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THE CALCULATION OF LATTICE PARAMETERS WITH X-RAY DIFFRACTION OF CRYSTALLINE POLYETHYLENE

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SUMMARY

Crystalline sizes and unit cell dimensions may be changed under the prepared conditions of the polymers. In the present study, structural changing of two crystalline polyethylene samples which are prepared under different conditions have been investigated by using x-ray diffraction methods. Unit cell dimensions and crystalline sizes of the samples have been obtained and these results have been compared with each other.

KRİSTALLİ POLİETİLENİN X-IŞINI KIRINIMI İLE ÖRGÜ PARAMETRELERİNİN HESAPLANMASI

ÖZET

Polimerlerin kristalleşme boyutları ve birim hücre boyutları hazırlanma şartlarına göre değişebilir. Bu çalışmada, farklı şartlarda hazırlanmış iki kristalleşmiş polietilen örneğinin yapısal değişimi x-ışını difraksiyon metodları ile incelenmiştir. Örneklerin birim hücre boyutları ve kristalleşme boyutları elde edilmiş ve bu sonuçlar karşılaştırılmıştır.

1- INTRODUCTION

Polyethylene is an important material in industry because of its transparancy. The crystalline cell formed in polyethylene is orthorhombic spatial unit cell [1]. But some structural changes may be occured in the polymers under the prepared conditions of the samples [2,3]. Structural changes caused by the prepared conditions of polimers have been investigated by many authors i.e. on the orientation of the crystallites [2-7], deformation mechanism [8-14], crystallinity and crystal size [15-17].

In the present study, the changing of unit cell dimensions and crystallite sizes along the unit axes of two polyethylene samples have been investigated by x-ray diffraction methods.

2- MATERIALS AND METHODS

The simplest organic polymer is polyethylene which is the polimerization product of ethylene. Ethylene polimerizes upon heating (100°C-400°C) under high pressure (1000 atm); the product is called polyethylene. The chemical formulea of polyethylene is is $n(CH_2=CH_2) \longrightarrow [-CH_2-CH_2-]_n$ [1]. Two polyethylene samples have been used in this study which were prepared in the Leeds university laboratories under the conditions; pressure annealed 234°C for 1 hour at $4^3/_4$ Kbar and extruded at 6 mm/min with draw ratio 7:1 (sample I) and 10:1 (sample II). Drawing is a commercially important process, since it is the means by which the physical properties of a soft isotropic polymer may became enhanced to form a synthetic fibre. This process was explained extensively by Jungnitz[15].

A Siemens diffractometer was used to measure profiles of x-ray reflections. A fine slit was used in addition to the primary collimator. The fine slit was also closer to the sample than the primary slit. Then, the profiles were registered under the appropriate experimental conditions: Cu target tube with the wavelenght, λ =1.5418, slits with fine slit, 1/2°, 0.2 mm apertures.

Crystalline cell of polyethylene is orthorhombic [1] and determining unit cell dimensions from an orthorhombic pattern can establish by using the orthorhombic space relation. Determination of crystal sizes from x-ray diffraction is based upon the broadening of a diffraction profile. The simplest relation, to describe x-ray profile broadening is Scherrer equation as

$$\beta(2\theta) = K(\lambda/L \cos\theta) \qquad -1-$$

where $\beta(2\theta)$ is full width at half maximum of the profile, λ is wavelength, 2θ is diffraction angle, and L is the crystal size [16]. The equation contains a constant K which was taken as unity throughought this study.

The measured broadening $B(2\theta)$ of the profile is usually corrected for istrumental broadening $b(2\theta)$ to obtain the true width $\beta(2\theta)$ by using the relation

$$\beta^2(2\theta) = B^2(2\theta) - b^2(2\theta) \qquad -2-$$

if the profiles are Gaussian, or by using the relation

$$\beta(2\theta) = B(2\theta) - b(2\theta) \qquad -3-$$

if the profiles are Lorentzian or Cauchy [9,14].

