

APPLICATION OF THE MOMENT METHODS TO ANALYSIS OF X-RAY DIFFRACTION LINE PROFILE FOR PA1010-BMI SYSTEM*

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ABSTRACT

Pure X-ray diffraction profiles have been analysed for polyamide 1010 and PA1010-BMI system by means of multipeak fitting resolution of X-ray diffraction. The methods of variance and fourth moment have been applied to determine the particle size and strain values for the paracrystalline materials. The results indicated that both variance and fourth moment of X-ray diffraction line profile yielded approximately the same values of the particle size and the strain. The particle sizes of (100) reflection have been found to decrease with increasing BMI content, whereas the strain values increased.

INTRODUCTION

Polyamide (PA) 1010 as the important polyamide engineering plastics produced commercially in China has been used in many fields. PA1010 possesses lower moisture absorption and thus higher dimensional stability,

* This work was supported by the National Natural Science Foundation of China and by the National Basic Research Project-Macromolecular Condensed State

Received January 16, 1994

but its service temperature is low, because of the additional hydrocarbon segments in the decanedioic acid and decamethylene diamine. The interest to improve its properties by transforming it into a network polymer has attracted considerable attention. Special attention was paid to specimens of PA1010 containing crosslinking agent N, N'-bismaleimide-4, 4'-diphenyl methane (BMI). In the present paper, the methods of variance and fourth moment were applied to analysis of X-ray diffraction line profile, which involved the particle size and strain values of the system with different BMI content. It is known that the molecular ordering and microstructure in a polymer play an important role in determining its mechanical properties. In a polymer, especially polymer blend which generally has paracrystalline structures, the state of atomic arrangement in paracrystalline polymers can be analysed with the help of X-ray diffraction line profile. The methods of the variance and fourth central moment of the line profile can be done independently^[1]. The methods overcame the major practical difficulty in a line profile analysis of a polymer which are generally the absence of higher-order reflections. It has been demonstrated that such an analysis can be carried out on the basis of a single-line technique alone^[2]. And it was shown that the single-line profile method yields values which are often more accurate than those yielded by multiple-order profile method^[3]. Also the central moments can avoid the encounter of the termination error of voigt function^[4]. The single-line profile method has been successfully used for many metals and alloys, but application of this method to a polymer blend seldom connected^[5].

EXPERIMENTAL

PA1010 with molecular weight $\bar{M}_n = 1.34 \times 10^4$ used in this work was a commercial product of Jilin Union Chemical Works in China. BMI with difunctional monomer was friendly provided from Hubei Chemical Institute. BMI was used to enhance the crosslinking agent by mixing thoroughly its acetone solution with powdered PA1010 in a motar. BMI content in PA1010—BMI blends samples is 0, 1, 2.5, and 5 (wt%) respectively. After vacuum drying, films of about 1.0 mm thickness were prepared by compression moulding at 220°C and 9.8MPa for 10min.

X-ray diffraction curves were recorded with the help of Rigaku D/max-IIB X-ray diffractometer. $\text{CuK}_{\alpha 1}$ radiation with a bent-quartz

monochromator at 40kV and 20mA was used for recording X-ray diffraction profiles. X-ray diffraction profiles for PA1010 and PA1010-BMI system were found to be partially overlapped. The diffraction curves corrected for Lorentz and polarization factors, absorption and background scattering were separated by means of the method of multipeak fitting resolution of X-ray diffraction.

RESULTS AND DISCUSSION

The diffraction intensity in the direction s can be written as^[6]

$$\begin{aligned} I(s) &= c \int_0^M V(t)Y(t)\cos(2\pi st)dt \\ &= c \int_0^M A(t)\cos(2\pi st)dt \end{aligned} \quad (1)$$

where $V(t) = M - |t|$, $Y(t) = \exp(-Dt)$.

The expression for the variance W , as given by Wilson^[6], is as follows:

$$W = \frac{1}{4\pi^2} \left[2\sigma \frac{A'(O)}{A(O)} + \frac{A''(O)}{A(O)} \right] \quad (2)$$

By some calculation and substitution, Equation (2) was changed as follows:

$$W = K_0\sigma + W_0 \quad (3)$$

where

$$\begin{aligned} K_0 &= \frac{1}{2\pi^2} \left(D + \frac{1}{L} \right) \\ W_0 &= \frac{1}{4\pi^2} \left(D^2 + \frac{2D}{L} \right) \end{aligned} \quad (4)$$

σ being the angular range over which the intensity is measured. L the particle average size in a direction normal to the reflection plane, D ($D = 2\pi^2 g^2/d$) the distortion parameter which depends on strain g , d the distance between the reflection planes. L and D or g are important parameters for paracrystalline substance in which distortions of second kind are present^[7].

