

Variation of long periodicity in blends of styrene butadiene, styrene copolymer/polyaniline using small angle X-ray scattering data

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MS received 28 August 2006; revised 3 May 2007; accepted 8 June 2007

Abstract. Small angle X-ray scattering data have been recorded for the blends of styrene butadiene, styrene copolymer/polyaniline using the beamline of the LNLS (Laboratorio Nacional de Luz sincrotron-Campinas, Brazil). Employing one-dimensional Hosemann's paracrystalline model, we have simulated the meridional reflections of these blends in order to compute the long periodicity and hence to find the variation with concentrations of the blends. Within the region of available experimental data we observe that there is a linear relationship between long periodicity and concentration of blends. These parameters are compared with physical measurements like tensile strength to find the structure–property relation in these blends.

Keywords. Long periodicity; polyaniline; SBS copolymer; emulsion polymerization; melt mixing.

PACS Nos 61.10.-i; 61.10.Eq; 87.15.-v

1. Introduction

Polyaniline (Pani) is a well-known conducting polymer. It shows unique features such as electric conductivity, chemical or electrochemical redox reversibility and thus it exhibits a great potential to be used in many fields, such as electrode materials [1], static electricity dissipation [2], metal anti-corrosion and marine-fouling prevention [3]. Because Pani is insoluble or infusible, great efforts have been made to realize its solution processing or melt processing by improving its solubility

in organic solvent and its miscibility with other melt-processable polymers. Two methods were adopted. One was to introduce flexible substituents onto the benzene rings or nitrogen atoms [4–6] of Pani. The other was doping Pani with functional organic acid such as camphor sulphonic acid (CSA) and dodecyl benzene sulphonic acid (DBSA) [7]. In the latter case, based on the improved processability of Pani caused by the solubility of the dopants in organic solvents or miscibility with conventional polymers, conducting composites of Pani with other insulating polymers were made with quite low conduction percolation threshold [8,9]. The melt blends of conducting polymers with rubbery, non-polar host polymers, such as SBS block copolymers, are widely used by the cable industry, and it is one of the major potential customers for conducting polymers [10].

2. Experimental

The blends of styrene butadiene, styrene copolymer/polyaniline are prepared as per the procedure reported in refs [11,12].

2.1 Material

SBS (TR-1061, PBD content=70 wt%, Mw=120,000, density=0.98 g/cm³) was kindly supplied by Petroflex S.A. (Rio de Janeiro, Brazil). Aniline (analytical grade from Vetec, Brazil), ammonium peroxydisulphate (APS) (analytical grade from Vetec, Brazil) and dodecyl benzene sulphonic acid (DBSA) (commercial grade from Solquim LTDA, Brazil) were used without further purification. Tensile experiments were performed in an Instron 5569 tensile machine (Boston, MA) at room temperature in accordance with ASTM D638.

2.2 Recording of X-ray diffraction pattern

The X-ray scattering measurements were performed at the SAXS beamline of the LNLS. A monochromatic beam of wavelength 1.7433 Å was used and the scattering intensity was registered using a one-dimensional position-sensitive gas detector for a sample-detector distance of 1641.5 mm. The range of scattering vectors measured was $0.005 < q < 0.17$ Å.

3. Theory

The linear paracrystalline model of polymer morphology of blends comprises stacks containing a finite number of crystalline lamellae separated by amorphous segments. These are used to analyse the SAXS data here. The thicknesses of successive lamellae along a stack are randomly selected from a certain probability density function, even though the lengths of the amorphous segments may be distributed according to a different function. It is assumed that the transverse width of a

stack is infinite and that the lamellae boundaries are flat and normal to the axis. An X-ray beam incident normal to the stack axis will be scattered along a line in reciprocal space parallel to the stack axis and the distribution of intensity along this line will be given at small angles. The equation is given by [13]

$$\frac{2I(\pi s)^2}{\Delta\rho^2} = \text{Re} \left[\frac{(1 - H_Y)}{(1 - H_Y J_Z)} \left\{ N(1 - J_Z) + \frac{J_Z(1 - H_Y)(1 - H_Y J_Z)^N}{(1 - H_Y J_Z)} \right\} \right], \quad (1)$$

where H_Y and J_Z are respectively the Fourier transforms of the normalized distribution function of the lengths Y , Z of the amorphous and crystalline segments, s ($s = 2 \sin \theta / \lambda$) is the scattering vector, 2θ is the scattering angle and λ is the wavelength of radiation, N is the number of repeating units in a stack, $\Delta\rho$ is the difference between the electron densities of the phases and $I(s)$ is the scattering intensity as a function of scattering angle parallel to the stack axis. If it is assumed that a blend comprises parallel stacks, incoherently arranged, there will be distribution of intensity scattered by the blend. A correction for broadening of the intensity profile has been reported in [14], and has been incorporated here.

