▼ Journal of Research (Science), Bahauddin Zakariya University, Multan, Pakistan.
Vol.13, No.2, December 2002, pp. 167-175 ISSN 1021-1012

INTERFACIAL STRUCTURE AND KINETIC MIXING OF Li-SPS/PC BLEND STUDIED BY NEUTRON REFLECTIVITY

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Abstract: Neutron reflectivity have been used as a tool to investigate polymer-polymer interdiffusion as a result of the interfacial structure and kinetic mixing of a partially miscible system polycarbonate and a lightly sulfonated polystyrene ionomer. The diffusion in this system with annealing at a temperature above the glass transition temperature of both polymers has been measured. The interfacial profiles obtained for this system are described by symmetric Gaussian interfaces and the diffusion process can be expected to follow the function of square root time, until a thermodynamical equilibrium is reached. In this case results suggest that the changes in the thickness layer are very slow and non-linearly dependent on the square roots time and ratio of the diffusion is extremely slow.

Keywords: Diffusion, neutron reflectivity, polycarbonate, sulfonated polystyrene ionomer.

INTRODUCTION

The concentration profile at polymer-polymer interfaces characterizes the interfacial structure. It not only is an important parameter for understanding the chemical and physical interactions at the interface, but also governs the interfacial adhesion, which ultimately controls the physical and mechanical properties of the blend [Paul and Sperling 1986]. Interfacial mixing begins when two polymer surfaces are brought into contact with each other and the extent and rate of interdiffusion depend on the interaction between the two polymers [de Gennes 1981]. General theories regarding polymer interdiffusion and the techniques used to study polymer-polymer interfacial mixing and the measurement of diffusion coefficients are described in recent reviews [Kausch and Tirrell 1989, Jabbari and Peppas 1994, Higgins and Bucknall 1997]. The present work falls within the area of the interfacial composition profile and the diffusion of the interface during interfacial mixing of a polymer pair with a large mismatch in their respective molecular mobilities and for which intermolecular interactions occur.

In this work, we focus our attention on polymer-polymer interdiffusion as the result of the interfacial mixing of a partially miscible system polycarbonate and a lightly sulfonated polystyrene ionomer pair. The interfacial development was investigated as a function of annealing time at 200°C and 220°C. The interfacial width obtained after annealing the sample for time t_0 at 200°C and 220°C can be correlated with different times and temperatures at one temperature by using the WLF (Williams-Landel-Ferry) empirical equation as given below:

$$\log \frac{t}{t_0} = \frac{c_1(T-200)}{c_2+(T-200)} \qquad (1)$$

The constants c_1 and c_2 depend on the temperature range and can be found in the literature [Ferry 1980].

It is known that polystyrene is immiscible with bisphenol-A polycarbonate, whereas blends of sulfonated polystyrene with polycarbonate are miscible at all concentrations in the range of 8.7-13.7 mol.% sulfonation whereas blends of lightly sulfonated polystyrene ionomers (SPS) and bisphenol-A polycarbonate (PC) were partially miscible for a narrow range of the sulfonation of the ionomers [Lu and Weiss 1993, 1996, Rui Xie and Weiss 1998]. This system exhibits upper critical solution temperature (UCST) phase behavior and a miscibility gap with respect to the sulfonate concentration. Fourier transform infrared spectroscopy revealed that no specific interactions involving either the carbonate carbonyl group or the metal sulfonate group occurred in these blends [Lu and Weiss 1996]. The miscibility was attributed to intramolecular repulsive interaction within the ionomers, the so-called copolymer effect.

A high-resolution technique is required to probe the interface between the polystyrene ionomers and the polycarbonate. Therefore we have used neutron reflectivity to investigate the polymer-polymer interfaces since it provides subnanometer resolution and high contrast when one of the two polymer components is selectively deuterium-labeled [Karim *et al*. 1990, Russell 1990]. This study reports some preliminary results from the application of specular reflection of neutrons used to investigate the nature of interface between lithium deuterated polystyrene and polycarbonate [Fernandez 1990].

