Evaluation of Structural Parameters in Semicrystalline Polymer Three-Phase Systems by Small-Angle X-Ray Scattering

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Abstract The structural parameters in a semicrystalline polymer three-phase system have been evaluated using small angle X-ray scattering technique. The crystallinity and the lamellar thickness are not consistent with those in two-phase system. The analysis of some semicrystalline polymer samples indicates that the Bragg long period approaches to the sum of the correlation function long period and the thickness of the transition layer. It is also consistent with the conclusion that the interphase layers exist in semicrystalline polymers.

Key words small-angle X-ray scattering, crystal polymer, three-phase structure, correlation function

1 Introduction

Small angle X-ray scattering (SAXS) is a powerful tool to research the structure of semicrystalline polymers since the fundamental work of Porod[1] and Debye et al[2]. The determination procedure of semicrystalline polymer's structural parameters was dependent on specific model in the past. Tsvankin[3] compared model scattering curves to experimental data. Vonk[4] developed fitting procedures for the correlation function. Until Strobl and Schneider[5] found a model-independent method, the correlation function can directly yield by using a simple geometrical construction the following structural parameters: the specific inner surface, the crystallinity, the average lamellar thickness, the long spacing and, if scattering intensities are measured in absolute values, the electron density difference between crystalline and amorphous regions. Nowadays the correlation function is one of the most applied methods for the evaluation of the structural parameters of semicrystalline polymers.

Strobl and Schneider's work originally aimed at the "corresponding ideal two-phase system" with sharp boundaries, though their results are applied to three-phase structure samples frequently. At present theory and experiment show the conclusion that a crystal-amorphous interphase exists in lamellar semicrystalline polymers[6—9]. The work of Zhang Hongfang et al from SAXS analysis also supported that a crystalline amorphous interphase exists in the lamellae of semicrystalline polymers, so that a three-phase model instead of the traditional two-phase model should be used [10,11]. When using a three-phase model with an interphase of linear electron density variation to reinvestigate the work, it is found that most concepts in two-phase system can be applied without any change, but the crystallinity and the average lamellar thickness need new considerations.

Some parameters can be derived either from the scattering curve of a sample directly or, after Fourier transformation, from the correlation function. Such as the long spacing, it can be obtained from the scattering curve by using Bragg law, or from the correlation function. Nevertheless long spacing obtained from the two methods are remarkably different. Their difference is successfully interpreted with SAXS. In the same time, it also shows that the interphase layer indeed exists.

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2 The correlation function of three-phase system

The lamellar three-phase structure model is used to describe the lamellar structure sample. This model consists of alternating parallel crystalline and amorphous lamellae connected by transition layers which are placed in stacks large enough not to perturb the small angle X-ray scattering. We assume that the electron density variation occur predominantly along the direction perpendicular to the lamellae, as long as we stay within a lamellar stack. Amorphous regions with density η_a and crystallites with a density η_c in the core alternate along the lamellar direction with interlayers, density of which changes linearly from η_a to η_c, between them. The profile of electron density for the model is shown in Fig. 1. In this case, the density distribution along the direction normal to lamellae z can be represented by

$$\eta(z) = \begin{cases} \eta_c, & |z| < \dfrac{d}{2}; \\ \eta_c - \dfrac{\eta_c - \eta_a}{E} \cdot \left(|z| - \dfrac{d}{2} \right), & \dfrac{d}{2} < |z| < \dfrac{d}{2} + E; \\ \eta_a, & \dfrac{d}{2} + E < |z| < \dfrac{L}{2}. \end{cases}$$

$$\eta(z + L) \quad \eta(z).$$

Here E is the interphase width, d the lamellar thickness, and L the long period. The average density within a stack (and that of the whole system) is $\langle \eta \rangle$. Therefore, our discussion is restricted to one dimensional electron density correlation function $K(z)$

$$K(z) = \langle [\eta(z') - \langle \eta \rangle][\eta(z' + z) - \langle \eta \rangle] \rangle,$$

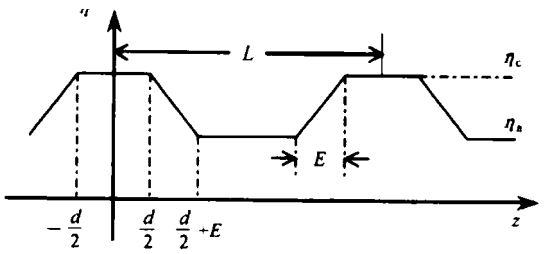

Fig. 1. Electron density profile of the lamellar three-phase structure; η_c and η_a are the electron densities of the crystalline and amorphous phases respectively.