From the elementary theory of Fourier transforms, H_Y and J_Z may always be expressed as

$$H_Y = A \exp(-i\chi) \quad (2)$$

$$J_Z = B \exp(-i\phi) \quad (3)$$

and

$$X = \chi + \phi. \quad (4)$$

Here X is the distribution width.

Hosemann's equation may be expressed in a form which is amenable to computational analysis. By substituting eqs (2)–(4) in eq. (1) and evaluating the real part of the expression on the right-hand side of the equation, Hall *et al* [15] have shown that, it reduces to

$$\frac{2I(\pi s)^2}{\Delta\rho^2} = \frac{C}{F} + \frac{D + E}{F^2}, \quad (5)$$

where

$$F = 1 + A^2 B^2 - 2AB \cos X, \quad (6)$$

$$C = N \{ 1 - A^2 B^2 - A(1 - B^2) \cos \phi - B(1 - A^2) \cos \chi \} \quad (7)$$

$$D = \frac{B[(1 - A^2)(1 - A^2 B^2) \sin X \sin \phi + \{(1 + A^2 B^2) \cos X - 2AB\} \times \{(1 + A^2) \cos \phi - 2A\}]}{G} \quad (8)$$

$$G = 1 - A^N B^N \cos NX \quad (9)$$

$$E = A^N B^{N+1} \sin NX [(1 - A^2 B^2) \{(1 + A^2) \cos \phi - 2A\} \sin X - (1 - A^2) \{(1 + A^2 B^2) \cos X - 2AB\} \sin \phi]. \quad (10)$$

For given values of A, B, χ and ϕ , $I(s)$ can be evaluated from eqs (5)–(10). A, B, χ and ϕ are the values of the Fourier transforms of the probability distributions of the amorphous and the crystalline phase lengths. A and χ are related to a distribution of phase Y segment lengths and B and ϕ to that of phase Z [15]. The following gives the necessary expression for A, B, χ and $\phi, I(s)$ corresponding to exponential distribution functions.

Here, we have used normalized exponential distribution function for both amorphous and crystalline lengths and the lengths $\langle Y \rangle$ of the segments of one phase are distributed according to the equation [16]

$$h(Y) = \alpha_Y \exp(-\alpha_Y (Y - \epsilon_Y)), \quad (11)$$

where $\alpha_Y = 1/2\gamma_Y \langle Y \rangle$, γ_Y is a parameter controlling both the skew and the dispersion of the distribution, $\epsilon_Y = \langle Y \rangle (1 - 2\gamma_Y)$ and $\langle Y \rangle$ is the mean length, suffix Y refers to the phase present in blends, provided $0 < \gamma_Y < 0.5$. Lengths less than ϵ_Y are not possible, since this would cause $h(Y)$ to be negative. The formula for $j(Z)$ for the lengths of the segments of the other phase is similar. From eqs (5) and (11), it is therefore necessary to obtain the model parameters ($N, \langle Y \rangle, \langle Z \rangle, \gamma_Y, \gamma_Z$) which will give the best fit to the experimental data. The formula was put into a form suitable for numerical analysis and a stepping refinement procedure was written in FORTRAN language to adjust the paracrystalline parameters so that the discrepancy between the calculated and the measured intensity was minimized. Here $\langle Y \rangle$ corresponds to amorphous phase and $\langle Z \rangle$ to crystalline phase region. The long periodicity is given by $L = (\langle Y \rangle + \langle Z \rangle)$. We have compiled necessary FORTRAN program to run on a PC for computing the model parameters from the input data of SAXS meridional reflection profile.

