

## Effect of Density Fluctuating Supercritical Carbon Dioxide on Polymer Interfaces

Tadanori Koga,<sup>\*,†</sup> J. L. Jerome,<sup>†</sup> Y.-S. Seo,<sup>†,‡</sup> M. H. Rafailovich,<sup>†</sup>  
J. C. Sokolov,<sup>†</sup> and S. K. Satija<sup>‡</sup>

*Department of Materials Science & Engineering, State University of New York at Stony Brook, Stony Brook, New York 11794-2275, and Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899*

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We investigated an effect of CO<sub>2</sub> sorption on the compatibility of immiscible polystyrene (PS) and polybutadiene (PB) bilayers by using in situ neutron reflectivity. By labeling either polymer with deuterium, we found that the excess CO<sub>2</sub> molecules were adsorbed to both top PS and bottom PB layers when the bilayers were exposed to CO<sub>2</sub> at the narrow *T* and *P* regime near the critical point of pure CO<sub>2</sub>. Furthermore, we clarified that this excess sorption of CO<sub>2</sub> molecules increased the interfacial width between the layers up to 100 Å even near room temperature, while the interfacial width without CO<sub>2</sub> exposure has been reported to be at most 40 Å even at the highest temperature (*T* ≈ 175 °C).

Supercritical carbon dioxide (scCO<sub>2</sub>) is currently being used widely as a regeneration solvent in a range of technical and chemical processes, such as chromatography, extraction, reactor cleanup, and preparation of pharmaceutical products.<sup>1</sup> In contrast to the liquid state, the well-known benefit of the supercritical regime is the large compressibility which permits sensitive control of density-dependent solvent properties, such as dielectric constant, viscosity, and diffusivity. However, even under high compression, CO<sub>2</sub> is generally a poor solvent for most polymers, which still places severe restriction on its widespread use. Recently, by utilizing in situ neutron reflectivity (NR), we found that a wide variety of polymer thin films could swell as much as 30–60% in CO<sub>2</sub> along the pressure/temperature line known as the “density fluctuation ridge” which defines the maximum isothermal compressibility (or density fluctuations) in pure CO<sub>2</sub>. Along this ridge, we established that miscibility of polymer thin films with CO<sub>2</sub> was greatly enhanced even when the bulk miscibility of the polymers was very poor.<sup>2</sup> The degree of CO<sub>2</sub> sorption seemed to depend more on the mechanical, rather than the chemical nature of the polymers.<sup>3</sup> For example, the sorption in rubbery polymers, whose glass transition temperature (*T*<sub>g</sub>) was much below ambient, exceeded 60%, whereas the sorption in glassy polymers with *T*<sub>g</sub> ~ 100 °C was at most 30%, regardless of the miscibility in the bulk.<sup>2,3</sup> Since the excess sorption of scCO<sub>2</sub> appears to be a general phenomenon which is nonspecific to any polymers, we postulate that it may also serve as a cosolvent for thin polymer blend films.

In the bulk, scCO<sub>2</sub> is known to act as an agent for either enhancing miscibility or accelerating phase separation, in polymer blends. For miscible polymer blends which exhibit lower critical solution temperature (LCST) behavior, such as PS/poly(vinyl methyl ether) (PVME),<sup>4,5</sup>

polybutadiene (PB)/PI<sup>6</sup> or poly(methyl methacrylate) (PMMA)/poly(vinylidene fluoride),<sup>7</sup> the sorption of CO<sub>2</sub> has been reported to significantly reduce the miscibility. On the other hand, Walker et al. have reported that CO<sub>2</sub> can promote miscibility in low-molecular-weight polystyrene (PS)/polyisoprene (PI) blends which exhibit upper critical solution temperature (UCST) behavior.<sup>8</sup> They postulated that CO<sub>2</sub> molecules were adsorbed to the polymer/polymer interfaces, thereby screening unfavorable interactions. To study this phenomenon more closely, we chose to measure interfacial structures between PS and polybutadiene (PB) films, which form an immiscible polymer blend with an UCST phase diagram. We chose to use in situ NR and start by directly measuring the interface between the two polymers. This was most conveniently achieved using planar thin film geometry. With this technique we can deuterate either polymer and measure the interfacial profile and the CO<sub>2</sub> volume fraction as a function of pressure and temperature in order to determine whether a correlation exists between enhanced miscibility and the density fluctuation ridge.

