Diffusion in Polymer Blends by Raman Microscopy

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Received April 18, 2008
Revised Manuscript Received June 3, 2008

Polymer blending is a popular industrial route to obtain target product properties without going through possibly expensive synthesis steps. In most cases, the microstructure of a polymer blend is characterized by micron-sized droplets of one phase dispersed into the other one. Polymer interdiffusion plays a major role in polymer blend microstructure, even in systems that are usually considered immiscible for practical purposes. In particular, by studying single droplet deformation under shear flow, it has been shown that the actual viscosity ratio between the dispersed and the continuous phase of a polymer blend is an increasing function of time from mixing, starting from the value calculated from the viscosities of the pure components and leveling off at some point.[1,2] This process, which is accompanied by a parallel increase of interfacial tension, has been attributed to a selective migration of chains, according to their molecular weights. Indeed, the smaller chains diffuse out at a faster rate, thus enriching the droplets with higher, more viscous molecular weight species and eliciting a corresponding rise in interfacial tension, which is an increasing function of molecular weight. These conclusions, though quite reasonable, have been reached by indirect evidence due to the lack of data of polymer−polymer diffusion in droplet-based systems.

In this work, we tackle the problem of diffusion in polymer blends by using Raman microscopy.[3−6] This technique is a well-established and powerful tool for the chemical characterization of materials, providing narrow spectral features, which constitute a sort of fingerprint of the investigated sample. When applied to polymer science, it presents many relevant advantages with respect to other conventional techniques, such as fluorescence microscopy. For instance, in Raman analysis no polymer labeling is needed, which is prone to introduce artifacts in the phase behavior and the mobility of the polymer chains. Within this framework, we have investigated the weight fraction profiles of the diffusing species outside a micron-sized droplet of the dispersed phase, by using a micro-Raman optical setup. This approach allows the investigation of the diffusion process, occurring at a micrometric scale, in a polymer blend of two “immiscible” phases. In particular, we have measured the weight fractions in the mixture due to molecular diffusion as a function of both time and distance from the droplet interface, in a geometry which has a close correspondence to the actual microstructure of a polymer blend.

The experimental setup used in this work has been presented in detail elsewhere.[7,8] Briefly, the spectroscopic analysis has been performed by using a homemade Raman microscope (inverted configuration) equipped with a frequency-doubled Nd-YVO laser (532 nm). The laser beam was focused by an objective lens (Olympus 40×, 0.65 N.A., dry, infinity corrected) on the sample. The Raman scattered radiation was focused through a 50 μm pinhole aperture for confocal geometry and, then, sent onto the entrance slit (set at an aperture of 50 μm) of a spectrometer (TRIAX 180, Jobin-Yvon). In such a way, the measured lateral and axial resolutions resulted ~0.52 and ~1.55 μm, respectively. The polymer blend used in our experiments is the polyisobutylene/poly(dimethylsiloxane) pair, which is a model system widely used in the literature.[9,10] The polyisobutylene (PB) was provided by BP Chemicals with $M_w = 2200$ and $M_w/M_n = 1.7$ ($T_g = 200$ K). Poly(dimethylsiloxane) (PDMS) was supplied by Rhone-Poulenc with $M_w = 133\,000$ and $M_w/M_n = 1.8$ ($T_g = 150$ K).[11] Both the PB and PDMS samples used in this work are transparent, Newtonian liquids at room temperature. The small density difference between the two polymers (around 0.08 g/cm^3) and the high viscosity (88 Pa s for PDMS, at 23 °C) ensure that buoyancy effects are negligible. The sample was prepared by depositing a thin layer of PDMS on a microscope coverslip, followed by injection of a few drops of PB into the PDMS layer by using a tiny glass capillary. Finally, the sample was sealed off with a microscope slide forming a chamber of about 4 μL with a thickness of 200 μm. The droplet diameter selected for this investigation was around 45 μm with a distance of around 60 μm from the coverslip surface (see Figure 1).

Our measurements consisted in acquiring Raman spectra at different times and distances from the droplet surface. In particular, spatial and temporal polymers weight fractions were monitored in the PB droplet equatorial plane, in which the diffusion process is radial (see Figure 1). It is worth to be noticed that, when using dry objectives, spherical aberrations may affect the correct estimation of this plane due to the apparent compression of the axial scale.[12] However, it is possible to demonstrate that this effect produces an indetermination on our measurements which is within the experimental errors.

