THE DEGREE OF CRYSTALLINITY IN POLYMERS BY X-RAY DIFFRACTION ANALYSIS

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Abstract - Based on the X-ray scattering intensity theory, the correction factors of the degree of crystallinity formulae of the crystalline polymers have been clearly defined. The formula of degree of crystallinity are derived in terms of the WAXD theory and improved graphic multipeak resolution methods. The results are discussed with some typical example.

Key words WAXD, crystalline polymers, formula of degree of crystallinity, correction factor

Introduction

The degree of crystallinity $W_{c,x}$ is an important parameter for crystalline polymers. The physical and mechanical properties of polymers are profoundly dependent on the degree of crystallinity. It is well known that the degree of crystallinity can be determined by a variety of physical methods, for example, X-ray diffraction, calorimetry, density measurements, infrared (IR), and nuclear magnetic resonance (NMR) spectroscopy. While the determination of degree of crystallinity by X-ray diffraction were claimed inherently superior to others. Based on the X-ray scattering intensity theory, the attempt of this paper describes that the formula of degree of crystallinity of polymers, which is derived in terms of the WAXD theory and improved graphic multipeak resolution methods.

Theoretical Basis

The degree of crystallinity, $W_{c,x}$ is given by

$$W_{c,x} = \frac{I_c}{I_c + K_x I_a} \quad (1)$$

where I_c and I_a are the integrated intensities scattered over a suitable angular interval by the crystalline and the amorphous phases, respectively, and K_x is a calibration constant. If the sample is anisotropic, a suitable average of the diffracted intensity in reciprocal space must be obtained.

The degree of crystallinity determined by X-ray diffraction is calculated by Graphic multipeak resolution method previously established[1] as follows:

$$W_{c,x} = \frac{\sum_i C_{i,hkl}(\theta) I_{i,hkl}(\theta)}{\sum_i C_{i,hkl}(\theta) I_{i,hkl}(\theta) + k_i C_l(\theta) I_l(\theta)} \quad (2)$$

where $I_{i,hkl}$ = relative intensity of the crystalline peaks, $I_l(\theta)$ = relative intensity of the amorphous peak; $C_{i,hkl}(\theta)$ = correction factor of crystalline peaks; $C_l(\theta)$ = correction factor of amorphous peak; the total correction factor $K = C_l(\theta) \cdot k_i$, $k_i = \sum I_{i,cal} / \sum I_{i,total}$ ($k_i \leq 1$).

$C_{i,hkl}$ or $C_l(\theta)$ can be calculated by following equation:

$$\begin{aligned} C_{i,hkl}^{-1} \text{ or } C_l^{-1}(\theta) &= \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} f^2 \cdot e^{-2B(\sin^2 \theta / \lambda)^2} \\ &= \sum_i N_i f_i^2 \frac{1 + \cos^2 2\theta}{\cos \theta \sin^2 \theta} e^{-2B(\sin \theta / \lambda)^2} \end{aligned} \quad (3)$$

where f = atomic scattering factor of a repeating unit, f_i = scattering factor of the i th atom, N_i = number of the i th atom in a repeating unit, 2θ = Bragg angle, $(1 + \cos^2 2\theta) / \sin^2 \theta \cos \theta$ = angle factor (LP), $e^{-2B(\sin \theta / \lambda)^2}$ = temperature factor (T), and $-2B = 10$. The atomic scattering factor f_i can be expressed approximately by:

$$f_i(\sin \theta / \lambda) = \sum_{i=1}^4 a_i e^{-b_i (\sin \theta / \lambda)^2} + C \quad (4)$$

where values of a_i , b_i and c are given in Ref[2].

Although X-ray diffraction analysis has been widely used to determine $W_{c,x}$ for homopolymers, the $W_{c,x}$ for the multicomponent polymers have not correctly determined so far. In our recent paper[4], the formula of the multicomponent polymer $W_{c,x}$ was derived in terms of the X-ray scattering intensity theory and improved graphic multipeak resolution methods. The $W_{c,x}$ of the multicomponent polymers is defined as

$$W_{c,x} = \frac{\sum_{i=1}^M \sum_{j=1}^{POD} C_{i,j}(\theta) I_{i,j}(P)}{\sum_{i=1}^M \sum_{j=1}^{POD} C_{i,j}(\theta) I_{i,j}(P) + \sum_{i=1}^M \sum_{l=1}^{NOO} k_l C_{i,l}(\theta) I_{i,l}(N)} \quad (5)$$

where M is the number of the components in the multicomponent polymers, P is the number of Bragg peaks, N is the number of amorphous peaks. The $C_{i,j}(\theta)$ is the correction factor of type j Bragg peak, the $C_{i,l}$ is the correction factor of type l amorphous peak in the i component. $I_{i,j}(\theta)$ is the Bragg peak intensity of type j ; the $I_{i,l}(\theta)$ is the amorphous peak intensity of type l in the i component. $k_l = \sum I_{i,am} / \sum I_{i,tot} (k_l \leq 1)$. The $C(\theta)$ value can be calculated by equation(3)