Two kinds of bilayers were prepared for the in situ NR experiments: hPB (*M*<sub>w</sub> = 200000 g/mol, 515 Å thickness)/dPS (*M*<sub>w</sub> = 690000 g/mol, 505 Å thickness) and dPB (*M*<sub>w</sub> = 264000 g/mol, 654 Å thickness)/hPS (*M*<sub>w</sub> = 200000 g/mol, 490 Å thickness). All polymers used were obtained from Polymer Source Inc. (Montreal, Canada), and their polydispersity indices were 1.1 or less. The characters “d” and “h” are hereafter used to distinguish deuterium labeled and hydrogenated polymers. PB films were first spun cast from toluene solution onto HF etched Si wafers (8 mm thickness and 75 mm diameter). PS films were spun cast onto glass plates and then floated from distilled water onto the polymer-coated Si wafers. The resulting bilayers were annealed in high vacuum (10<sup>-5</sup> Torr) at *T* = 140 °C

\* Correspondence author: tkoga@notes.cc.sunysb.edu.

<sup>†</sup> State University of New York at Stony Brook.

<sup>‡</sup> National Institute of Standards and Technology.

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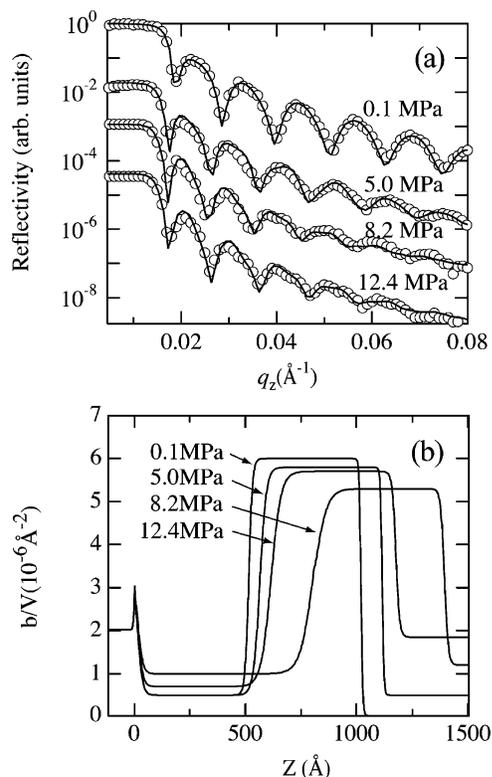
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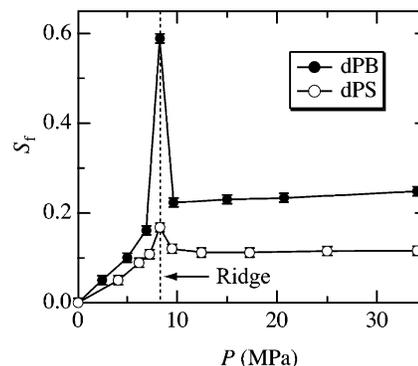
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**Figure 1.** (a) Representative NR curves for hPB/dPS at  $T = 36$  °C. Reflectivities have been offset from each other for clarity. The solid lines are calculated reflectivity based on the corresponding SLD profiles shown in Figure 1b. Note that the SLD values of  $\text{CO}_2$  increase with increasing pressure, i.e., the density of  $\text{CO}_2$ .

