initiation of the chlorination[8-12]. Some authors found that the crystallinity of the original material changed during the course of the reaction[13-14], but others reported that it did not, even after long reaction times[7,15].

In this work, measurements of the crystallinity of a polyethylene-based matrix were carried out during the course of a sulphochlorination reaction, and an attempt was made to explain the conflicting results obtained by other authors[13-15].

EXPERIMENTAL

Materials

Polyethylene fibres (the Israel Fiber Institute) and polyethylene sheets (Petrochemical Industries, Israel) were used as the starting materials. The fibres were melt spun and cold drawn at a ratio of 4:1. (This type of ion-exchange fibres was developed by our laboratory for industrial applications[16-17].) The fibres were photochemically reacted with SO_2 and Cl_2 (1:4) at 60°C for various times up to 20 h after preswelling in decaline (decahydronaphthalene)[17]. The polyethylene sheets were treated in the same way.

Although the fibres and sheets were both produced from low-density polyethylene, there were marked structural differences between them. These differences were reflected by that fact that the width of the diffraction peaks for the fibres was more than twice that for the sheets (the broadening being a function of the lattice distortion and the small size of the crystallites in the polyethylene[18]).

For example, the half-height width of the 110 peak was 1.10° for the fibres and only 0.5° for the sheets. We did not attempt to separate the effects of lattice distortion and crystallite size, although it seems likely that both effects were present, since the value of the half-height width of the 220 peak was intermediate between one for a pure distortion effect and one for a pure size effect. The increased lattice distortion in fibres is apparently the result of plastic deformation of material during cold drawing. Annealing considerably reduces the half-width of the 110 peak—to 0.9° at an annealing temperature of 60°C and to 0.6° at 90°C.

Methods of analysis

Three different methods are in common use for the determination of the crystallinity of polymers: X-ray diffraction, measurements of density and determination of the heat of fusion. In our case, X-ray diffraction seems to be preferable, since the determination of density or heat of fusion does not seem viable for the following reasons. The measurement of density is based on the fact that the density of crystalline polyethylene differs from that of the amorphous polymer by 15%. Since introduction of the comparatibely heavy atoms S and Cl into the polyethylene matrix during sulphochlorination may cause a change in density of about the same magnitude, the method is obviously not practicable for the determination of crystallinity. The heat-of-fusion method is based on a comparison of the heat of fusion of a pure crystalline phase and that of the sample under investigation. Since the effect of sulphochlorination on the heat of fusion of the polymer is not known, it is not possible to use this method.

We therefore chose to use an X-ray method similar to that of Hermans and Weidinger[19]. Some difficulties arose due to changes in absorption, preferred orientation, density and the dimensions of the sample resulting from the sulphochlorination of the polyethylene. These difficulties were overcome by means of the following

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treatment of the results. For each phase (crystalline or amorphous) in any sample, we can write the following equation[20]:

$$I_{ij} = \frac{K_i}{\rho_{ij}} X_{ij} A_{ij} \qquad (1)$$

where I_{ij} is the intensity of the diffraction peak of the ith phase in the jth sample; K_i is a constant for the ith phase; X_{ij} is the weight fraction of the ith phase in the jth sample; ρ_{ij} is the density of the ith phase in the jth sample; A_{ij} is the absorption factor.

From two equations of the form of equation (1) written for two samples with different crystallinities and two equations of the kind:

$$\sum_{i=1}^{n} X_{ij} = 1 \qquad (2)$$

written for the same samples, we can derive an equation for any X_{ij}

For example $$X_{11} = \frac{L_c(1-L_a)}{L_c - L_a} \qquad (3)$$

where $$L_c = (I_{11}\rho_{11}/A_{11}):(I_{12}\rho_{12}/A_{12})$$
$$L_a = (I_{21}\rho_{21}/A_{21}):(I_{22}\rho_{22}/A_{22})$$

As was shown in ref 21 the error in analysis increases drastically if $L_c \simeq L_a$. Therefore, in order to reduce this kind of error, we chose from the samples to be analysed, two pairs of samples with the largest and smallest values of L_c and L_a. The samples chosen were:

Pair 1: Untreated fibres and fibres treated for 10 h and
Pair 2: Untreated fibres and untreated sheets.

