

DETERMINATION OF DEGREE OF CRYSTALLINITY OF NYLON 1212 BY WIDE-ANGLE X-RAY DIFFRACTION*

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Abstract Based on the X-ray scattering intensity theory and using the approximate expression for the atomic scattering factor, the correction factors for three crystalline peaks and an amorphous peak of Nylon 1212 were calculated and the formula of degree of crystallinity of Nylon 1212 was derived by a graphic multipeak resolution method. The degree of crystallinity calculated from the WAXD method is compatible with those obtained by density and calorimetry methods.

Keyword Degree of crystallinity, WAXD, Nylon 1212

INTRODUCTION

Nylon 1212 is one of the important engineering plastics in the family of even-even series Nylons. It has superior physical and chemical properties: low density, lower water absorption, excellent size stability, acid and alkali resistance, good low temperature flexibility, a wide processing temperature range, and high temperature stability. Because of its impermeability, Nylon 1212 is used in frozen food packaging and pharmaceutical packaging. Powder Nylon 1212 can be processed into powder coatings, which have excellent abrasion resistance and self-lubrication, strong metal bonding and good leveling properties^[1]. But the literature on the degree of crystallinity of Nylon 1212 is very limited. Jones *et al.*^[2] have studied the structure of a series of even-even nylons and found that Nylon 1212 shows two crystalline forms: α -form: $a = 0.49$ nm, $b = 0.52$ nm, $c = 3.23$ nm, $\alpha = 50^\circ$, $\beta = 77^\circ$, $\gamma = 64^\circ$, and β -form: $a = 0.49$ nm, $b = 0.802$ nm, $c = 3.23$ nm, $\alpha = 90^\circ$, $\beta = 77^\circ$, $\gamma = 67^\circ$. The Brill transition temperature of Nylon 1212 is about 130°C when heated from room temperature to melting temperature^[3]. The equilibrium melting temperature T_m^0 of Nylon 1212 is 188°C ^[4]. In Nylon 1212/montmorillonite blend, the existence of montmorillonite causes Nylon 1212 to have higher crystalline rate and short crystallization induction time. At the same time, the spherulites of Nylon 1212/montmorillonite were bigger than that of Nylon 1212 homopolymer^[5]. In this paper, we try to determine the degree of crystallinity of Nylon 1212 by wide-angle X-ray diffraction (WAXD), density and calorimetry (DSC) methods and derive the WAXD formula for the degree of crystallinity.

EXPERIMENTAL

Material

Nylon 1212 granules were provided by Zhengzhou University, with η_i of 1.76 measured in 96% H_2SO_4 . The

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samples were dried in vacuum at 70 °C for 24 h before used.

WAXD pattern of Nylon 1212 (Fig. 1) shows that there are two strong and one weak diffraction peaks. It indicates that the Nylon 1212 samples belong to the α -form^[2]. For the sake of attaining the change of the degree of crystallinity, the Nylon 1212 samples were melted into sheets at 224 °C for 10 min to eliminate thermal history, then annealed for 1.5 h at 165 °C, 160 °C, 155 °C, 150 °C, 145 °C and 140 °C, respectively.

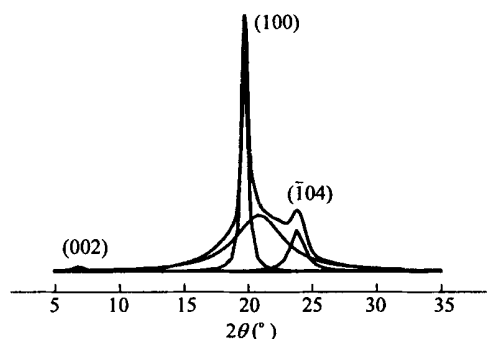


Fig. 1 WAXD pattern of Nylon 1212 (α -form)

The amorphous Nylon 1212 sample was prepared by melting at 224 °C for 10 min and quenching in liquid nitrogen. The WAXD pattern of the amorphous sample exhibits a broad peak at about $2\theta = 20.72^\circ$.

X-Ray Diffraction

WAXD experiments were performed at room temperature using a Rigaku D/max 2500V PC X-ray diffractometer in combination with a 18 kW rotating-anode generator operated at 40 kV and 200 mA, and curved graphite crystal filtered, $\text{CuK}_{\alpha 1}$ radiation ($\lambda = 0.15406$ nm). WAXD data were collected from $2\theta = 3^\circ$ – 45° with a step interval of 0.02° .