for 2 h to remove residual solvent and relax strains induced by spinning.<sup>9</sup> The samples were then placed in a chamber with temperature and pressure controls, specifically designed for high-pressure NR experiments.<sup>3</sup> Specular NR measurements were performed on the NG7 neutron reflection spectrometer at NIST with a wavelength ( $\lambda$ ) of 4.76 Å and  $\Delta\lambda/\lambda$  of 2.5%. The details of the high-pressure NR experiments have been described elsewhere. The NR experiments were conducted at  $T = 36$  °C with elevated pressures up to  $P = 35$  MPa. The samples were exposed to  $\text{CO}_2$ , prior to data acquisition, for up to 4 h in order to ensure that the equilibrium swelling had been achieved.<sup>2,3</sup> The NR data were corrected for the scattering from pure  $\text{CO}_2$ , and was analyzed by comparing the observed reflectivities with calculated ones based on a hyperbolic-tangent model density profile with three fitting parameters for each layer: film thickness, scattering length density (SLD), and roughness between the layers.<sup>10</sup> A four-layer model, i.e., a silicon substrate, a native oxide layer (typically  $\sim 15$  Å thickness), a PB layer, and a PS layer, was used to fit the NR data. The errors of the thicknesses are 3–5 Å. The errors of the interfacial widths are relatively larger (about 20% of the value) since the interfacial widths are rather larger, and thus we are not so sensitive to the large  $q_z$  values.

Figure 1a shows the representative NR profiles for the hPB/dPS bilayer at four different pressures and  $T = 36$  °C, where the reflected scattering intensity is plotted as a function of the momentum transfer normal to the surface,  $q_z = 4\pi \sin \theta/\lambda$ , where  $\theta$  is the grazing angle of incidence



**Figure 2.** Pressure dependence of  $S_f$  at  $T = 36$  °C: filled and open circles correspond to the dPS film for hPB/dPS and the dPB film for dPB/hPS, respectively.

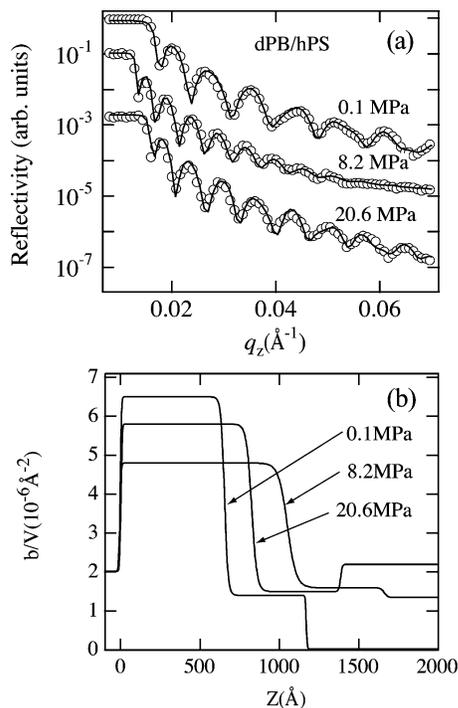
and  $\lambda$  is the neutron wavelength, respectively. From the figure we can clearly see that the film thickness, i.e., the frequency of Kiessig fringes, and the interface roughness between the two polymers, i.e., the damping of the fringes, sensitively change as a function of the  $\text{CO}_2$  pressure. From the best fit (solid lines) to the data based on the corresponding SLD profiles shown in Figure 1b, the film thickness of the dPS layer increased from the initial film thickness of 505 Å to 530 Å at  $P = 5$  MPa, 591 Å at  $P = 8.2$  MPa, and 561 Å at  $P = 12.4$  MPa. It should be noted that the swelling behavior of the bottom hPB film was assumed to be identical to that of the single dPB film reported previously<sup>3</sup> and, as will be discussed below, this assumption was valid for this study. As shown in Figure 2, the linear dilation ( $S_f$ ) of the dPS film in the direction normal to the surface, which was calculated from the definition  $S_f = (L - L_0)/L_0$ , where  $L$  and  $L_0$  are the measured thickness of the swollen and unswollen films, respectively, showed a relatively small maximum of  $S_f = 0.18$  at the density fluctuation ridge ( $P = 8.2$  MPa) and the overall swelling behavior was in good agreement with that reported for the single dPS layer.<sup>2,3</sup> As shown in Figure 1b, in all cases, the dilation was uniform, indicating that  $\text{CO}_2$  did not segregate to either the vacuum or PB interface.