From Equation (3) one can get that the plots of W vs. σ will be a straight line with a slope K_0 and an intercept W_0 . From K_0 and W_0 , the structural parameters L and D or g can be determined using a single line only.

The expression for the fourth moment is given by Mitra^[8,9] as

$$\mu(\sigma) = \frac{\sigma^3}{24\pi^2} \left(\frac{1}{L} + D \right) + \frac{\sigma}{8\pi^4} \left(D^3 + \frac{3D^2}{L} \right) + \frac{1}{16\pi^4} \left(D^4 + \frac{4D^3}{L} \right) \quad (5)$$

Thus,

$$\begin{aligned}\frac{d\mu(\sigma)}{d\sigma} &= \frac{1}{8\pi^2} \left(\frac{1}{L} + D \right) \sigma^2 + \frac{1}{8\pi^4} \left(D^3 + \frac{3D^2}{L} \right) \\ &= A_1 \sigma^2 + A_2\end{aligned}\quad (6)$$

where

$$\begin{aligned}A_1 &= \frac{1}{8\pi^2} \left(\frac{1}{L} + D \right) \\ A_2 &= \frac{1}{8\pi^4} \left(D^3 + \frac{3D^2}{L} \right)\end{aligned}\quad (7)$$

The plots of $d\mu/d\sigma$ vs. σ^2 will be obtained as a straight line with the slope A_1 intercept A_2 . From A_1 and A_2 , the structural parameters L and D or g can be also got.

Fig. 1 was X-ray diffraction pattern for PA1010—BMI and carried out multipeak fitting resolution for (100) and (010) reflections.

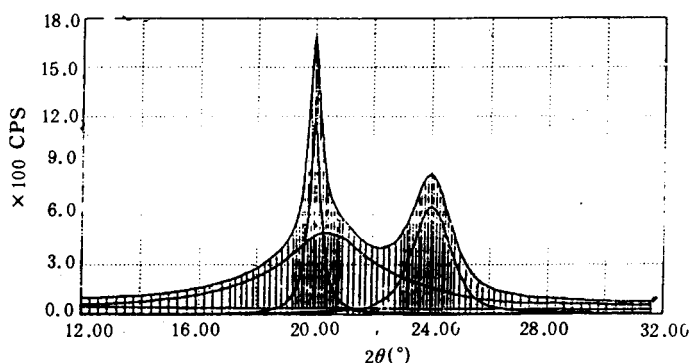


Fig. 1 WAXD pattern of PA1010+1% BMI blend and its multipeak fitting resolution

Its two main diffraction peaks are (100) and (010) at corresponding diffraction angles of $2\theta = 20.0^\circ$ and 24.05° . On the basis of the Fig. 1, the variance range functions for PA1010—BMI blends with various BMI contents were calculated by Equation (3). The plots of variance W vs. range σ were shown in Fig. 2. One can observe that W vs. σ are the straight lines. The slope of the straight line is K_0 , and the intercept W_0 . According to Equation (4), the particle sizes L and the distortion parameters D or g of lattice site of second kind of the paracrystalline structure were determined, and listed in Table 1. Table 1 also gave out other L' values calculated from Scherrer equation. Comparing both L and L' one can find $L' > L$. As a result of the weight-average size L' derived from the Scherrer equation is larger than the corresponding number-average size L derived from the variance

range function^[10]. Fourth moment μ vs. range σ functions from the observed profiles were shown in Fig. 3 and thus the first derivative of μ with respect to σ , $d\mu/d\sigma$ vs. σ^2 curves were shown in Fig. 4.