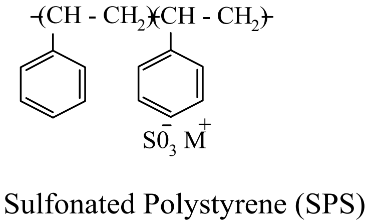
MATERIALS AND METHODS

MATERIALS

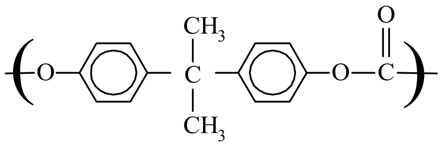
The polymers used in this work were polycarbonate and deuterated sulfonated polystyrene with Lithium metal cation. Polycarbonate (PC) was obtained from Aldrich Chemical Co., Inc. Deuterated polystyrene (d-PS), was synthesized by Dr. Robson Storey at the University of Southern Mississippi, USA. Sulfonation level was determined by elemental sulfur analysis at Galbraith Laboratories, Inc. USA. The structure of these polymers is shown below and the characteristics of these samples are listed in Table 1. The neutron scattering length densities (Nb) were calculated from the respective elemental composition and mass density.

Table 1: Characteristics of samples used in neutron reflectivity experiments.

Polymer	M_n (g mol^{-1})	M_w (g mol^{-1})	T_g (°C)	Density (g cm^{-3})	Nb x 10^{-6} (Å^{-2})
PC	12,100	22,600	155	1.20	2.03
d-LiSPS	18,620	18,750	120	1.17	5.97



Sulfonated Polystyrene (SPS)



Polycarbonate (PC)

SAMPLE PREPARATION

The samples prepared for the neutron reflection experiment consisted of a bilayer film of d-LiSPS on the top of thick layer of PC, both layers were cast on a silicon wafer. The sulfonation level of these dSPS was 11.2 mol.%. Prior to spin-coating, the silicon disks were cleaned in a 70/30 sulfuric acid / hydrogen peroxide solution for 45 min. They were then rinsed thoroughly in deionized water and blown dry. The bottom layer was prepared by spin-coated (at 1350 rpm) from a 1% (weight) solution in a solvent methylene chloride directly on to a polished silicon wafer, with the aim to achieve a layer thickness of ~100 nm. After spin-coating, the thin PC film was first air-dried and then dried in a vacuum oven for 45 min. at room temperature. These wafers were then coated with d-LiSPS. A 1% solution of d-LiSPS in solvent mixture 90/10 toluene/methanol, was then spun cast onto the PC layer at 1750 rpm, leaving a coat of approximately 40 nm. Samples were stored in a desecrator until the time of the experiment to protect the samples from moisture.

Interfacial mixing were measured by placing the bilayer samples at the annealing temperatures of 200 and 220°C in a vacuum oven for different periods of time. One of these samples was not annealed (as made) to compare to the annealed samples. A list of the annealing times is given in Table 2. After prescribed annealing period, specimens were quenched by natural cooling to the room temperature for the neutron reflectivity measurements. The annealing temperature was chosen so that it was above the glass transition temperatures of both polymers where the polymer chains were mobile, in order to allow interfacial mixing to occur.

Table 2: Annealing times for the bilayer d-LiSPS/PC.

Annealing Code	Cumulative annealing time at 200° C (hrs)
As made	0
B	1
C	3
D	5
E	7
F	17
G	60

NEUTRON REFLECTIVITY MEASUREMENTS

The neutron reflectivity measurements were carried out at the ISIS pulsed neutron source, Rutherford Appleton Laboratory, on the CRISP reflectometer [Penfold 1989]. Data were collected at three different incident angles, 0.25, 0.6 and 1.5°, and then merged to form a single reflectivity curve. The reflection from the film was measured at the specular angle by a single well-collimated detector. The wavelength dependence of the reflected neutron intensity is obtained by a time-of-flight analysis. The reflected intensity is converted to reflectivity by removal of the incident spectral shape (using an incident beam monitor), corrected for the detector efficiency and normalized to unity at total reflection. The procedure of modeling and fitting the reflectivity spectrum is documented elsewhere [Ankner 1992].

DATA ANALYSIS

The NR data analysis was carried out using a combination of the model fitting techniques. Model fitting is the standard approach towards NR data analysis. It works relatively well when there is enough prior knowledge of the system but it gives model dependent results for the interfacial profile.