Finally, the crystallinity of a sample of untreated fibres was determined and served as a reference for the crystallinity of other samples determined according to equation (1).

Instrumentation

Diffraction patterns were obtained with a Philips diffractometer equipped with a copper tube and a proportional counter. The divergence slit was set at 1° and the receiving slit, at 0.2 mm. Both transmission and reflection geometries were used. The samples were taken either from a single sheet or from a row of parallel fibres. For each sample, the diffraction pattern was also obtained with a Philips pinhole flat-film camera, and the distribution of the intensity along the 110 ring was measured by means of a Joyce and Loeb microdensitometer.

The distribution of sulphur and chlorine in the sulphochlorinated sheets and fibres was examined with a JEOL (JSM-35) scanning electron microscope with an EDAX attachment for X-ray spectrochemical analysis.

Intensity measurements

The integral intensity of the 110 and 200 peaks represented the scattering by the crystalline phase, and the halo between $2\theta = 10°$ and 30° gives the intensity of the scattering by the amorphous phase.

The separation of the diffraction peaks from the diffuse halo was not difficult for the treated samples because the diffuse halo was clearly visible (*Figure 1b*). The problem was more complicated for the untreated samples of fibres, for which the diffuse halo was hidden under the tails of the very strong and very broad 110 peak (*Figure 1a*). In this case the diffuse halo obtained during the transmission meridional run of the untreated sample, i.e. the scattering of the amorphous phase, was subtracted (after absorption corrections) from the pattern obtained by reflection geometry.

For the treated samples, an additional correction was introduced for the scattering of the heavy atoms (SO_2 groups and Cl_2). It seems reasonable to assume that SO_2 and Cl would be concentrated in the amorphous part of the material. The content of these atoms was rather low, between 1 and 2 atomic %, and their positions were irregular with respect to each other. We could, therefore, consider the scattering of these atoms as gas scattering and subtract it from the diffuse halo in the following way. A scattering angle of $\theta \approx 50°$ far from the sharp diffraction peaks was chosen, and the intensity I measured at this angle was approximated as the sum of the following items:

$$I = C_1 f_1^2 + C_2 f_2^2 + C_3 f_3^2 + C_1 i_1 + C_2 i_2 + C_3 i_3 \qquad (4)$$

where C_1, C_2, C_3—molar concentrations of CH_2, SO_2 and Cl_2, respectively; f_1 f_2, f_3—scattering factors of these groups; i_1, i_2, i_3—incoherent scattering of these groups.

The quantities C_1–C_3 are known from chemical analysis, and f_1–f_3 and i_1–i_3 may be obtained from ref 22. It is then possible to divide the intensity I between all the items of equation (4). After this step, it is possible to subtract the scattering caused by the heavy atoms and the incoherent scattering from the intensity of the diffuse halo at the angular range 10–30° by using the known[22] dependence of f and i on 2θ angle.

Absorption correction

For symmetrical reflection geometry and for a sample of thickness t_j, the absorption factor A_{ij}[20] may be calculated from

$$A_{ij} = \frac{1}{2\mu_j^*}[1 - \exp - (2\mu_j t_j/\sin\theta_i)] =$$
$$\left(\frac{\rho_j t_j}{2\mu_j t_j}\right)[1 - \exp - (2\mu_j t_j/\sin\theta_i)] \qquad (5)$$

where μ_j—linear absorption coefficient of sample j; μ_j^* = mass absorption coefficient; ρ_j—density of the