To measure the profile directly in PB, we also measured NR from the reverse labeled bilayer, i.e., dPB/hPS. Their typical NR profiles are shown in Figure 3a, where we find that in this case as well the dilation is uniform (see Figure 3b), indicating that  $\text{scCO}_2$  does not segregate to either the silicon oxide or polymer interfaces. Furthermore, as can be seen from the frequency of the Kiessig fringes, the dilation is much larger than that observed in the dPS film. The dilation of the dPB film is plotted in Figure 2 (filled circles). Here we can see that a large increase occurs at the density fluctuation ridge. The magnitude of the increase, 60%, is consistent with that previously reported for the single layer film.<sup>3</sup> The difference in the magnitude of the dilation between the dPS and dPB films was explained previously as being due to the difference in elasticity of the polymer.<sup>3</sup> We have previously shown that the dilation in  $\text{scCO}_2$  is largest for films of thickness  $2R_g$  or less,<sup>2</sup> where  $R_g$  is the radius of polymer gyration. Furthermore, the gradient of the dilation with thickness was found to be larger in rigid polymers than that in flexible ones.<sup>3</sup> However, since the dilation of dPB is relatively independent of film thickness,<sup>3</sup> we are not sensitive to the effect of the PS overlayer on the dilation on the bottom PB layer.

On the basis of the SLD values obtained from the NR curves, we determined the volume fraction of the  $\text{CO}_2$  component in the mixtures ( $\phi$ ), assuming that the SLD values for the polymer- $\text{CO}_2$  mixtures ( $\text{SLD}_{\text{mix}}$ ) were

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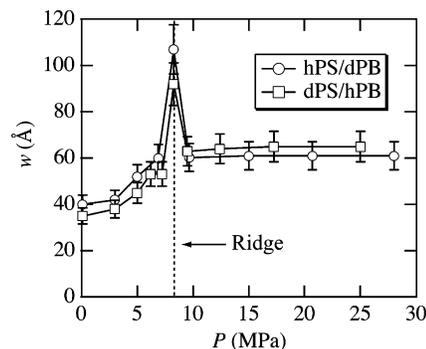
**Figure 3.** (a) Representative NR curves for dPB/hPS at  $T = 36$  °C. The solid lines are calculated reflectivity based on the corresponding SLD profiles shown in Figure 3b.

homogeneous through the entire films.  $SLD_{\text{mix}}$  can be then expressed as follows

$$SLD_{\text{mix}} = SLD_{\text{co}}\phi + SLD_{\text{p}}(1 - \phi) \quad (1)$$

where  $SLD_{\text{p}}$  and  $SLD_{\text{co}}$  are the SLD values for the bulk polymers and  $\text{CO}_2$ , respectively. The density of  $\text{CO}_2$  dissolved in the polymers was taken to be  $0.956 \text{ g/cm}^3$ .<sup>11</sup> Substitution of the observed  $SLD_{\text{mix}}$  values of the dPB layer for dPB/hPS ( $SLD_{\text{mix}}^{\text{dPB}} = 4.8 \times 10^{-6} \text{ \AA}^{-2}$ ) and the dPS layer for hPB/dPS ( $SLD_{\text{mix}}^{\text{dPS}} = 5.3 \times 10^{-6} \text{ \AA}^{-2}$ ) provided the  $\phi$  values of 42% for the dPB layer and 22% for the dPS layer at the ridge, respectively, with  $SLD_{\text{dPS}} = 6.1 \times 10^{-6} \text{ \AA}^{-2}$  and  $SLD_{\text{dPB}} = 6.5 \times 10^{-6} \text{ \AA}^{-2}$ . Note that these SLD values of the pure polymers were obtained from the NR results without  $\text{CO}_2$  exposure. Hence we can see that  $\text{CO}_2$  penetrates throughout the samples and the concentration is much larger inside the PB films.

Let us focus on the interfacial width between the layers in the presence of  $\text{CO}_2$ . From the best fits to the data shown in Figure 1, we found that the interfacial width ( $w$ ), which is expressed as  $w = 2w_{\text{h}}$ , where  $w_{\text{h}}$  is the width of the hyperbolic tangent function used for the fitting, shows a drastic pressure dependence:  $w = 35 \text{ \AA}$  at  $P = 0.1 \text{ MPa}$ ,  $w = 45 \text{ \AA}$  at  $P = 5 \text{ MPa}$ ,  $w = 92 \text{ \AA}$  at  $P = 8.2 \text{ MPa}$ , and  $w = 64 \text{ \AA}$  at  $P = 12.4 \text{ MPa}$ . Data were obtained both by successively increasing the pressure and then by slowly decreasing the pressure. The results were identical, indicating that the interfacial structures were reversible and an equilibrium quantity, which was a function only of the  $\text{CO}_2$  pressure and temperature. As summarized in Figure 4, we can see that the  $w$  values for the hPB/dPS bilayer increased with increasing pressure approaching the ridge and rapidly dropped and then became a plateau after crossing the ridge. Interestingly, the  $w$  value at the ridge was more than two times larger than those reported



