Morphological Parameter Study of Polymer By Using Small Angle X-Ray Scattering Method

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ABSTRACT

Thermoplastic natural rubber sample is found isotropic based on SAXS pattern. Morphological parameter was obtained based on ideal lamellar morphology using 1-D correlation function. The fitting was carried out using Porod tail model and Vonk for back-extrapolated model. It is found that the long period value is 15.7nm which is comparable to results obtained from Lorents corrected profile, 20nm. Crystalline thickness and amorphous thickness was found as 13.4 and 2.31nm respectively.

ABSTRAK

Sampel getah asli termoplastik didapati isotropi berdasarkan corak SAXS. Parameter mofologikal diperolehi berdasarkan morfologi lamela unggul dengan menggunakan rangkap korelasi 1-D. Pemadanan dijalankan menggunakan ekor Porod model dan Vonk untuk belakang mengekstrapolasikan model. Ia didapati bahawa nilai jangka masa yang panjang ialah 15.7nm keputusan-keputusan setanding dengan yang mana diperolehi dari Lorents membetulkan profil, 20nm. Ketebalan berhablur dan ketebalan amorfus didapati kerana 13.4 dan 2.31nm masing-masing.

Keywords: *Thermoplastic natural rubber, SAXS, Porod model, lamellar morphology*

INTRODUCTION

Structural parameters such as long spacing, amorphous and crystal length of a sample could be derived from SAXS data by using a correlation function analysis (Strobl, G. R. and Schneider, M. J., 1980; Balta Calleja, F.J. and Vonk, C. G., 1989). The correlation function is simply the Fourier Transform of the SAXS curve which is related to the electron density distribution within the sample. The structural parameters are obtained by interpretation of the 1-D correlation function. The interpretation assumes that the sample has an ideal lamellar morphology (Glatter, O. and Kratky, O., 1982). The morphology consists of an ensemble of isotropically distributed stacks of alternating crystalline and amorphous lamellae. The stacks are assumed to be of dimensions that are large enough not to affect the small angle scattering.

There are three stages involved in the correlation function analysis:

i. Extrapolation of the data to q = 0 and q = ∞.

ii. Calculation of the Fourier transform of the extrapolated data.

iii. Interpretation of step ii.

The SAXS data must first be extrapolated to q = 0 and q = ∞ prior to calculating the Fourier transform to avoid the introduction of series termination errors in the transform. Extrapolation to q = ∞ is performed by fitting either a Porod (Balta Calleja, F.J. and Vonk, C. G., 1989) or sigmoid (Koberstein, J. and Stein R. J., 1983) function to the tail of the

SAXS data. The tail-fit affects the correlation function in the most important region for the extraction of ideal lamellar morphology parameters. The tail fitting functions are given as:

$$I(q) = B + \frac{K}{q^4} e^{-q^2\theta^2} \qquad \text{Sigmoid}$$

$$I(q) = B + \frac{K}{q^4} \qquad \text{Porod}$$

where;

B = Bonart thermal background.

K= Porod constant

The data are extrapolated to q = 0 by fitting a Guinier or Vonk model to the first few genuine data points after the beamstop. If the experimental data do not increase in intensity as the beamstop is approached, back-extrapolation may fail. Fitting functions for back-extrapolation are given as:

$$I(q) = Ae^{Bq^2} \qquad \text{Guinier}$$

$$I(q) = H_1 - H_2 q^2 \qquad \text{Vonk}$$

The joint between the original SAXS data and tail-fit is smoothed using a Savitzky-Golay (Press W. H. et. al., 1986) smoothing algorithm that smooths the data without greatly altering higher moments. This avoids the formation of ripples in the correlation function that would occur with a period matching the d-spacing of the join. No smoothing is used at the join of the back-extrapolation to the SAXS data.