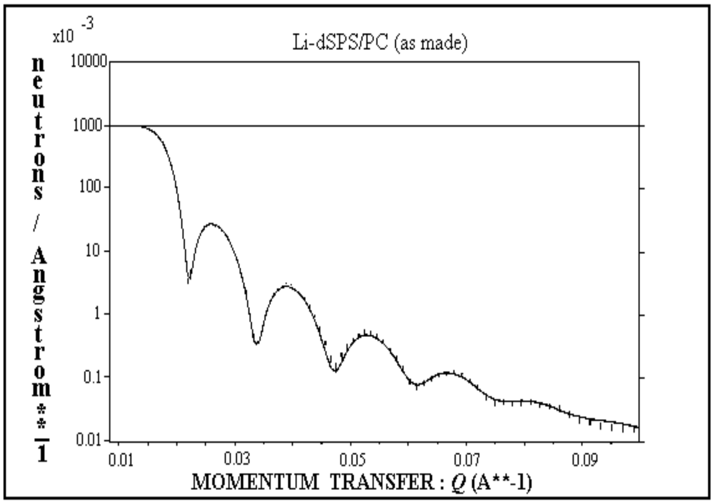


Fig. 1: Neutron reflectivity profile of a d-LiSPS/PC bilayer “as made” on a silicon wafer. The error bars represent the experimental points and the solid line curve is the best fit by using a symmetric interfacial model shown in the Fig. 2.

RESULTS AND DISCUSSION

Fig. 1 shows the reflectivity data (error bars) and the best fitting (solid line) obtained for the “as made” sample from d-LiSPS/PC bilayer. The interface can be described by a perfect Gaussian function whose interfacial width is 4 Å and surface roughness is 30 Å (Fig. 2). The top d-LiSPS layer is 427 Å thick and the bottom PC layer is approximately 1300Å. This indicates that the surface of “as made” sample is not smooth. Figs. 3 and 4 show the reflectivity profiles and their best model fits for the d-LiSPS/PC bilayer following the annealing sequences as shown in Table 2. The reflectivity data in these figures have been scaled for clarity. The interference patterns arise from waves reflected at each interface. The dominant lower frequency fringes arise from the thinner top layer d-LiSPS, whereas the superimposed high frequency fringes arise from the bottom thick PC layer. The rate at which these fringes damp depend on the interfacial width and nature of the polymer-polymer interface. The fits are very sensitive to the parameters describing the top d-LiSPS layer but they are not sensitive to the parameters of the bottom PC layer and the density of the substrate, these parameters have been held constant in the refinement procedure.

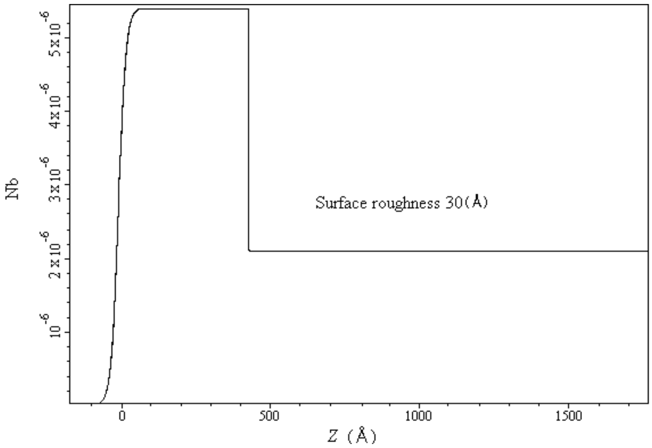


Fig. 2: The profile of scattering length density as a function of the layer depth (*Z*) for a d-LiSPS/PC bilayer on a silicon wafer, as made. The profile indicates d-LiSPS layer thickness of 427 Å and an air / ionomer interfacial roughness of 30 Å and was used to calculate the solid line curve of Fig. 1.

Table 3: Parameters used in the two-layer fits of reflectivity profiles, where Nb and d are the scattering length density and thickness of the d-LiSPS, $\sigma 1$ and $\sigma 2$ are the air- top layer and top layer-bottom layer root mean square roughness values, respectively. All the profiles have been fitted with the following constant parameters: Nb (PC) = 2.05×10^{-6} Å^{-2}, d (PC) = 1300 Å and Nb (silicon) = 2.07×10^{-6} Å^{-2}.

Annealing code	d (Å) d-LiSPS	Nb$\times 10^{-6}$ Å^{-2} d-LiSPS	$\sigma 1$ Å	$\sigma 2$ Å
As made	427	5.38	30	4.1
B	412	5.50	22	5.2
C	416	5.64	11	21.0
D	416	5.75	11	22.4
E	402	5.78	11	23.1
F	402	5.75	13	26.8
G	402	5.75	15	34.0