where the angular brackets indicate averaging over all coordinates z' within a lamellar stack. This function was evaluated from the small-angle scattering intensity distribution $J(q)$, that is

$$K(z) = \frac{\int_0^\infty J(q) q^2 \cos qz \, dq}{\int_0^\infty J(q) q^2 \, dq}, \tag{3}$$

q denotes the scattering wector

$$q = \frac{4\pi \sin\theta}{\lambda}, \tag{4}$$

where λ and θ are the wavelength and the Bragg angle respectively. In order to obtain the correlation function, we evaluate the integral

$$K(z) = \frac{1}{\Delta} \int_{-\Delta/2}^{\Delta/2} [\eta(z') - \langle \eta \rangle][\eta(z' + z) - \langle \eta \rangle] dz' \tag{5}$$

Here Δ denotes the averaging range for z'. It gives

$$K(z) = \begin{cases} \dfrac{1}{L}(\eta_c - \eta_a)^2 \left[\dfrac{1}{3} \dfrac{z^3}{E^2} - \dfrac{z^2}{E} + d + \dfrac{2}{3}E - \dfrac{(d+E)^2}{L} \right], & |z| < E; \\ \dfrac{1}{L}(\eta_c - \eta_a)^2 \left[-z + d + E - \dfrac{(d+E)^2}{L} \right], & E < |z| < d; \\ \dfrac{1}{LE^2}(\eta_c - \eta_a)^2 \left[\dfrac{1}{6}(z-d)^3 - E^2(z-d) + E^3 - \dfrac{E^2(d+E)^2}{L} \right], & d < |z| < d + E \\ \dfrac{1}{6LE^2}(\eta_c - \eta_a)^2 \left[-z + d + 2E - \dfrac{6E^2(d+E)^2}{L} \right]^3 & d + E < |z| < \min\left(d + 2E, \dfrac{L}{2} \right); \\ -\dfrac{1}{L}(\eta_c - \eta_a)^2 \dfrac{(d+E)^2}{L}, & d + 2E < |z| < \dfrac{L}{2}, \\ & \text{only when } d + 2E < \dfrac{L}{2}. \end{cases}$$

$$K(L + z) = K(z). \tag{6}$$

The result is shown in Fig. 2. In this case there is a straight line segment in the central section of $K(z)$. Its slope is related to the specific inner surface O_s by

$$\frac{dK}{dz} = -\frac{O_s}{2}(\eta_c - \eta_a)^2. \tag{7}$$

After extrapolation the line reaches $z = 0$ at the invariant

$$Q = w(1 - w)(\eta_c - \eta_a)^2 \tag{8}$$

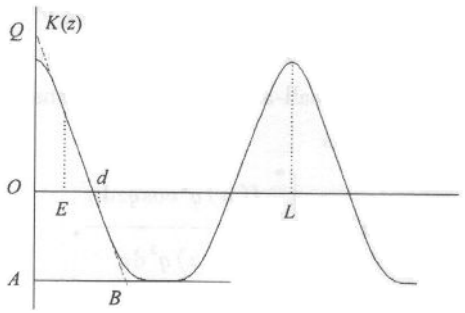

Fig.2. Schematic plot of the correlation function of the three-phase structure system. Q, E, d and L are the invariant, the transition thickness, the lamellar thickness and the long period respectively.

with $w = \dfrac{d + E/2}{L}$ which does not represent the crystallinity $w_c = \dfrac{d}{L}$ of the sample of two-phase structure yet[5]. This should be advertent. We notice that extrapolation of the other side of the line does not intersect the base line AB at the abscissa $z = d$. According to Eq.(6), it is the second end point of the straight-line segment in the correlation function curve whose abscissa denotes the lamellar thickness d. From the drawing, we can also obtain the transition thickness E, which is the abscissa of the first end point of the straight-line segment, and the long period L, which is the position of the first peak.

3 Experiments

The polymer samples used for experiments were obtained from Beijing Research Institute of Chemical Industry, which were neat isotactic polypropenes prepared with different metallocene catalyst systems (i-PP). The samples were extruded into slices with a thickness of 2mm at 220℃. All slices were found to be macroscopically homogeneous and to exhibit excellent optical clarity.

SAXS experiments were performed with a long-slit collimation system at Beamline 4B9A of Beijing Synchrotron Radiation Facility. The incident X-ray wavelength was 0.154nm, and the scattering angle range was 0°—3° approximately. The distance between the sample chamber and the detector was 1.52m. Two ionization chambers were used to measure the sample transmission. The scattered X-ray intensities were recorede using the image plate detector. The absorption of the sample and the background scattering was corrected[12].

4 Results and discussion

The long period can be obtained directly from the scattering curve. An interference maximum can be seen on the scattering curve of the semicrystalline polymer. From the angle position of the maximum, the long spacing can be obtained with Bragg law, which is called the Bragg long period here. As an example, the SAXS curve of sample No 7 is shown in Fig.3. The interference peak corresponds to scatter vector $q = 0.41\text{nm}^{-1}$. The Bragg long period L_b is 15.3nm.