4. Results and discussion

Figure 1 shows SAXS X-ray diffraction patterns of SBS, Pani and their blends. Figure 2 indicates the experimental and simulated profiles of SBS, Pani and their blends for finite stacks of lamellae at room temperature, with crystal width ranging from 294 Å to 594 Å using one-dimensional paracrystalline model. The normalized exponential probability distribution of the phases (a) γ_Y (amorphous) and (b) γ_Z (crystalline) are shown in figure 3. In fact lamellae thickness turns out be 37 Å in the case of pure Pani, which is not observed in other samples. It is clear that the simple lamellae stack model presented here is capable of producing qualitatively similar behavior observed experimentally. Even though the present model is not an exact one, we have tried to incorporate the variation in width and thickness by using exponential distributions for amorphous and crystalline regions, while refining against the experimental SAXS data. From our computation it turns out that

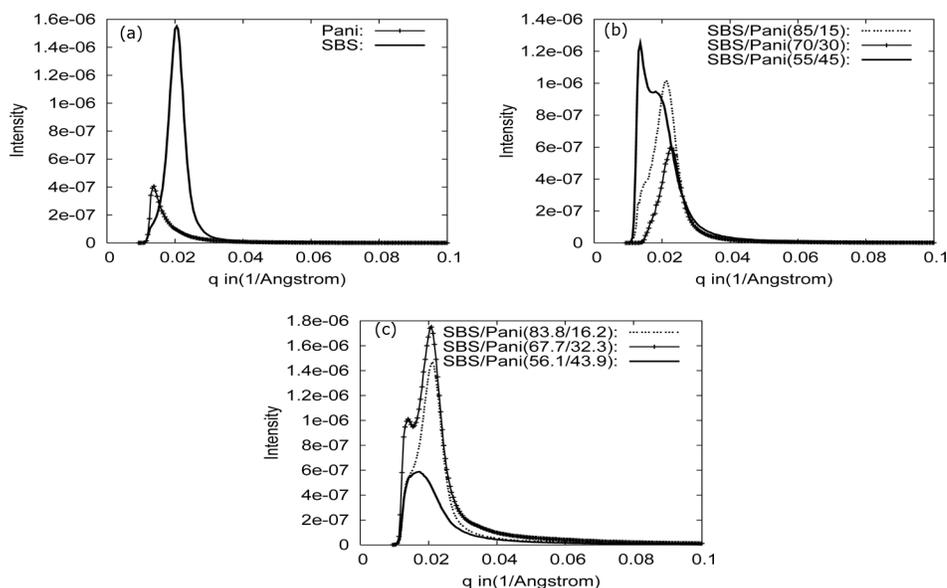


Figure 1. SAXS X-ray diffraction patterns of (a) Pani and SBS, (b) SBS/Pani (85/15), SBS/Pani (70/30), SBS/Pani (55/45), (c) SBS/Pani (83.8/16.2), SBS/Pani (67.7/32.3), SBS/Pani (56.1/43.9).

stack of 10–30 lamellae would be appropriate which is also observed in electron microscope studies of different polymers. We have selected 15, 30 and 45% because (i) with increase of Pani content in blends, there is a gradual reduction in mechanical properties like tensile strength and elongation at break [17]. (ii) Less than 15% Pani is not useful to achieve conductivity since volume resistivity is greater than 10^{12} ohm-cm. Pani incorporation of 15–30% shows drastic reduction in volume resistivity, i.e., from 10^{12} to 10^6 ohm-cm. But 30–45% of Pani incorporation yields reduction in volume resistivity from 10^6 to 10^4 ohm-cm. This has been reported in table 2 and figure 7 of ref. [17]. These are the optimized formulations range. Hence, in order to balance processing behavior, mechanical and electrical properties of the composites, we have selected 15–45% Pani. Within the region of available data we observe that there is a linear relationship between long periodicity and concentration of blends. In this region of our experimental data, we observe that there is a linear variation of crystalline thickness with the measured tenacity of polymer blends. The microstructure parameters obtained are given in table 1. It is evident from table 1 that blends (melt mixing) leads to an uneven polymer networking and uneven variation of long periodicity with increase in the concentration of Pani. So, it is more significant to consider the blends formed by chemical method which shows a linear variation of long periodicity with increase in concentration of Pani in the range of 15–45%. Essentially this indicates an increase in long range order of the polymer network. It was also observed [17] that blends formed by chemical method/polymerization resulted in lower resistivity. A comparison of long periodicity obtained in samples prepared by chemical method with the physical property like tensile strength indicates that the tensile strength decreases with increase in