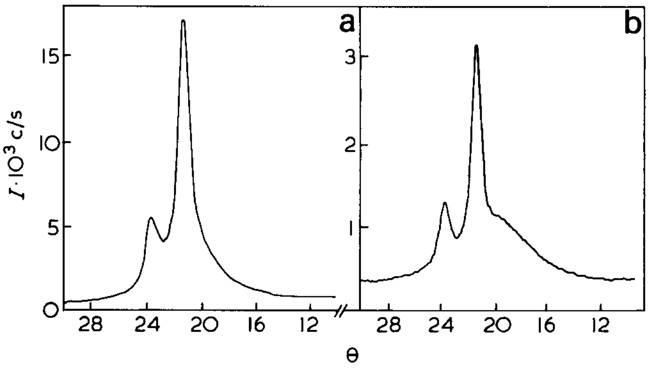

Figure 1 X-ray diffraction patterns of untreated polyethylene sheets (a) and fibres (b)

Table 1 Crystallinity of polyethylene fibres and sheets

Sample	Preswelling	Time of treatment (h)	Integral intensity of 110 and 200 peaks counts x10^5	$\int_0^{\pi/2} f(\alpha)\cos\alpha\,d\alpha$	Crystallinity (%)
Fibre	–	0	19.0	0.45	51
"	+	1	9.70	0.45	37
"	+	4	6.90	0.50	29
"	+	10	2.80	0.57	17.5
Film	–	0	7.3	1.00	31
"	+	4	3.20	1.00	21.5
"	+	10	3.00	1.00	21.5
"	+	20	2.30	1.00	19.5
"	–	1	5.2	1.00	26
"	–	10	3.80	1.00	24
"	–	20	3.30	1.00	24

sample, t_j—thickness of the sample. θ_j—scattering angle of phase i.

For symmetrical transmission geometry

$$A_{ij}=\rho_j t_j \exp-(\mu_j t_j/\cos\theta_i) \tag{6}$$

The quantity $\mu_j t_j$ was obtained experimentally by direct measurement of the absorption of monochromatic CuK$_\alpha$ radiation by the sample. The quantity $\rho_j t_j$ (the 'surface density') could be measured without difficulty: if U_j is the area of the sample (approximately 4 x 3 cm^2) and G_j—the weight of the sample, then:

$$\rho_j t_j = G_j/U_j \tag{7}$$

Preferred orientation correction

In polyethylene fibres, the direction (001) is approximately parallel to the fibre axis, and the distribution of the poles to any *hk*0 plane has an axial symmetry. This distribution can be described by the function $f(\alpha)$ where α is the latitude of the pole. If the function $f(\alpha)$ is normalized so that $f(0)=1$, then the average intensity of reflection from planes *hk*0 is given by:

$$I_{ij}=I_{ij}(0)\int_0^{\pi/2} f(\alpha)\cos\alpha\,d\alpha \tag{8}$$

where $I_{ij}(0)$—intensity of diffraction for the equatorial ($\alpha=0$) run in the diffractometer.

The function $f(\alpha)$ was obtained by measuring the intensity distribution along the 110 Debye ring, and the correction was applied according to equation (8). The validity of preferred orientation correction was confirmed by comparing the intensities I_{ij} for untreated fibres with those of the same fibres annealed at 60°C.

RESULTS AND DISCUSSION

The crystallinity of the untreated fibres was obtained according to equation (3): for this equation the first member of each pair of samples was taken as untreated fibres; the second member of the one pair was a sample of untreated sheet; and the second member of the other pair was a sample of fibre after 10 h of treatment. Two independent results obtained for the crystallinity of the untreated fibres—51% and 50.5%—were in excellent agreement. The crystallinity of the untreated sheet and fibres after 10 h of treatment was 31% and 17.5%, respectively. The crystallinity of the other samples was determined according to equation (1) with samples of untreated fibres and untreated sheet serving as standards.

From the results summarized in *Table 1*, we can see that the crystallinity of both the polyethylene fibres and sheets decreased as the sulphochlorination reaction proceeded. Preswelling of the polyethylene matrix facilitated a further decrease in crystallinity. The latter phenomenon is not unexpected since preswelling will enhance matrix relaxation which will in turn tend to facilitate the diffusion of gases into the matrix during the reaction.