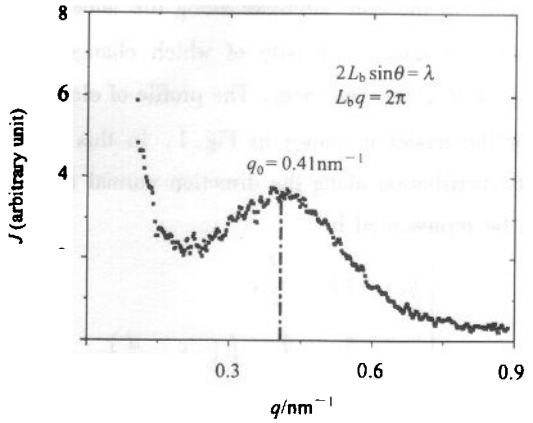

Fig.3. The scattering curve of sample No 7.

The corresponding correlation function curve of sample No 7 is shown in Fig.4. When using correlation function method to determine structure parameters of a sample, allowance must be made for the fact that the correlation function in the origin is very sensitive to experimental errors in the tail of the scattering curve[13]. In order to decrease the effect of errors at large values of q, Porod's law is used to correct the data. Porod's law for smeared data in the case of slit collimation is $J(q) = K_P q^{-3}$ exp

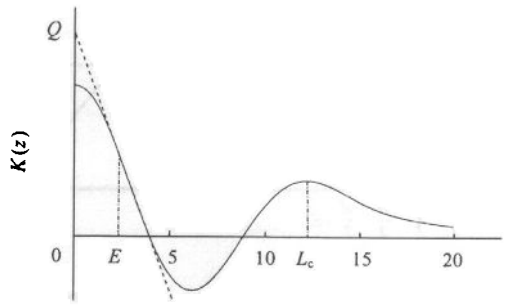

Fig.4. The correlation function curve of sample No 7.

Table 1. Evaluation and analysis of structure parameters of polymer samples (nm).

Sample No	1	2	3	4	5	6	7	8
E	2.15	2.18	1.83	2.02	2.19	2.56	2.42	2.34
L_c	11.66	11.84	11.70	14.33	15.17	14.61	12.19	12.90
$E + L_c$	13.81	14.02	13.53	16.35	17.36	17.17	14.61	15.24
L_b	14.63	14.43	14.68	15.98	17.86	17.43	15.32	16.16

$(-\sigma^2 q^2)$, here K_P is Porod's constant, and σ is a parameter pertaining to the thickness of transition layers. This law is employed to predict the scattering data of a sample at high angles. On the other hand, since we blocked the central rays up in the experimental procedure, the scattering data around 0 degree was lost. This part of data was extrapolated to makeup by using Guinier law[14]. From Fig.4, some structural parameters can be got: the correlation function long period L_c = 12.19nm, and the transition layer thickness E = 2.42nm. Comparing L_c with L_b, it is found that they are not equal. All experimental samples' results are listed in table 1. From the results, it is found that the Bragg long period of the samples are close to the sum of its correlation function long period and the thickness of the transition layers.

The existence of the transition layers in a periodic polymer will broaden the interference peak or even form a high platform on the scattering curve. The thicker the transition layer, the wider the interference peak or the platform on the scattering curve will be[13]. When the thickness of transition layers is E, the interference peak or the platform will broaden to be E. However, the high platform or the broadening peak is not seen on the scattering curve. This is because the platform can only be formed with a uniform distribution of X-ray scattering intensity, while at the high angle, the intensity distribution obeys Porod's law, and decreases in proportion to q^{-3} for the slit collimation system. If a platform exists, the platform will lower its height from right to left on the scattering curve. Therefore, we only see a peak on the scattering curve instead of the platform. At the same time, the peak moves to the left about E. As using Bragg's law to calculate the long period, the Bragg long period will be longer, and approaches to the sum of the correlation function long period and E.

5 Conclusion

Using the correlation function to evaluate structural parameters of semicrystalline polymer, although most results with the three-phase model are the same as those with the two-phase model, the crystallinity in the three-phase system should be replaced by $w = \frac{d + E/2}{L}$. At the same time, the lamellar thickness d is equal to the abscissa of the second end point of the straight-line segment in the correlation function curve. The Bragg long period of a semicrystalline polymer is not equal to its correlation function long period because of the existence of an interphase layer. It approaches to $L_c + E$.

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三相系统部分结晶聚合物结构参数小角X射线散射分析

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摘要 使用小角X射线散射技术分析了部分结晶聚合物结构参数.结晶度和片层厚度与两相系统中的结果不一致.对一些部分结晶聚合物样品的分析表明它们的Bragg长周期接近相关函数长周期与过渡层厚度的和.这个结论也与部分结晶聚合物存在中间过渡层一致.

关键词 小角X射线散射 结晶聚合物 三相结构 相关函数

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