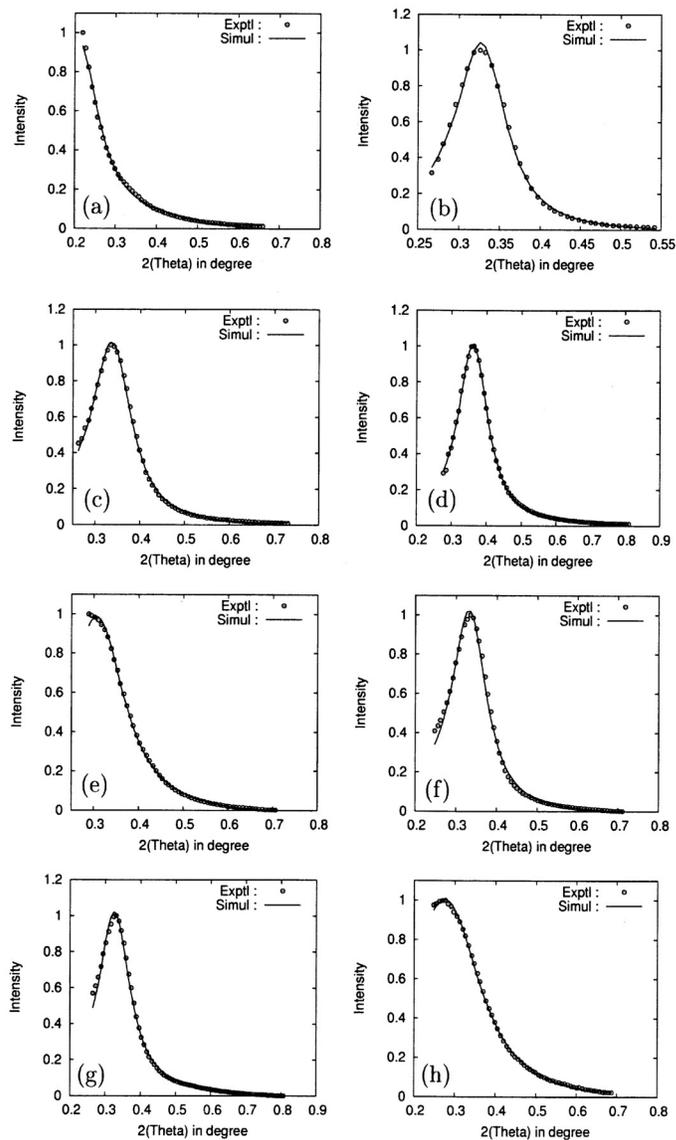


Figure 2. Experimental and simulated SAXS profiles using paracrystalline model. (a) Pani ($2\theta = 0.22$), (b) SBS ($2\theta = 0.32$), (c) SBS/Pani (85/15) ($2\theta = 0.33$), (d) SBS/Pani (70/30) ($2\theta = 0.36$), (e) SBS/Pani (55/45) ($2\theta = 0.29$), (f) SBS/Pani (83.8/16.2) ($2\theta = 0.34$), (g) SBS/Pani (67.7/32.3) ($2\theta = 0.33$), (h) SBS/Pani (56.1/43.9) ($2\theta = 0.28$).

long periodicity. The increase in long periodicity observed in chemically modified blends can be understood by the fact that the chain mobility within the crystalline regions at room temperature is such that the chains from the surrounding

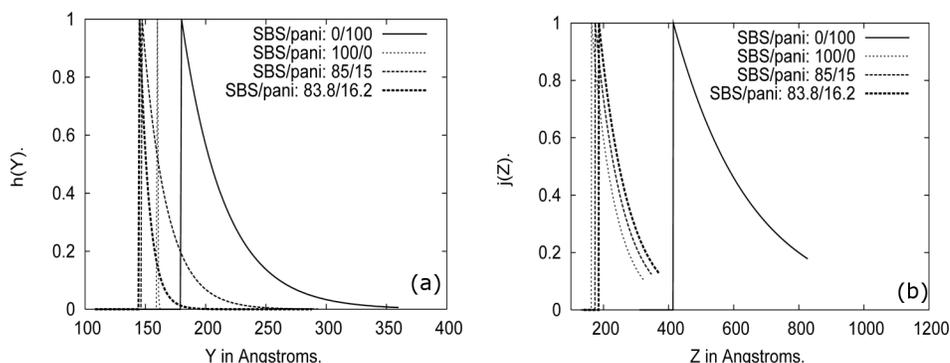


Figure 3. The normalized exponential probability distribution of the lengths of the phases. (a) γ_Y (amorphous) and (b) γ_Z (crystalline).

