

THE DEGREE OF CRYSTALLINITY OF NYLON-1010 BY WAXD*

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ABSTRACT

Based on the X-ray scattering intensity theory and using the atomic scattering factor approximate expression, the correction factors for three main crystalline peaks and an amorphous peak of Nylon-1010 were calculated and the formula of degree of crystallinity of Nylon-1010 was derived by graphic multipeak resolution method.

The results calculated are compatible with the density measurement and calorimetry.

INTRODUCTION

Nylon-1010 is one of the important polyamide engineering plastics specifically produced and widely used in industry in China. In addition to a combination of high strength, elasticity, toughness and abrasion resistance in common with other polyamides, it features lower moisture absorption and thus higher dimensional stability. Its crystal structure, crystal density ρ_c , amorphous density ρ_a , equilibrium heat of fusion H_m^0 and equilibrium melting temperature T_m^0 have been reported^[1-3]. In the present paper, an effort has been made to determine the degree of crystallinity of Nylon-1010 by Wide Angle X-ray Diffraction (WAXD).

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EXPERIMENTAL

Sample

Nylon-1010 used in this study was a granular commercial product of Jilin Union Chemical Works. The $\bar{M}_n$ determined by dissolving it in m-cresol was 1.34×10^4 [1]. The Nylon-1010 samples were treated by two methods. Method I: granular samples were melt-molded into sheets, at 230°C for 10 min before annealing in air at 195, 185, 175, 165 and 150°C for 1.5 hr. Method II: the melt-molded samples were quenched at room temperature (18°C) for 5 min before annealing again with the same temperature series above for 1.5 hr.

The amorphous sample of Nylon-1010 was prepared by melting the sample at 230°C for 10 min and quenching in ice-salt water. WAXD pattern of amorphous sample exhibits only a wide peak at about $2\theta = 21.5^\circ$ (Fig. 1).

WAXD

The WAXD patterns of heat treated samples were scanned using a Rigaku D/max-IIIC diffractometer and scanning was performed from $2\theta = 5$ to 50 degrees. The diffractometer which is equipped with a graphite monochromator gives $\text{CuK}\alpha_1$ radiation ($\lambda = 0.15406 \text{ nm}$) by 2 kW Philips X-ray tube (40 kV, 20 mA).

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 integrating 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 diffraction intensity in reciprocal space must be obtained.

By means of graphic multipeak resolution method previously established [4,5], the degree of crystallinity determined by X-ray diffraction is as follows:

$$W_{c,x} = \frac{\sum_i C_{i,hkl}(\theta) I_{i,hkl}(\theta)}{\sum_i C_{i,hkl}(\theta) I_{i,hkl}(\theta) + K C_a(\theta) I_a(\theta)} \quad (2)$$

where $I_{i,hkl}$ = relative intensities of the crystalline peaks, $I_a(\theta)$ = relative

intensity of the amorphous peak; $C_{i,hkl}(\theta)$ = correction factors of crystalline peaks; $C_a(\theta)$ = correction factor of amorphous peak; the total correction factor $K = C_a(\theta) \cdot k_i$, k_i is the relative scattering coefficient, which is a ratio of calculating diffraction intensity ($\sum I_{i,cal}$) to total scattering intensity ($\sum I_{i,total}$) for unit weight crystalline polymer $k_i = \sum I_{i,cal} / \sum I_{i,total}$ ($k_i \leq 1$). $C_{i,hkl}$ or $C_a(\theta)$ can be calculated by the following equation:

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

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 approximately expressed 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[6].

RESULTS AND DISCUSSION

1. WAXD curve resolution

WAXD of the isothermal crystallization of Nylon -1010 shows three distinct peaks at 2θ of 8.5° , 20.05° , 23.92° , respectively (Fig. 1). These three peaks correspond to the 002 ; $\bar{1}00$, 100 ; and 110 , $0\bar{1}0$, 010 crystal planes. The last two were overlapping peaks^[2].

Interplanar spacings indices and observed intensities for Nylon-1010 by triclinic unit cell: $a = 0.49\text{nm}$, $b = 0.54\text{nm}$, $c = 2.78\text{nm}$, $\alpha = 49^\circ$, $\beta = 77^\circ$, $\gamma = 63.5^\circ$, were given in Table 1.

Base line AE connects A to E and crystalline intensity was assumed to drop to zero. ABCDE was amorphous curve with peak value point C at about $2\theta = 21.5^\circ$. The relative intensities (relative area) of I_{002} , $I_{\bar{1}00}$, I_{010} and I_a respectively were calculated by planimeter (Fig. 1).