In Figure 2A,B, we report typical Raman spectra of pure PB and pure PDMS as acquired in the spectral region between 650 and 1350 cm^{-1}. All the spectra here shown were acquired at

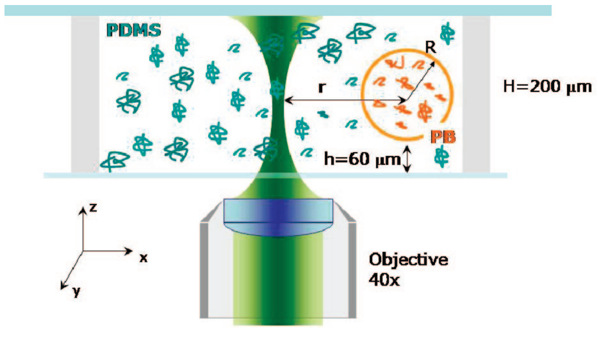

Figure 1. Schematic of the experimental setup: ($r - R$) is the distance of the laser focus from the PB droplet interface, h is the droplet bottom position from the coverslip surface, and H is the distance between the two coverslips.

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10.1021/ma800866m CCC: $40.75

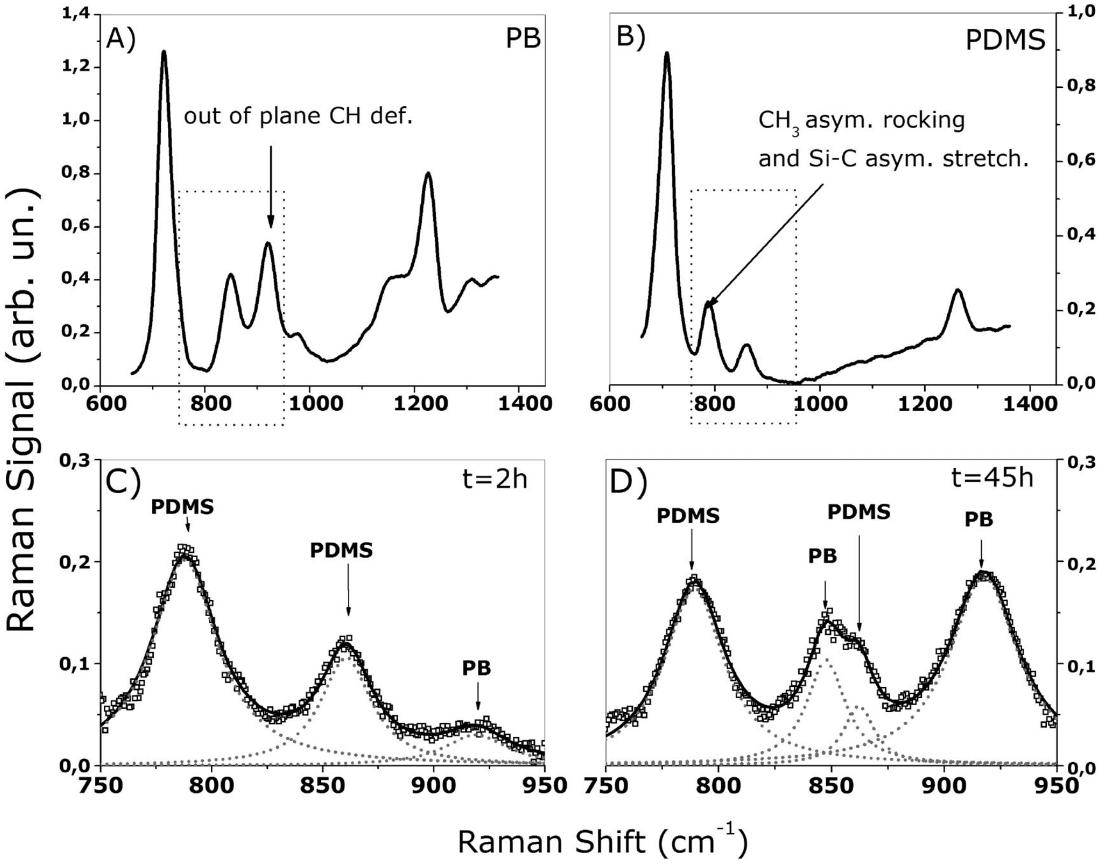

Figure 2. (A) Raman spectra of pure polyisobutylene (PB) and (B) pure polydimethylsiloxane (PDMS). The out-of-plane CH deformation of PB at ~915 cm^{-1} and the CH_3 asymmetric rocking + Si−C asymmetric stretching of PDMS at ~790 cm^{-1} were used to monitor molecular diffusion of the two polymers. (C) Raman spectra of PDMS/PB blend in the spectral region between 750 and 950 cm^{-1} (dashed region of parts A and B) at a distance of 4 μm from the droplet interface in the beginning (t = 2 h) and (D) at the end of the experiment (t = 45 h). The Raman peaks have been fitted by a combination of Lorentzian line shapes (solid and dashed lines).