**Figure 4.** Pressure dependence of  $w$  for dPB/hPS (circles) and hPB/dPS (squares) at  $T = 36$  °C.

for the PS/PB bilayers ( $w \approx 40 \text{ \AA}$ ) annealed at the highest temperature ( $T \approx 175$  °C).<sup>12,13</sup> This is consistent with our hypothesis that  $\text{scCO}_2$  behaves like a cosolvent along the density fluctuation ridge, rather than a physical barrier segregating the two polymers from each other. Hence we can prove that the interfacial broadening is an effect directly correlated to the density fluctuation ridge. In addition, as shown in Figure 4, we found that the pressure dependence of  $w$  for dPB/hPS was in good agreement with that for hPB/dPS including the excess broadening at the ridge. We can therefore conclude that density fluctuating  $\text{scCO}_2$  can be used to promote the compatibility between PS and PB drastically even near room temperature, offering potential benefits for processing thin polymer blend films as not only “environmentally friendly” but “polymer friendly” means.

As we have previously reported, the Flory–Huggins interaction parameter ( $\chi$ ) for the dPB thin film/ $\text{CO}_2$  binary mixture is estimated to be about 0.9 at the ridge.<sup>3</sup> Interestingly, this  $\chi$  value is almost equivalent to that reported for the bulk silicone rubber,<sup>14</sup> which is one of the “ $\text{CO}_2$ -philic” polymers under moderate  $\text{CO}_2$  conditions. In the case of the PS film, although the solvent quality of  $\text{scCO}_2$  is still poor even at the ridge,<sup>15</sup> the excess sorption of  $\text{CO}_2$  sufficiently plasticized the PS film so that its glass transition temperature approaches or drops below the experimental temperature used.<sup>16</sup> In addition to these roles as the effective solvent and plasticizer, the excess sorption of  $\text{CO}_2$  in both layers could screen the unfavorable segment interactions at the polymer/polymer interfaces as a compatibilizing agent. Further NR experiments for PS/PMMA bilayers showed a similar enhancement in the interfacial width between the layers at the density fluctuation ridge (the data is not shown here), indicating that the cosolvent effect of  $\text{scCO}_2$  may be a characteristic feature for immiscible thin polymer blend films exhibiting upper critical solution behavior. Interestingly, the magnitude of the enhancement for PS/PMMA was much smaller ( $w \approx 50 \text{ \AA}$ ) than that for the PS/PB bilayers mentioned above. In this case, the  $\phi$  value for the bottom PMMA layer was estimated to be 20%, suggesting that the increased degree of the compatibilization would be directly proportional to the  $\text{CO}_2$  volume fraction.

In conclusion, we investigated the effect of  $\text{CO}_2$  sorption on the compatibility of immiscible polymer bilayers, PB/

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PS, by using the in situ neutron reflectivity. By labeling either polymer with deuterium, we found that the excess CO<sub>2</sub> molecules were adsorbed to both top PS and bottom PB layers when the bilayers were exposed to CO<sub>2</sub> at the narrow  $T$  and  $P$  regime near the critical point of pure CO<sub>2</sub>. Furthermore, we clarified that this excess sorption of CO<sub>2</sub> molecules increased the interfacial width between the layers up to 100 Å even near room temperature, while the interfacial width without CO<sub>2</sub> exposure has been reported to be at most 40 Å even at the highest temperature ( $T \cong$

175 °C) measured.<sup>12,13</sup> This finding opens new avenues to thin polymer blend film processing, which is typically operated at high temperatures so that most of polymers are easily degraded. We are currently studying the effect of the density fluctuating scCO<sub>2</sub> on miscible thin polymer blend films.

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