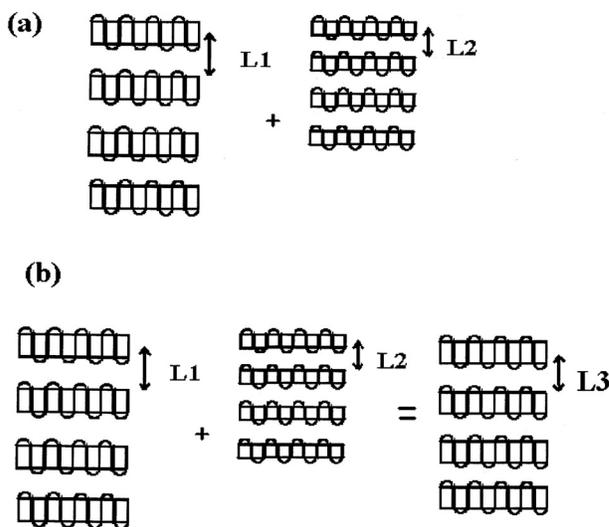


Figure 4. Illustrated models of stacked lamellar structures with different long periodicity.

amorphous matrix or microcrystals are incorporated into the crystalline lamellae [18]. This results in the crystal thickening process.

A simple calculation of mixing of two different two-phase lamellar stacking models with appropriate composition of Pani and SBS indicates combination of lamellar stacking model which is shown in figure 4a. For both melt mixing and chemical methods, we observe a new lamellar stacking model with a different long periodicity as shown in figure 4b. In the case of SBS/Pani (55/45) in melt mixing and SBS/Pani (67.7/32.3) in chemical method we observed a shoulder in the small angle X-ray recording with the periodicities of 44.5 and 41.1 nm, which indicates the co-existence of two different two-phase lamellar structure models as shown in figure 4. Such co-existence of lamellar phases have been reported earlier [19].

Table 1. Microstructural parameters of SBS, Pani and their blends using SAXS.

Composition of blends (SBS/Pani) (wt/wt%)	2Θ (deg)	Periodicity (Å)	Phase ratio	γ_Y	γ_Z	$\langle Y \rangle$ (Å)	$\langle Z \rangle$ (Å)	Crystallinity	N	Tensile strength (MPa)
0/100 (Pani)	0.22	594	0.3	0.098	0.289	180	414	0.70	10	–
	3.58	27.9	0.92	0.052	0.001	25.76	2.2	0.92	30	–
100/0 (SBS)	0.32	323	0.5	0.001	0.217	160	163	0.91	15	16.8 ± 1.1
<i>(a) Blends (Melt mixing)</i>										
85/15	0.33	321	0.5	0.067	0.238	147	174	0.54	15	7.2 ± 0.3
70/30	0.36	294	0.4	0.081	0.202	128	167	0.57	15	2.4 ± 0.8
55/45	0.29	393	0.4	0.030	0.302	146	248	0.63	15	2.0 ± 0.2
<i>(b) Blends (Chemical method)</i>										
83.8/16.2	0.34	329.7	0.44	0.027	0.242	144.3	185.3	0.56	15	4.6 ± 0.9
67.7/32.3	0.33	341.9	0.39	0.025	0.231	130.9	211	0.94	15	3.7 ± 0.4
56.1/43.9	0.28	471.2	0.32	0.098	0.347	149.4	322	0.68	15	3.0 ± 0.1

5. Conclusion

From our SAXS studies in the region of 15–45% of Pani in SBS, we observe that the long periodicity increases with increase in the content of Pani in the blends obtained by chemical method. This also favors lowering of the tensile strength in these blends. This is due to the formation of microcrystals at the expense of the unoriented amorphous chains between the lamellae. These microcrystals inhibit the mobility of polymer chains in both the amorphous and crystalline domains resulting in decreasing tensile strength. We also observe from these studies that blends formed by chemical method is more suitable than blends formed by melt mixing or mechanical method.

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