These scattering density profiles shows the decrease in amplitude of the fringes with annealing time indicates the presence of an interface. The period of the higher frequency fringes increases as a result of thinning of the d-LiSPS layer. The entire model fitting has been made using a single bilayer with a diffuse Gaussian interface at the d-LiSPS/PC interfaces. The fitted parameters (thickness and density) of the d-LiSPS layer, and the width of the interface are summarized in Table 3. The effect of annealing on the reflectivity data can be seen directly in Figs. 3 and 4. The amplitude of the fringes decreases, which indicates the presence of an interface that increases in size with annealing time. Moreover, the period of the low frequency fringes increases indicating a thinning of the top d-LiSPS layer. The top film gets thinner with annealing while initially its scattering length density increases and eventually reaches a constant value. However from the fitting parameters (Table 3) one can extract the following information about the system:

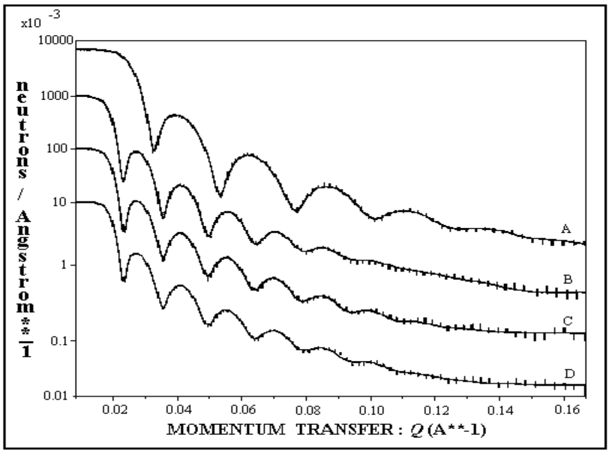


Fig. 3: Neutron reflectivity profiles with best fits of d-LiSPS/PC annealed at 200°C for different periods of times. Curve (A) as made, (B) 1 hrs, (C) 3 hrs, (D) 5 hrs.

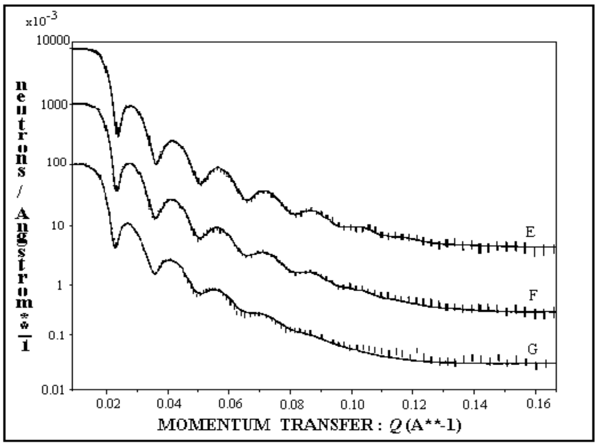


Fig. 4: Reflectivity data and their best fits after annealing at 200ºC, curve (E): for 7 hrs, curve (F): for 14 hrs and curve (G): for 60 hrs.

During annealing B, C and D thickness of the top layer increases. After annealing B the scattering length density of the d-LiSPS increases and then remains approximately constant during all annealing steps. This suggests that during first three annealing processes the d-LiSPS layer is stabilizing and that chains are allowed to move and arrange themselves until they reach equilibrium.

After annealing E, F and G thickness of the top layer decreases and its scattering length density mostly remains constant. Width of the interface increases continuously and the air-ionomer roughness remains approximately constant. Several conclusions can be drawn from the results obtained before and after annealing the samples.

The top d-LiSPS layer gets thinner with annealing while its scattering length density increases slightly and than remains constant. The surface undulations are larger at the initial stages of annealing and the quality of the sample improves gradually. The d-LiSPS chains are allowed to move and arrange, and hence the root-mean-square roughness d-LiSPS/PC changes gradually. The surface of the top layer becomes again more wavy with annealing and as d-LiSPS diffuses into the bottom layer. The shape of interface remains the same but the position of the interface moves towards the d-LiSPS layer. These effects are clear from changes in the period of fringes with annealing. We should also point out that why interface appears large, then decreases and subsequently increases again. Because the top layer was prepared by spin coating directly onto the layer already on the substrate, it is quite likely that the solvent has swollen the interface so that in the first couple of hours of annealing the system is simply changing to a new equilibrium state.

The d-LiSPS/PC interface has been modeled as a symmetrical Gaussian, implying that there is some mixing on both sides of the interface. As shown by the fitting parameters (Table 3) the top d-LiSPS layer gets thinner as the PC, which is the more mobile polymer, starts swelling the less mobile PC. The PC has higher molecular weight than the d-LiSPS. The direction of the shift of the interface is therefore always towards the fastest moving components, clearly indicating the occurrence of a swelling mechanism.