3- RESULTS AND DISCUSSIONS

The polyethylene structure is a fiber structure which has equatorial which means hk0 reflections and meridional which means 001 reflections, separately. The equatorial reflections were examined in reflection, and the meridional reflections were examined in transmission. The profiles have been measured at 1°/min scanning rate for the detector. As shown in figure 1; each of the samples have 8 equatorial reflections and one meridional reflection.

The patterns can index by using the unit cell dimensions of an ordinary poliethylene sample. The unit cell dimensions of an ordinary polyethylene sample are a=7.40, b= 4.9, c=2.53 in angström units [1]. Measured peak positions and their hkl indices of the patterns have been given in table 1. The accurate unit cell dimensions of these patterns have been obtained by using the orthorhombic space relation and these results have been given in table 2.

As shown in table 1, the patterns of the samples have 200, 020, and 002 peaks along the unit axes. The crystalline sizes of the samples based on the broadening of diffraction profiles have been calculated from these reflections. These profiles of the samples have been measured again at (1/8)°/min scanning rate. The measured broadening B(2θ) of a diffraction profile is corrected for istrumental broadening b(2θ) to obtain the true width β(2θ). The instrumental broadening b(2θ) of a chosen profile is full width at half maximum of the nearest peak to chosen profile in the peak positions of a standart sample. A Cu standart sample has been used to determine instrumental broadening of the profiles. There are four peaks of a Cu standart sample at 43.27°, 50.48°, 74.15°, 89.95° by using Cu$K_{\alpha 1}$ radiation. The peaks at 43.27° and 74.15° of Cu standart sample are the nearest peaks to 200, 020 profiles and 002 profile of the samples respectively. These peaks broadenings have been taken as instrumental broadening b(2θ). Standart profiles measurements under the condition (1/4)°/min scanning rate have been taken in the same time with every sample measurements. All of these profiles have been shown in figure 2.

Pure peak broadening (i.e. β(2θ)) of 200, 020, 002 peaks have been determined by using equation 2. After that, by using equation 1, crystal sizes along the unit axes of the samples have been obtained as shown in table 3.

As shown in table 2, the results of unit cell dimensions of the samples are not different from each other and these results are very near to the unit cell dimensions of an ordinary polyethlene sample. From the results in table 3, the crystalline sizes along a and b directions are the same but along c direction the crystalline sizes are different from each other of the samples. Then it can be say that crystallinity and crystal sizes of the polyethylene samples highly dependent on the preparation condition of the samples. Stiffness and transparancy of the samples can be changed under the prepared conditions [2,3]. This is an important property of polyethylene because the material is used in industry extensively.

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sample I 2θ	sample II 2θ	hkl
21.75	21.80	110
24.20	24.15	200
30.60	30.35	210
36.55	36.50	020
41.00	41.00	310
44.25	44.25	220
49.45	49.60	400
52.60	52.65	320
74.70	74.20	002

Table 1: Measured 2θ values and their hkl indices of polyethylene samples.

samples	a	b	c
I	7.35	4.91	2.54
II	7.35	4.93	2.56

Table 2: Unit cell parameters in angströms of the samples.

hkl	B(2θ)	b(2θ)	β(2θ)	θ	L size
		Sample I			
200	0.50	0.19	0.00809	12.10	195
020	0.60	0.19	0.00994	18.28	163
002	0.45	0.16	0.00732	37.35	265
		Sample II			
200	0.54	0.26	0.00818	12.08	192
020	0.63	0.26	0.00990	18.25	164
002	0.49	0.16	0.00802	37.10	241

Table 3: Crystallite sizes of the samples (here: B(2θ), b(2θ) and θ in degree, β(2θ) in radian, L in angström units).

Figure 1: Diffraction patterns of polyethylene samples.

a) equatorial and b) meridional reflections of sample I.

c) equitorial and d) meridional reflections of sample II.

Figure 2: 200, 020, 002 diffraction profiles of polyethylene samples and Cu standart profiles at 43.27°and 74.15°.

a) Sample I.

b) Sample II.