The decrease of crystallinity in the fibres was considerably larger than that in the sheets for comparable reaction times. Let us now examine the three main factors which may contribute to the rate of decomposition of the crystalline phase, i.e. the initial concentration of the crystalline phase in the sample, the specific (external) surface area of the sample and the reactivity of the crystalline phase, defined by size of the crystallites and the extent of lattice distortion. The average rate of decomposition of the crystalline phase in fibres is 3.4% per hour for the 10 h period, as opposed to 1% for the sheets. The ratio of the initial crystallinity in these samples is 1.5 which is much lower than the ratio of the decomposition rates (3.4). Furthermore, the crystallinity of fibres dropped below that of sheets after the same time of reaction. It is thus clear that difference in the initial crystallinity cannot be the only factor causing the greater rate of decomposition of the crystalline phase in our fibres, and the remaining two factors should be considered.

The specific surface area S_f of the fibres with diameter d and density ρ is equal to $4/\rho d$. Consequently, for sheets of thickness t, provided that t is very much less than the planar dimensions of the sheet, $S_{sh}=2/\rho t$. In our case $d\approx0.18$ mm, $t\approx0.2$ mm and ratio $s_f/S_{sh}\approx2$, i.e. the difference in the specific surface area between fibres and sheets is considerable. At this stage, it became necessary to determine the mechanism of the sulphochlorination reaction, since a diffusion-controlled mechanism would imply that the specific surface area would exert a considerable influence on the sulphochlorination reaction and thus on the crystallinity, whereas a reaction rate dependent entirely on the sulphochlorination mechanism would imply that the specific surface area does not play an important role.

In order to elucidate the mechanism of reaction, we performed line-scan profiles of the chlorine and sulphur contents in fibres and sheets by means of a scanning

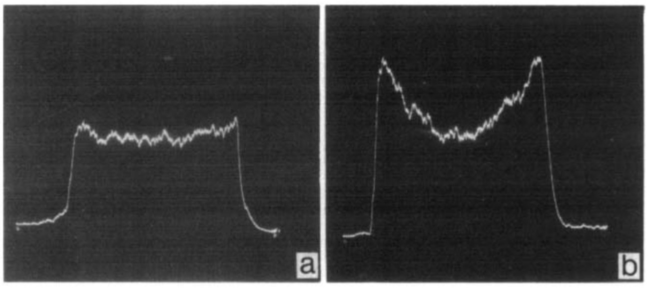

Figure 2 Distribution of chlorine (a) ahd sulphur (b) across the sulphochlorinated polyethylene sheet

electron microscope with an EDAX attachment (*Figure 2*). The direction of scan was normal to the plane of the sheet or along the diameter of the fibre cross section. Uniform distribution of chlorine or sulphur along the cross section would show that the mechanism of sulphochlorination is reaction-kinetics controlled and a decrease of concentration towards the middle of the sheet cross section or the centre of the fibre cross section would imply a completely or partially diffusion-controlled mechanism. According to our results (*Figure 2*) the chlorination process is reaction-kinetics controlled, but sulphochlorination is at least partially diffusion controlled.

If the line-scan profile of sulphur is known, the average concentration of sulphur can be calculated as follows.

For fibres $$\bar{C}_f = \frac{1}{v}\int_0^{d/2} 2\pi X L C(X) \mathrm{d}X$$

For sheets $$\bar{C}_{sh} = \frac{1}{v}\int_0^{t} L^2 C(X) \mathrm{d}X$$

where v is the volume of the fibre or sheet; L is the length of the fibre or sides of the rectangular sheet; $C(X)$ is the distribution of the sulphur concentration along the diameter of the fibre or along the axis normal to the plane of the sheet.

According to equations (9) and (10) and distribution $C(X)$ shown in *Figure 2b*, the ratio of the average concentrations C_f/C_{sh} is only ~1.10. Thus, in our case the difference in specific surface area between fibres and sheets has only a minor influence on the average concentration of sulphur and chlorine and, consequently, on the rate of decomposition of crystalline phase.