Results and Discussion

Some typical examples for the homopolymers are given in the following:

(1) Homopolymer

(a) PE[3]

Polyethylene(PE) samples were heat-molded into sheets. Wide angle X-ray diffraction(WAXD) curve of PE shows two crystalline peaks at 2θ of 21.36° and 23.78° , one amorphous peak(A) at 2θ of 19.5° , respectively. These two crystalline peaks correspond to 110 and 200 spacings. The total WAXD curve is resolved into crystalline and amorphous portions (Fig.1).

Using eqs. (2)-(4), the correction factors for the crystalline and amorphous peaks were calculated and listed in Tab.1. With the Tab.1 correction factors, Eq.(2) can be further reduced to give PE formula of the degree of crystallinity (Eq.6).

$$W_{c,x} = \frac{I_{110} + 1.42 I_{200}}{I_{110} + 1.42 I_{200} + 0.75 I_A} \quad (6)$$

Fig.1 Resolution of the WAXD curve of PE into crystalline and amorphous portions

Tab.1 calculation values of correction factor $C(\theta)$ of PE

	A	110	200
$2\theta^\circ$	19.5	21.36	23.78
θ°	9.75	10.68	11.89
$e^{-2B(\sin\theta/\lambda)^2} = T$	0.8864	0.8655	0.8365
f_H^2	0.6063	0.5518	0.4900
f_C^2	24.1971	22.5415	20.6455
$f^2 = 4f_H^2 + 2f_C^2$	50.8194	47.2902	43.2510
$\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} = Lp$	66.8166	55.3287	44.2333
$f^2 Lp T$	3009.8432	2264.5861	1600.3386
$C(\theta)$	0.75	1	1.42

(b) st-1,2 PB

WAXD curve of syndiotactic 1,2-polybutadiene (st-1,2 PB) shows four crystalline peaks at $2\theta_{010}=13.75^\circ$, $2\theta_{110}=16.3^\circ$, $2\theta_{210}=21.45^\circ$, $2\theta_{201}=23.8^\circ$, and one amorphous peak at $2\theta_a=19.4^\circ$, respectively. The total WAXD curve is resolved into crystalline and amorphous portions (Fig.2). There are four carbon atoms and six hydrogen atoms in a repeating unit, the total atomic scattering factor $f^2=4f_C^2+6f_H^2$. Using the data above, Eq(2) can be reduced to give

$$W_{c,x} = \frac{I_{010} + 1.56I_{110} + 3.51I_{210} + 4.93I_{201}}{I_{010} + 1.56I_{110} + 3.51I_{210} + 4.93I_{201} + 1.02I_a} \quad (7)$$

Equation(7) was used for calculating the degree of crystallinity of st-1,2 PB samples.

Fig.2 WAXD curve of st-1,2 PB

ED//AB, point C (at $2\theta=19.1^\circ$) where the intensity of amorphous is large and crystalline intensity is assumed to drop to zero, amorphous peak (at $2\theta=19.4^\circ$)

Based on the X-ray diffraction intensity theory, we considered that the K value should be defined as $K=C(\theta) \cdot k_1$, K is the relative scattering coefficient for unit weight of crystalline and amorphous polymer i.e. total correction factor, $C(\theta)$, which has been corrected by atomic scattering factor, angle factor and temperature factor, is correction factor of crystalline peaks or amorphous peaks. k_1 is the relative scattering coefficient, which is the ratio of calculated diffraction intensity ($\sum I_{i,cal}$) to total scattering intensity ($\sum I_{i,total}$) for unit weight crystalline polymer specimen. Thus k_1 is defined as $k_1 = \sum I_{i,cal} / \sum I_{i,total}$ ($k_1 \leq 1$). The correction of lost coherent intensity in this method is very important.

The results of ten polymers studied have been reported[1]. The correction factors of formulae for the degree of crystallinity have been clearly defined. The formulae of the degree of crystallinity was derived by graphic multipeak resolution methods. The degree of crystallinity of crystalline polymers can be easily evaluated by our method.