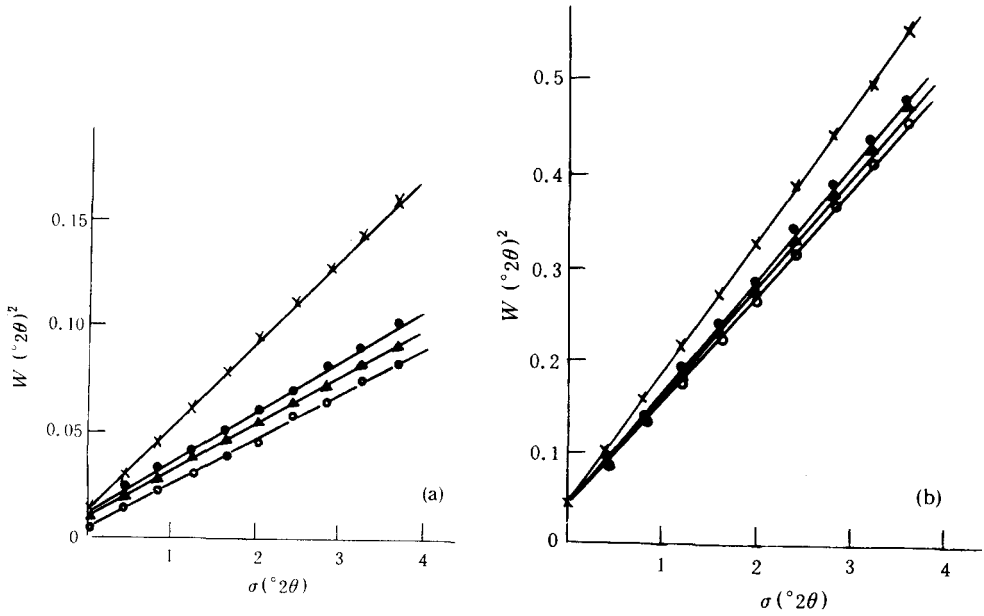


Fig. 2 The plots of W vs. σ as function of BMI content for PA1010—BMI system

- a: (100) reflection

● PA1010

× PA1010+2.5%BMI

b: (010) reflection

△ PA1010+1%BMI

○ PA1010+5%BMI

Table 1 W_0, K_0, L, L' and g values obtained by variance range function

Sample	W_0		K_0		$L(\text{nm})$		$g(\%)$		$L'(\text{nm})$	
	100 ^a	010	100	010	100	010	100	010	100	010
PA1010	0.1090	0.0250	0.0451	0.1208	15.08	4.16	2.6	7.7	16.90	5.52
PA1010+1%BMI ^b	0.0085	0.0235	0.0428	0.1193	14.47	4.20	4.5	7.7	15.55	4.72
PA1010+2.5%BMI	0.0120	0.0419	0.0480	0.1408	13.79	3.67	4.7	8.2	13.88	5.44
PA1010+5%BMI	0.0042	0.0221	0.0418	0.1158	12.51	4.33	4.4	7.6	12.96	5.10

a: 100 and 010 refer to the reflections of X-ray diffraction

b: Percent in the table is the weight ratio of BMI/PA1010

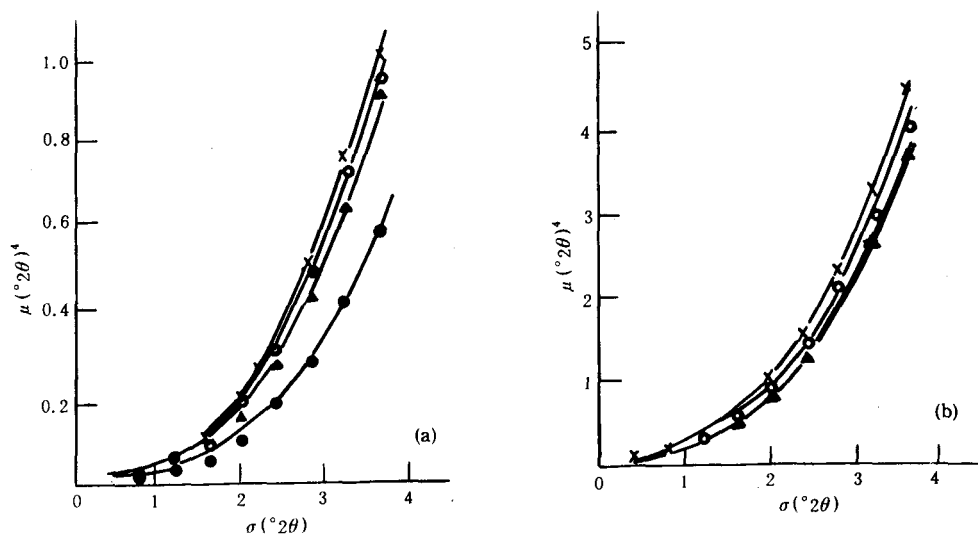


Fig. 3 The curves of fourth moment μ vs. range σ for PA1010-BMI system with different BMI