Now, we have to take into account the significance of the third remaining factor, size of crystallites and the extent of lattice distortion, on the process of decomposition of the crystalline phase. Although it is difficult to perform any calculations, it is obvious, at least qualitatively, that this factor must have an important effect on the decompositon of the crystalline phase: both increasing the concentration of lattice defects and increasing the surface area of crystalline phase will lead to increasing internal energy and chemical activity of the polyethylene.

In our process the decomposition of the crystalline phase is facilitated by the photochemical breakdown of the chlorine molecules within the polymer. The results presented in this paper will thus help to resolve the question of whether the crystalline phase of the polyethylene decomposes on sulphochlorination. In keeping with our resules Konishi *et al.*[13] found that the crystallinity of polyethylene decreased after sulphochlorination induced by irradiation. Similarly, Keller[14] found that a single crystal of polyethylene placed in a chlorine gas stream was completely destroyed at 60°C or higher. He deduced that chlorine radicals found their way into the crystal lamellae and disrupted their order. In contrast, Bickson *et al.*[7] did not find any change in crystallinity after their sulphochlorination process. The difference between our process and that of Bickson *et al.* may explain the incompatibility of the results: our reaction was carried out in the gas phase at 60°C, whereas that of Bickson *et al.* was carried out in the liquid phase at 15°C with an organic peroxide (methyl ethyl ketone hydroperoxide) as the initiator and cobalt naphthenate as the promotor. This latter reaction is sterically hindered since the large organic radical cannot find its way into the lamellae and thus attacks only the amorphous part of the matrix.

REFERENCES

1 Mackie, J. S. and Meares, P. *Proc. Roy. Soc.* 1955, **A232**, 298
2 Michaels, A. S. and Bixler, H. J. *J. Polym. Sci.* 1961, **50**, 413
3 Meares, P., Crank, J. and Park, G. S. (Eds.), 'Diffusion in Polymers', Academic Press, London, 1968, Ch. 10
4 Rogers, C. E., Stannett, V. and Szwarc, M. *Ind. Eng. Chem.* 1933, 1957, **49**
5 Korosy, F. de and Shorr, J. *Dechema Monog.* 1962, **47**, 477
6 Jagur-Grodzinski, J. and Vofsi, D. Isr. Patent No. 35838, 1973
7 Bikson, B., Jagur-Grodzinski, J. and Vofsi, D. *Polymer* 1979, **20**, 215
8 Reed, C. F. US Pat. 2046090; *Chem. Abst.* 1936, **30**, 5593
9 Walling, C. 'Free Radicals in Solutions', Wiley, New York, 1957
10 Wuckel, L., Sawchenko, L. and Seidel, A. 'Proceedings of the 1962 Tihany Symposium on Radiation Chemistry', Hungary, 1964, p. 301
11 Dzhazatspanyan, R. V., Yakomenko, L. M., Gershimovitch, A. I. and Zetkin, V. I. U.S.S.R. Pat. 150625 (1963)
12 Kroepelin *et al. Z. Angew. Chem.* 1952, **64**, 273
13 Konishi, K., Yamanguchi, X. and Takebisa, M. *J. Appl. Polym. Sci.* 1971, **15**, 257
14 Keller, A. *J. Polym. Sci.* 1962, **62**, 291
15 Jagur-Grodzinski, J., Bikson, B. and Vofsi, D. Proceedings 4th Int. Symp. on Fresh Water from the Sea, 1973, **4**, 171
16 Kedem, O. *Desalination* 1973, **16**, 105
17 Messalem, R., Forgacs, C., Michael, J. and Kedem, O. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* 1977, **31**, 383
18 Alexander, L. E. 'X-ray Diffraction Methods in Polymer Science', New York, Wiley, 1969
19 Hermans, P. S. and Weidinger, A. *Makromol. Chem.* 1961, **44–46**, 24
20 Klug, H. P. and Alexander, L. E. 'X-ray Diffraction Procedures', New York, Wiley, 1974
21 Zevin, L. S. *J. Appl. Crystalogr.* 1977, **10**, 147
22 'International Tables for X-Ray Crystallography', Vol. 3, Kynoch, London, 1962