(2) Multicomponent polymer

Using eq.(5), the degree of crystallinity of some typical multicomponent polymer were calculated. Fig.3 and 4 were WAXD curves of ethylene(E)-propylene(P) copolymer and ethylene(E)-propylene(P) blend, respectively. One of the common features of WAXD patterns of copolymer (Fig.3) and blend (Fig.4) is the retention of the modification of the monoclinic i-pp crystalline structure. Also diffraction of the PE crystal planes 110 and 200 is observed in Fig.3 and 4. The calculation of degree of crystallinity must consider the contribution from i-pp and PE, respectively. The amorphous peaks of i-pp and PE are at $2\theta=16.3^\circ$ and 19.5° , respectively. The $W_{c,x}$ was calculated from the data in Tab.2 and 3 by the following equation

$$W_{e,x} = \frac{\Delta_1 + \Delta_2}{\Delta_1 + \Delta_2 + \Delta_3} \quad (\text{for copolymer}) \quad (8)$$

$$\text{where, } \Delta_1 = (I_{110} + 1.64I_{040} + 2.16I_{130} + 2.73I_{\gamma} + 2.91I_{111})_{PP}$$

$$\Delta_2 = (5.37I_{110} + 6.86I_{200})_{PE} \quad \Delta_3 = 3.4I_{PE} + 1.29I_{PP}$$

$$W_{e,x} = \frac{\square_1 + \square_2}{\square_1 + \square_2 + \square_3} \quad (\text{for blend}) \quad (9)$$

$$\text{where, } \square_1 = (I_{110} + 1.60I_{040} + 2.16I_{130} + 2.68I_{\gamma} + 3.18I_{111})_{PP}$$

$$\square_2 = (5.29I_{110} + 6.88I_{200})_{PE} \quad \square_3 = 3.3I_{PE} + 1.27I_{PP}$$

Fig.3 Resolution of WAXD curve of ethylene-propylene copolymer

Fig.4 Resolution of WAXD curve of ethylene-propylene blend

Tab.2 The calibration Factor of $W_{e,x}$ in E-P Copolymer

samples	hkl	$2\theta^\circ$	θ°	T	Lp	f^2	C(θ)	I
PE	110	21.76	10.88	0.861	53.24	47.39	5.37	5.51
	200	23.45	11.73	0.841	45.55	44.38	6.86	3.52
	A	19.5	9.75	0.886	66.82	51.54	3.82	35.64
PP	110	13.89	6.95	0.940	133.84	92.69	1	6.70
	040	16.74	8.37	0.915	91.45	84.99	1.64	20.02
	130	18.44	9.22	0.898	74.98	80.26	2.16	6.05
	γ	19.95	9.98	0.881	63.74	75.06	2.73	16.92
	111	21.10	10.55	0.969	56.76	72.89	2.91	28.90
	A	16.30	8.15	0.919	96.57	86.20	1.52	81.40

Tab.3 The Calibration Factor of $W_{e,x}$ in E-P Blend

samples	hkl	$2\theta^\circ$	θ°	T	Lp	f^2	C(θ)	I
PE	110	21.84	10.92	0.860	52.83	47.25	5.29	20.1
	200	23.64	11.82	0.838	44.79	44.04	6.88	7.6
	A	19.50	9.75	0.886	66.82	51.54	3.72	90.7
PP	110	14.04	7.02	0.939	130.94	92.30	1	5.5
	040	16.76	8.38	0.916	91.23	84.93	1.60	28.4
	130	18.60	9.30	0.896	73.66	79.82	2.16	9.7
	γ	20.00	10.00	0.881	63.41	75.93	2.68	13.9
	111	21.14	10.57	0.868	56.53	72.78	3.18	33.7
	A	16.30	8.15	0.919	96.57	86.20	1.49	66.5

* A is amorphous peak; $C_{110}(\theta)$ is the standard of normalization for $C_{hkl}(\theta)$; γ peak is a contribution of long E and P sequences in EPR; $k_1(PE)=0.89$; $k_1(PP)=0.85$.

The PP/EPO and PE/EPO results calculated have been reported[4]

References

1. You-Lo Hsieh and Zhishen Mo, J. Appl. Polym. Sci., **33**, 1479 (1987);
Mo Zhishen and Zhang Hongfang, Polymeric Materials Science and Engineering(Chinese), **3**, 9 (1988).
2. International Tables for X-ray crystallography, Vol 4, P.71:101.
3. Mo Zhishen and Zhang Hongfang, Journal of Chinese User of the Rigaku X-ray Diffractometer. **1**, 1-15 (1991).
4. Zhishen Mo, Lixiao Wang, Hongfang Zhang, Ping Han and Baotong Huang, J. Polym. Sci., Part B: Polym. Physics, **25**, 1829 (1987);
Gao Huan, Mo Zhishen, Zhang Hongfang, Xue Xiaofu and Li Han, Chinese J. Appl. Chem, **7**(2), 35 (1990).