EXPERIMENTAL AND INSTRUMENTATION

Sample of polymer blend consists of 50% natural rubber (Nr), 10% liquid natural rubber (Lnr) and 40% high density polyethylene (HDPE). Nr (SMR L grade) was supplied by Malaysian rubber research institute, RRI (Malaysia). The density of Nr is 0.95g/cm^3. HDPE was supplied by Titan Chemicals Corp. Bhd. (Malaysia) with a density of 0.91g/cm^3. Lnr was produced from Nr with weight average molecular weight relative to polystyrene as Mw = 40 x 10^4.

SAXS experiments were performed using Hecus SWAX instrument, operated at 50kV and 1mA with the point collimation geometry. The radiation used was a Ni filtered CuKα radiation of wavelength 0.154nm (Seifert, Ahrensburg, Germany). The intensity profiles are recorded using a 2-D detector (Pilatus) and the scattering vector q, covers from 0.01 to 0.6 Å^{-1}. One-dimensional scans of I(q) were extracted from two- dimensional scattering patterns using the analysis package Fit2D (Hammersley, A. P., 2010). Angular calibration of the scattered intensities in the small angle regime for the detector is performed using silver stearate (d = 48.68 Å). Sample to detector distance is 271mm and sample exposure to the source is 600 seconds. All experiments are carried out at room temperature, 20 ºC. Validation experiment is carried out using a reference material, alumina type 150 (Al_2O_3) CRM BAM-PM-104.

Based on Fig. 1, there is no preferred orientation of the structure within the plane of the samples. This proves that the sample is fully isotropic. However, this does not exclude the possibilty that a preferred nematic type orientation exist perpendicular to the surface. Rings at larger angles are due to Be window.

Figure 2 shows the Lorentz-corrected SAXS profile for compatibilized 60/40 NR/HDPE blend. In this figure, the Iq^2 (arbitrary unit) is plotted against the scattering vector q where;

$$q = \frac{4\pi}{\lambda} \sin\theta \qquad (2)$$

and θ is scattering angle; λ is the incident wavelength.

It is observed that there are scattering peaks at q = 0.3 and 0.6 nm^{-1} caused by the inter-lamella interference from the lamella crystal structures in the HDPE domains. The peak corresponds to the first and second order peaks and from that

the lamella spacing l_s is calculated. In this work, the lamella spacing or long spacing is ca. 20 nm. This is in agreement with the previous result which is also ca. 20 nm (Kazuhiro et. al., 2005).