a: (100) reflection b: (010) reflection

The symbols are the same as in Fig. 2

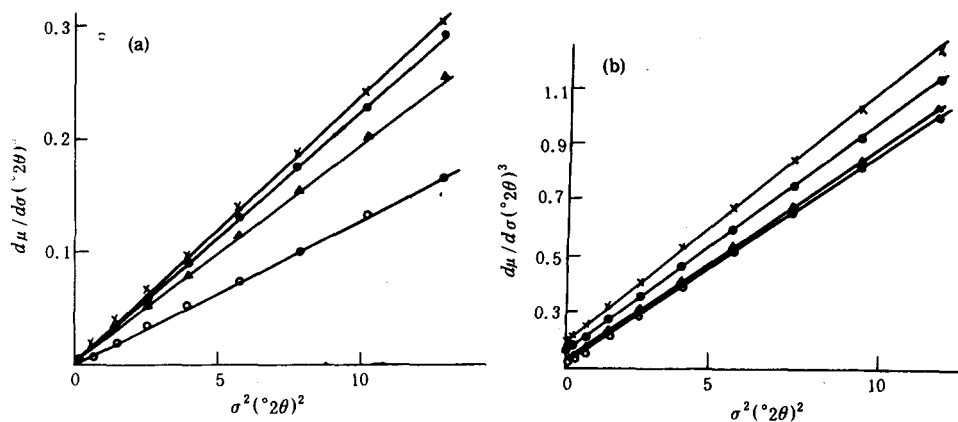


Fig. 4 The curves of $d\mu/d\sigma$ vs. σ^2 for PA1010-BMI system with different BMI content

a: (100) reflection b: (010) reflection

The symbols are the same as in Fig. 2

According to Equation (6), the slope A_1 and the intercept A_2 can be obtained, then in terms of Equation (7) can calculate the particle size L and the strain D or g . L and D or g values calculated by Equation (7) are listed in Table 2.

Table 2 A_1, A_2, L and g values by fourth moment for PA1010-BMI system

Sample	A_1		A_2		$L(\text{nm})$		$g(\%)$	
	100	010	100	010	100	010	100	010
PA1010	0.0126	0.0684	0.0004	0.1217	14.36	3.87	2.9	8.0
PA1010+1%BMI	0.0193	0.0690	0.0028	0.1333	14.03	4.11	4.6	8.2
PA1010+2.5%BMI	0.0227	0.0803	0.0050	0.2042	13.42	3.42	5.1	8.7
PA1010+5%BMI	0.0219	0.0741	0.0040	0.1672	12.09	3.86	4.8	8.5

From the results showed in Tables 1 and 2, they clearly indicated that the particle size and strain values obtained from variance range function and fourth moment were nearly equal or comparable.

The values of microstructural parameter from Tables 1 and 2 can be seen that L values determined from variance range are slight greater than those from fourth moment. From two tables one can also find that L values of (100) plane markedly decreased with increasing BMI content, however, g values of (100) plane then increased and those of (010) plane are nearly constant values. It can be concluded that microparacrystallite size and degree of order changed with changing BMI content, and that microparacrystallite size decreased with increasing disorder^[11]. Comparing the L and g values in Tables 1 and 2, it can be also found that the degree of the order in the (010) reflection was lower than in the (100) reflection, this may be so because, as these samples under preparation possessing inner strength, which would result in some extent damage of hydrogen bond plane (010)^[12], and the addition of BMI into PA1010 might be also to form the certain degree damage of (010) plane, therefore g values of (010) plane were larger than that of (100) plane, and L values of (010) plane were smaller than that of (100) plane. The result showed that chain folding might occur in (010) plane, and adding BMI into PA1010 might further make more vulnerable to structure distortion of (010) plane, because of the relative rotation of the molecular chain about their chain axes^[9]. The results led to that the atomic arrangement of this plane exhibit more or less tendency for deviation from its perfect lattice sites.

Keywords:

PA1010-BMI system; Central moment method; WAXD

REFERENCES

- [1] Kulshreshtha, A. K. ; Kothari, N. R. and Dweltz, N. E. ; *J. Appl. Cryst.* , **1971**, 4, 125.
- [2] Mitra, G. B. and Choudhuri, A. K. , *J. Appl. Cryst.* , **1974**, 7, 350.
- [3] Mitra, G. B. and Choudhuri, A. K. , *Indian J. Pure Appl. Phys.* , **1969**, 7, 158.
- [4] Langford, J. I. , *J. Appl. Cryst.* , **1978**, 11, 10.
- [5] Gao, H. ; Yang, B. Q. and Mo, Z. S. , *Acta Polymerica Sinica (in Chinese)* , **1993**, (2), 184.
- [6] Wilson, A. J. C. , "Mathematical Theory of X-Ray Power Diffractometry", Phillips Technical Library, New York, **1963**.
- [7] Hosemann, R. , *Z. Phys.* , **1950**, 128, 464.
- [8] Mitra, G. B. , *Brit. J. Appl. Phys.* , **1964**, 15, 917.
- [9] Mitra, G. B. and Mukherjee, P. S. , *J. Appl. Cryst.* , **1981**, 14, 421.
- [10] Guinier, A. , "X-ray Diffraction", Freeman, San Francisco, **1963**.
- [11] Hosemann, R. and Balta Calleja, F. J. , *Ber. Bunsenges. Phys. Chem.* , **1980**, 84, 91.
- [12] Zhang, L. H. ; Zhang, H. F. ; Yu, L. , et al. , *Polymer International* , **1994**. 35, 355.