DSC Measurement

The samples melt-crystallized at different temperature were studied by a Perkin-Elmer DSC-7 differential scanning calorimeter. The temperatures and heat flow scales were carefully calibrated using indium over a wide temperature range at a heating rate of 10 K/min. The weight of samples was typically 8–10 mg and the samples were encapsulated in hermetically sealed aluminum pans.

Density Measurement

The density of Nylon 1212 was measured by the suspension method in an ethanol/carbon tetrachloride solution with a PZ-B-5 liquid-density balance.

Theoretical Basis

The degree of crystallinity, $W_{c,x}$ determined by X-ray diffraction is calculated 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 the graphic multipeak resolution method^[6] previously established, the degree of crystallinity determined by X-ray diffraction is as follows:

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

Where $I_{i, hkl}(\theta)$ = relative intensities of the crystalline peaks, $I_a(\theta)$ = relative intensity of the amorphous peaks, $C_{i, hkl}(\theta)$ = correction factors of crystalline peaks, $C_a(\theta)$ = correction factor of amorphous peak. The total correction factor $K = k_i C_a(\theta)$, k_i is the relative scattering coefficient, which is a ratio of the calculated diffraction intensity ($\sum I_{i, cal}$) to total scattering intensity ($\sum I_{i, total}$) for unit weight crystalline polymer, $k_i = \sum I_{i, cal} / \sum I_{i, total}$ ($k_i \leq 1$). $C_{i, hkl}(\theta)$ or $C_a(\theta)$ can be calculated by the following Eq. (3):

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

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. [7].

RESULTS AND DISCUSSION

The Result of $W_{c, x}$

WAXD curve resolution

Interplanar spacing indices and observed intensities for Nylon 1212 (α -form) are shown in Table 1. We choose three strong peaks to calculate k_i .

Table 1. Interplanar spacing indices and relative intensities for Nylon 1212 (α -form)

n	$2\theta (^{\circ})$	$d_{obs} (\text{nm})$	$d_{cal} (\text{nm})$	$I/I_0 (\%)$	$h k l$	k_i
1	6.800	1.29879	1.23290	3.1	002	0.82
2	19.760	0.44892	0.43891	100.0	100	
3	23.880	0.37231	0.37236	20.0	$\bar{1} 04$	
4	31.461	0.28412	0.27869	0.3	$11 \bar{3}$	
5	34.142	0.26240	0.26343	0.3	$\bar{1} 13$	
6	35.943	0.24965	0.24886	0.4	$1 \bar{1} \bar{1}$	
7	37.800	0.23780	0.23896	2.6	211	
8	39.961	0.22543	0.22559	0.8	$\bar{2} \bar{1} 1$	
9	40.300	0.22361	0.22020	1.2	$20 \bar{1}$	

In Fig. 1, the WAXD pattern of the isothermal crystallized Nylon 1212 (α -form) shows three distinct peaks at 2θ of 6.80° , 19.76° , and 23.88° from small to high angles, respectively.

Correction factors of main peaks and $W_{c, x}$ calculation

Using Eqs. (2), (3), and (4), the correction factors in the formula of the degree of crystallinity for the crystalline and amorphous peaks were calculated and listed in Table 2. The total atomic scattering factor was $f_{hkl}^2 = 24f_c^2 + 46f_H^2 + 2f_O^2 + 2f_N^2$ in a repeating unit of Nylon 1212, $k_i = 0.82$, $C_1(\theta) = 0.075$, $C_2(\theta) = 1$, $C_3(\theta) = 1.82$, $C_a(\theta) = 1.15$, $K = k_i \cdot C_a(\theta) = 0.95$. Using the above data, Eq. (2) can be further reduced to give Eq. (5).

$$W_{c, x} = \frac{0.075I_{002} + I_{100} + 1.82I_{\bar{1}04}}{0.075I_{002} + I_{100} + 1.82I_{\bar{1}04} + 0.95I_a} \times 100 \% \quad (5)$$

Table 2. Correction factors of X-ray diffraction peaks for Nylon 1212 (α -form)

Reflection	$2\theta(^{\circ})$	I	T	LP	f^2	C_{θ}	K
002	6.80	1580.6	0.985	560.677	1081.937	0.075	0.95
100	19.76	76859.9	0.883	65.016	783.824	1	
$\bar{1}04$	23.88	44427.4	0.835	43.886	676.687	1.82	
A	20.72	208607	0.873	58.936	758.397	1.15	