RESULT AND DISCUSSIONS

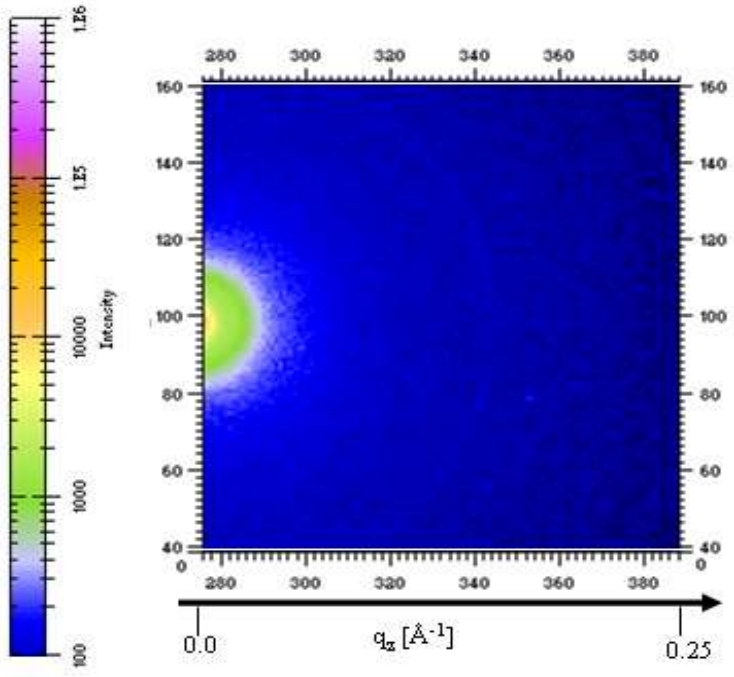

Figure 1: 2-D SAXS profile

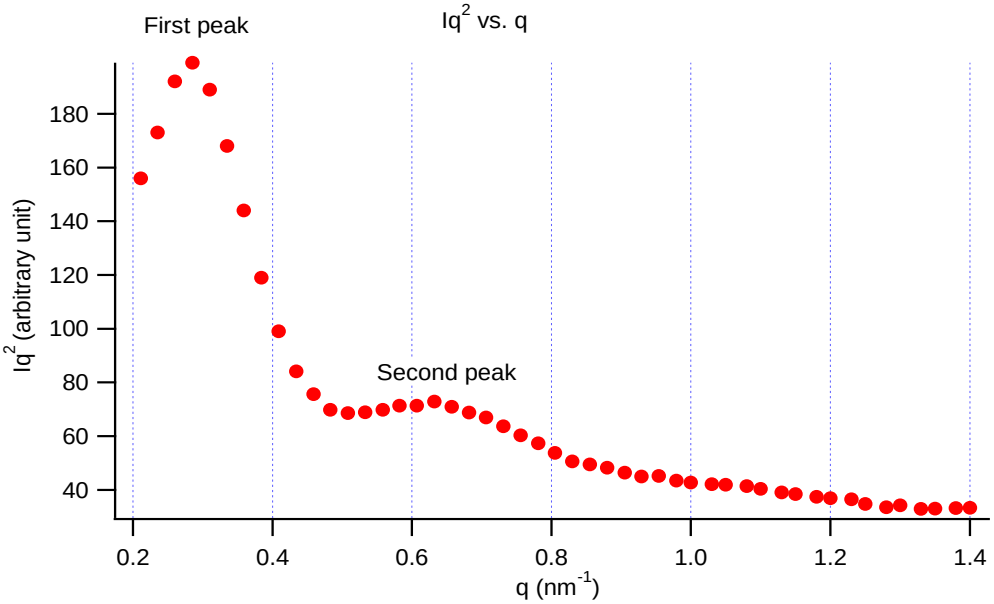

Figure 2: Lorentz-corrected SAXS profile for compatibilized TPNR blend

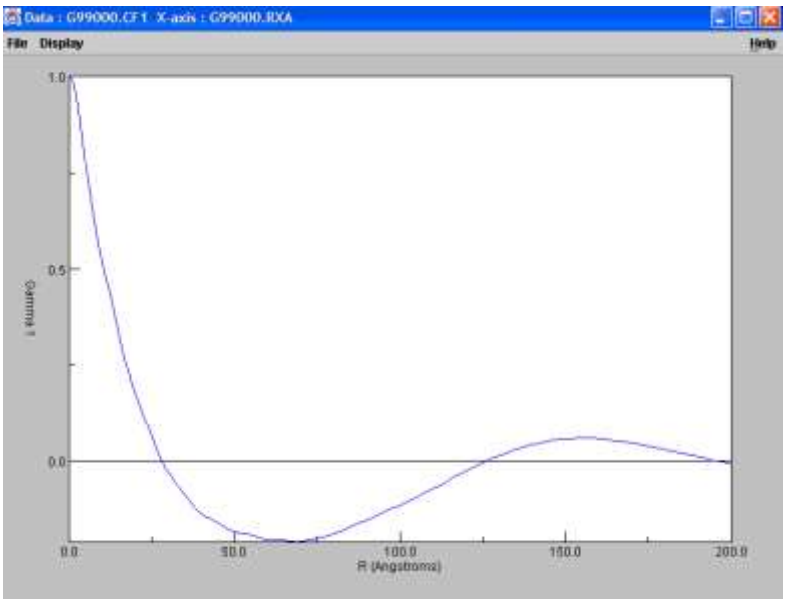

Figure 3: Result of correlation function

Morphological parameter is extracted from Fig. 3. It is found that long spacing is 15.7nm. Crystalline thickness and amorphous thicknes was found to be 13.4 and 2.31nm respectively.

CONCLUSION

The technique of using correlation function to probe morphological parameter is found to be promising and comparable with other technique. In this work, three parameters were successfully investigated namely long spacing, crystalline thickness and amorphous thickness.

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