2. Correction factors of main peaks and W_c , x calculation

Using equations 2, 3, 4 and 5, the correction factors at formula of the degree of crystallinity for the crystalline and amorphous peaks were

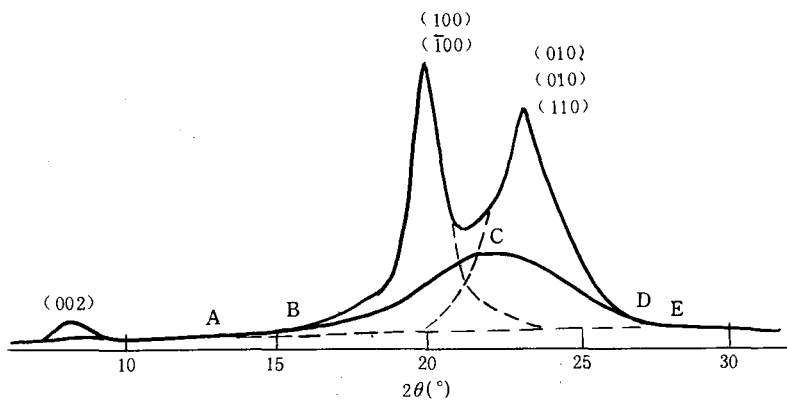


Fig. 1 WAXD curve resolution for Nylon-1010

calculated and listed in Table 2. The total atomic scattering factor was $f_{hkl}^2 = 20f_c^2 + 38f_H^2 + 2f_O^2 + 2f_N^2$ in a repeating unit of Nylon-1010 (Table 2), $k_i = 0.71$, $C_{002}(\theta) = 0.064$; $C_{100}^{100}(\theta) = 0.61$; $C_{010}^{010}(\theta) = 1.00$; $C_a(\theta) = 0.71$; $K = k_i \cdot C_a(\theta) = 0.504$. Using data above, equation 2 can be further reduced to give Equation(5).

Table 1 Interplanar spacings indices and relative intensities for Nylon-1010^[2]

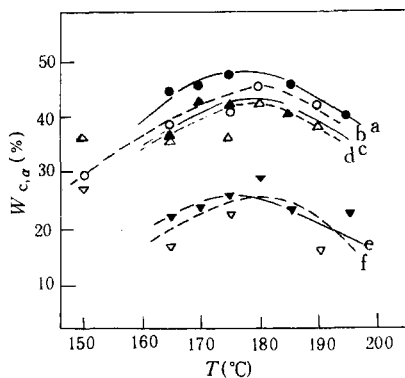
<i>n</i>	<i>2θ</i> (°)	<i>I</i> / <i>I</i> ₀	<i>hkl</i>	<i>k_i</i>
1	8.37	13	002	0.71
2	20.05	100	100, $\bar{1}00$	
3	23.92	87	010, $0\bar{1}0$	
4	24.10	8	110	
5	31.00	11	012, 105	
6	37.20	10	214	
7	37.70	11	014	
8	40.60	10	115	
9	45.02	9	203	
10	49.38	6	205	
11	49.75	8	220	
12	51.92	5	$\bar{1}25$	
13	52,30	3	$\bar{1}\bar{1}5$	
14	61.01	4	212, 321	
15	72.58	3	216	
16	74.00	2	031, $\bar{1}37$	
17	76.60	4	247, 148	

Table 2 Correction factors of X-ray diffraction peaks for Nylon-1010

hkl	$2\theta(^{\circ})$	T	LP	f^2	Correction factors
002	8.37	0.9779	372.568	915.98	0.064
100, $\bar{1}00$	20.05	0.8804	63.086	665.36	0.61
110, $0\bar{1}0, 010$	23.92	0.8350	43.771	589.35	1.00
A^+	21.5	0.8639	54.585	642.69	0.71

+ A amorphous peaks

$$W_{c,x} = \frac{0.064I_{002} + 0.61I_{100}^{100} + I_{110}^{110}}{0.064I_{002} + 0.61I_{100}^{100} + I_{110}^{110} + 0.504I_a} \cdot 100\% \quad (5)$$

**Fig. 2** Effect of heat treatment at various temperatures on the degree of crystallinity of Nylon-1010

- a, b $W_{c,x}$ ● annealing; ○ quenching;
 c, d $W_{c,d}$ ▲ annealing; △ quenching;
 e, f $W_{c,h}$ ■ annealing; □ quenching.

Based on Equation 5, the degree of crystallinity of Nylon-1010 samples with various heat treatment temperatures were calculated (Fig. 2). In order to confirm the results, we also showed the degree of crystallinity ($W_{c,d}$) from density measurement and the ($W_{c,h}$) from DSC measurement in Fig. 2. The $W_{c,\alpha}$ ($\alpha = x, d, h$) of every sample have values of the approximately normal distribution with the temperature change, indicating that both method I and method II have the most suitable annealing temperature (T_h) for crystallization of the samples. The $W_{c,x}$ of the sample from method I were higher than that from method II when the T_h was the same, indicating that method I is better than method II for the crystallization of Nylon-1010. Imperfections in crystals are not easily distinguished from the amorphous

phase. Also, the various techniques may be affected to different extents by imperfections and interfacial effects. Hence, some disagreement among the results of quantitative measurements of degree of crystallinity by different methods were frequently encountered. The degree of crystallinity ($W_{c,a}$) determined from density measurement ($W_{c,d}$) and X-ray diffraction ($W_{c,x}$) is equal to the sum of the crystalline and interphase content, while enthalpy of fusion measurement (DSC) by calorimetry yield values which are equal to just the crystalline content, as Fig. 2 showed at $W_{c,x} \geq W_{c,d} > W_{c,h}$.

Keywords:

Degree of crystallinity; Nylon-1010; WAXD

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