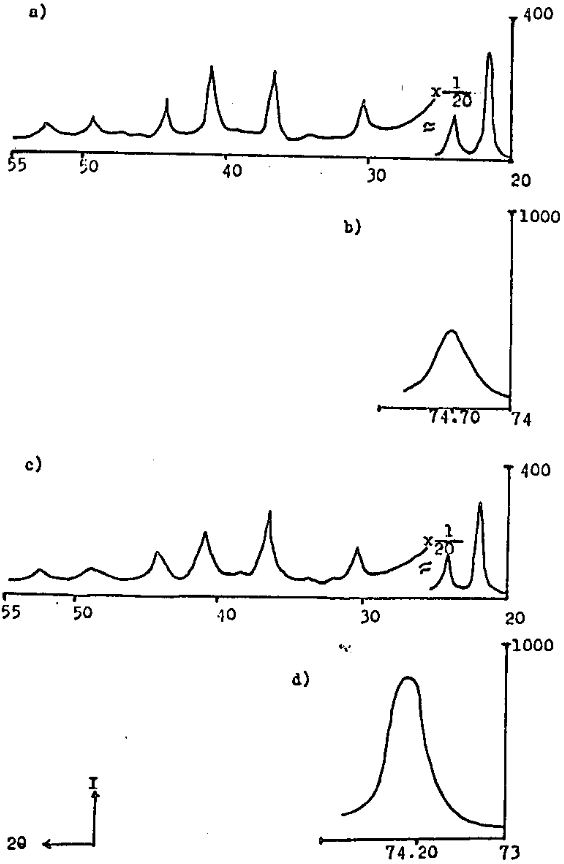
a)
400
x 1/20
55
50
40
30
20
b)
1000
74.70
74
c)
400
x 1/20
55
50
40
30
20
d)
1000
74.20
73
I
2θ

Figure 1:

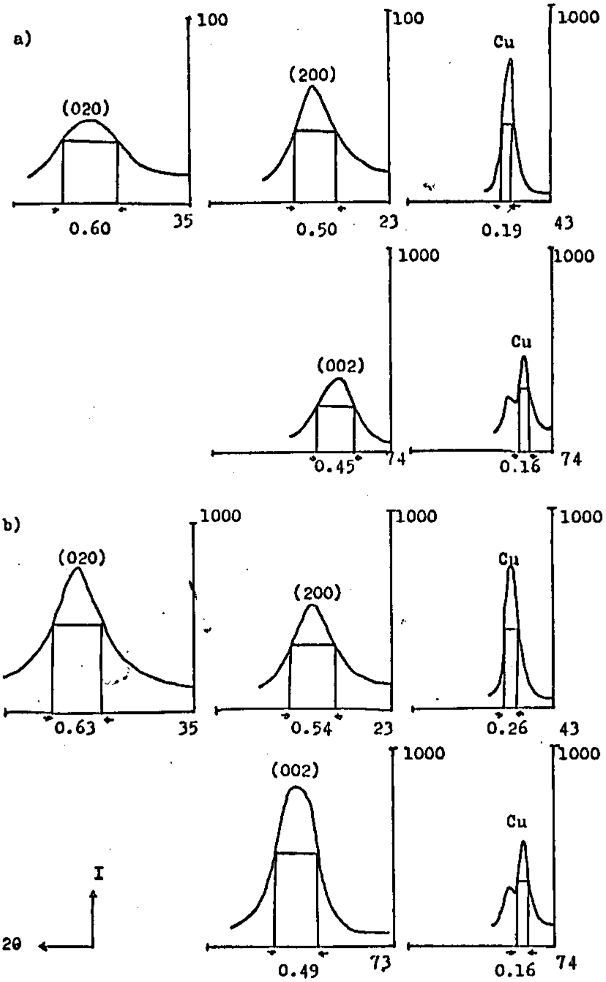
a)
100
(020)
0.60
35
100
(200)
0.50
23
1000
Cu
0.19
43
1000
(002)
0.45
74
1000
Cu
0.16
74
b)
1000
(020)
0.63
35
1000
(200)
0.54
23
1000
Cu
0.26
43
1000
(002)
0.49
73
1000
Cu
0.16
74
I
2θ

Figure 2:

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