A: amorphous peak

Table 3. The values of ΔH_m , ρ , $W_{c,x}$, $W_{c,d}$ and $W_{c,h}$ of Nylon 1212

$T(^{\circ}C)$	$\Delta H_m (J/g)$	$\rho (g/cm^3)$	$\bar{V}_{sp} (cm^3/g)$	$W_{c,x} (\%)$	$W_{c,d} (\%)$	$W_{c,h} (\%)$
140	49.178	1.0525	0.9501	42.8	36.8	17.6
145	59.897	1.0569	0.9462	46.6	39.9	21.5
150	62.805	1.0581	0.9451	47.6	40.7	22.5
155	64.015	1.0586	0.9446	48.0	41.0	22.9
160	64.982	1.0590	0.9443	48.2	41.3	23.3
165	63.047	1.0582	0.9450	47.7	40.8	22.6

Using the above Eq. (5), the values of $W_{c,x}$ at different crystallization temperature are calculated and listed in Table 3.

The Measurement of ΔH_m^0 and $W_{c,h}$

The ΔH_m^0 of Nylon 1212

A number of methods are now available to determine equilibrium melting enthalpy ΔH_m^0 of a crystalline polymer^[8]. Among them, the approach to extrapolate the linear relationship between enthalpy of fusion ΔH_m and the specific volume $\bar{V}_{sp}$ of samples with different degree of crystallinity to 100% crystalline condition has been proved to be successful in the determination of ΔH_m^0 for many linear semicrystalline polymers^[9]. Therefore, specimens with different degrees of crystallinity were prepared by annealing in different conditions. Enthalpy of fusions ΔH_m of the samples were determined by DSC and listed in Table 3. And their respective specific volumes $\bar{V}_{sp}$ were measured with a density gradient column and are tabulated in Table 3. Figure 2 shows the plot of ΔH_m against the corresponding $\bar{V}_{sp}$ of the differently annealed Nylon 1212 samples. The graph can be expressed as Eq. (6):

$$\Delta H_m = 2623.99 - 2709.99 \bar{V}_{sp}$$

(6)

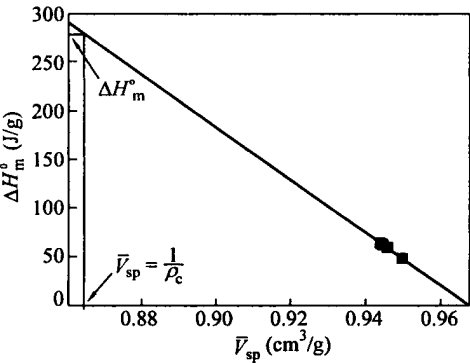


Fig. 2 The enthalpy of fusion of Nylon 1212 (α -form) isothermally crystallized at different temperatures

If $\bar{V}_{sp}$ is substituted with the specific volume of hypothetical 100% crystalline Nylon 1212, i.e.,

$\bar{V}_{sp} = 0.8652 \text{ cm}^3/\text{g}$ or $\rho_c = 1.1558 \text{ g/cm}^3$ calculated by unit cell parameter, $\Delta H_m^0 = 279.2 \text{ J/g}$ is derived. Generally speaking, for polyamides, there is a trend that the longer the hydrocarbon segment in the repeating unit, the higher is the value of ΔH_m^0 . Therefore, the value of ΔH_m^0 (279.2 J/g) can be regarded to be reasonable as compared with those of Nylon 66 (117.0 J/g)^[10], Nylon 610 (211.7 J/g)^[11] and Nylon 1010 (244.0 J/g)^[12].

The $W_{c, h}$ of Nylon 1212

The degree of crystallinity measured from calorimetry ($W_{c, h}$)^[7] was calculated by Eq. (7):

$$W_{c, h} = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \quad (7)$$

Where ΔH_m and ΔH_m^0 were regarded as the enthalpy of fusion of samples and the equilibrium melting enthalpy, respectively, at the same temperature. The values of ΔH_m are listed in Table 3., and the values of $W_{c, h}$ calculated are shown in Table 3.

The Result of Density Measurement

The $W_{c, d}$ is given by Eq. (8)^[6]

$$W_{c, d} = \frac{\frac{1}{\rho_a} - \frac{1}{\rho}}{\frac{1}{\rho_a} - \frac{1}{\rho_c}} \times 100\% \quad (8)$$

Where ρ_a is the density of an amorphous sample, determined by extrapolating the line of $W_{c, x}$ versus ρ as shown in Fig. 3, the value of ρ_a obtained is 1.0018 g/cm^3 when $W_{c, x}$ equals to zero. ρ is the density of the sample, ρ_c is the density of the sample crystallized completely. Using the above data, we can calculate the $W_{c, d}$ values of Nylon 1212, which are listed in Table 3.