Having discussed the interfacial structure, we now proceed to discuss the kinetics of the interfacial mixing. Fig. 5 plots interfacial shift $\left(\Delta Z_i\right)$ as a function of annealing time, t at 200°C for the d-LiSPS/PC bilayer. Line (a) in Fig. 5 corresponds to “case – II” $\left(\Delta Z_i \sim t\right)$ diffusion predictions. The experimental data do not clearly follows linear relationship with time, which indicates that the overall mixing process cannot be described solely by a polymer relaxation or a simple molecular diffusion mechanism. These results show that a relatively small increase in the interfacial width is observed. The initial fast increase is followed by a slow increase until the final constant width is reached.

Earlier Feng et al. [1996] used neutron reflectivity to study the kinetics of interfacial mixing between the Lithium-salt sulfonated polystyrene and polyamide (mPA). They interpreted their data with two suggested models of diffusion-controlled mechanisms of mixing kinetics for a different temperature range. We have also used the same models to fit our experimental data.

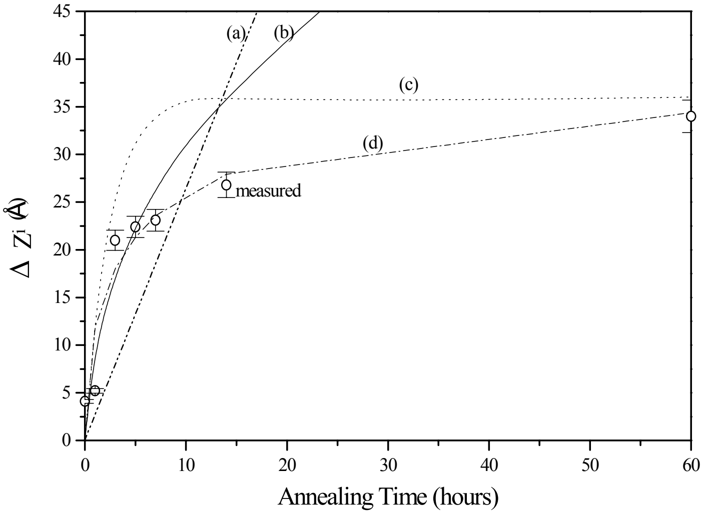


Fig. 5: Displacement of the d-LiSPS layer front at 200°C as a function of annealing time for a d-LiSPS/PC bilayer. Lines are the best fittings by using different kinetic models: (a) $\Delta Z_i = Bt$, (b) $\Delta Z_i = Bkt^{1/2}$; (c) $\Delta Z_i = B[1-\exp(-kt)]$; (d) $\Delta Z_i = B[1-\exp(-kt^{1/2})]$ where *t* is the annealing time, ΔZ_i the interface shift, *k* and *B* the fitting parameters.

In Fig. 5, lines (b) and (c) give the best fits by equations ($B[1-\exp(-kt)]$) and ($B[1-\exp(-kt^{1/2})]$), respectively. Within the experimental error, the expression ($B[1-\exp(-kt)]$) does not fit the experimental data. On the other hand the expression ($B[1-\exp(-kt^{1/2})]$) provided the best fit to our experimental data. The interpretation for this expression provided by Feng *et al.* [1996] was that the diffusion is gradually and significantly slowing down by cross-linking mechanism. This is unlikely to be the case in this system of PS/PC, but it is obviously some form of chemical reaction or molecular rearrangements, which are responsible for the observed effects. These results could be expected, as at 200°C polymers are immiscible. It will therefore be useful to repeat the experiment with samples annealed in the miscible range i.e. above the critical solution temperature (225°C) [Lu and Weiss 1996]. Another modification that might have been beneficial would be to change the different metal cation (i.e. Zinc) sulfonate polystyrene. This would provide more information about this system.

CONCLUSIONS

In this study, we have demonstrated the effects of introducing intermolecular complexation on the interface of sulfonated polystyrene (SPS) and polycarbonate (PC) blends with lithium metal cation. The diffusion in this system with annealing at a temperature above the glass transition temperature of both polymers has been measured. The interface can be simulated by a symmetric Gaussian interface. After a sufficiently long enough annealing time a constant interfacial width is observed. Also the observed changes in thickness of the layer are very slow and depend non-linearly on the square root of time. This indicates that the observed thickening of the interfacial layer is more affected by changes in planarity of the interface than by true diffusion. Therefore, it can be concluded with certainty that diffusion (if any) is extremely slow.

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