From Fig. 4 and Table 3, we can see that with increasing crystallization temperature in the same crystallization time (1.5 h), the degree of crystallinity Nylon 1212 also increases. At 160°C or so, the degree of crystallinity reaches its maximum value. As to this phenomenon, we assume that increasing annealing temperature may enhance the ability of second crystallization of Nylon 1212. Compared with the dominant crystalline layer, the melting point of second crystallization becomes lower. Along with the increase of annealing temperature, the degree of crystallinity of Nylon 1212 is enhanced and the crystal becomes perfect. But, when the temperature exceeds 160°C , the degree of crystallinity begins to decline. The reason is that high temperature is partly favorable for the formation of crystal, but many small and unstable crystal grains can easily transform into the amorphous state, so that the total degree of crystallinity decreases.

In order to confirm that the degree of crystallinity of the Nylon 1212 sample varies with heat treatment temperatures, we also calculate the degree of crystallinity ($W_{c, d}$) from density measurement (method II) and the ($W_{c, h}$) from DSC measurement (method III), the results of which are shown in Fig. 4. The values of $W_{c, \alpha}$ ($\alpha = x, d, h$) of every sample increase approximately with the temperature change. The values of $W_{c, x}$ of the samples measured by method I are higher than those of $W_{c, d}$ from method II and those of $W_{c, h}$ from method III when their annealing temperatures are the same, indicating that method I is better than method II and method III for the crystallization of Nylon 1212. Imperfection in crystals is not easily distinguishable from the amorphous phase. Also, various measuring techniques may be affected to different extents by imperfections and interfacial effects. Hence, some disagreements among the results of quantitative measurements of degree of crystallinity using different methods are frequently encountered. In addition, method I is based on the density difference of electrons between crystalline and amorphous phase, method II is based on the difference of ordered stacks of molecular chains in crystalline and amorphous phase, method III is based on the quantity of heat absorbed during the melting of crystalline phase of the sample, it only considers the contribution of crystalline phase. Therefore, we can conclude that $W_{c, x} > W_{c, d} > W_{c, h}$ and Eq. (5) can be used to calculate the degree of crystallinity of

Nylon 1212.

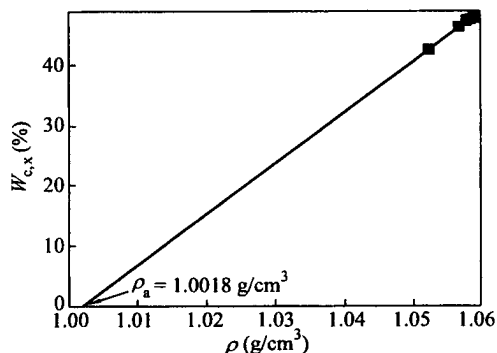


Fig. 3 Plots of $W_{c,x}$ versus ρ for Nylon 1212 (α -form) at different crystallization temperatures.

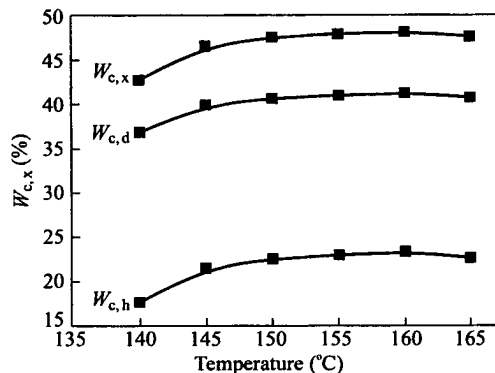


Fig. 4 Degree of crystallinity of Nylon 1212 determined by different methods.

CONCLUSION

The changes of degree of crystallinity for Nylon 1212 and the formula of degree of crystallinity are determined by graphic multipeak resolution. The values of degree of crystallinity, determined by graphic multipeak resolution using WAXD, reach a maximum at 160°C or so and are higher than those determined by DSC and density methods under the same conditions. By extrapolating the linear relationship between ΔH_m and the obtained specific volume $\bar{V}_{sp}$, the equilibrium melting enthalpy ΔH_m^0 is found to be 279.2 J/g.

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