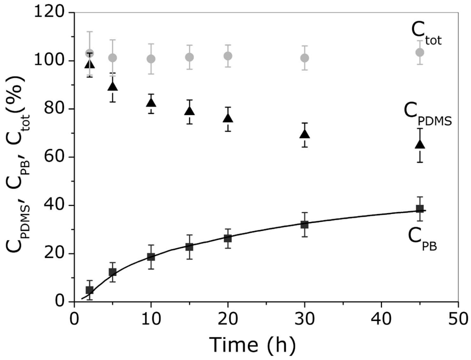

Figure 3. PB (C_{PB}), PDMS (C_{PDMS}), and the sum $C_{tot} = C_{PB} + C_{PDMS}$ as a function of the time at $(r - R) = 4$ μm from the droplet surface. The best fit to the C_{PB} data obtained by using the model of eq 5 is shown by the solid line.

room temperature, with a laser power of 20 mW (on the sample) and a CCD integration time of 20 s. Even though the two spectra look quite similar, there are two peaks (highlighted in Figure 1A,B by arrows) presenting a quite reduced spectral overlapping which are, therefore, good candidates to selectively monitor each polymer weight fraction. These Raman features correspond to the out-of-plane CH deformation around 915 cm^{-1} (for PB polymer)[13] and to the CH_3 asymmetric rocking plus the Si−C asymmetric stretching at ~790 cm^{-1} (for PDMS polymer).[4] Hereafter, these two peaks will be denoted as S_{PB} and S_{PDMS}, respectively.

Figure 2C,D shows the Raman spectra in a narrower interval (750−950 cm^{-1}) around the S_{PB} and S_{PDMS} peaks. Spectra C and D were recorded after t_1 = 2 h and t_2 = 45 h from PB droplet injection in PDMS, respectively, and focusing the laser beam at a distance $(r - R) = 4$ μm from the droplet interface. As can be noticed, the S_{PB} peak, already visible after 2 h, becomes clearly evident after 45 h, when it reaches its maximum intensity. On the contrary, the S_{PDMS} peak decreases during the observation time.

In order to determine PB and PDMS weight fractions, we fitted our spectra with an envelope of Lorentzian curves (solid and dashed lines in Figure 2). Once the best fit was achieved, the relative weight fractions of the two polymers, $C_{PB}(r,t)$ and $C_{PDMS}(r,t)$, were evaluated by dividing the areas under the S_{PB} and S_{PDMS} peaks by the corresponding values estimated from pure PB and PDMS samples, i.e.

$$C_{PB}(r,t) = \frac{A_{PB}(r,t)}{A_{PB}^{bulk}} \tag{1}$$

$$C_{PDMS}(r,t) = \frac{A_{PDMS}(r,t)}{A_{PDMS}^{bulk}} \tag{2}$$

being such areas proportional to weight fraction. The time evolutions of C_{PB} and C_{PDMS} at fixed distance (4 μm) from the droplet are shown in Figure 3. As expected, there is a progressive increase of C_{PB} with time while C_{PDMS} displays an opposite trend. As a check of data consistency, the sum $C_{tot} = C_{PB} +$

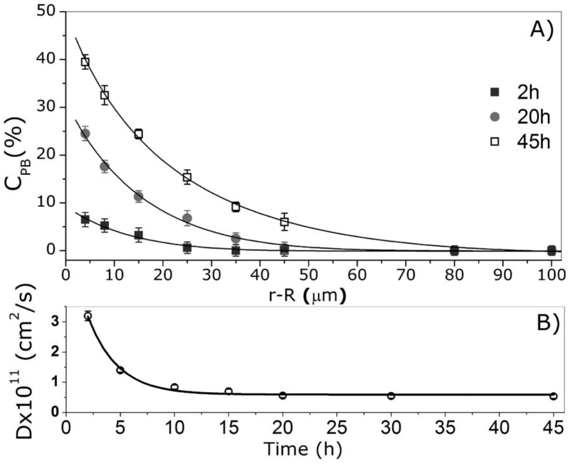

Figure 4. (A) Weight fraction of PB in PDMS at different times as a function of the distance from the drop surface (from 4 to 80 μm). For simplicity, only few experimental sets are reported. The fits with the model of eq 2 (solid lines) are also shown. (B) Plot of the diffusion coefficients, coming from the best-fit procedure, as a function of time for the PB/PDMS system. These values of D are well represented by an exponential decay fit, as shown by the solid line.

C_{PDMS} is also plotted in Figure 3 and is indeed constant with time.

To model this PB diffusion process in the continuous phase, we applied Fick's second law with a constant diffusion coefficient (D) in radial coordinates:

$$\frac{\partial C_{\mathrm{PB}}}{\partial t} = D\left[\frac{\partial^2 C_{\mathrm{PB}}}{\partial r^2} + \frac{2}{r}\frac{\partial C_{\mathrm{PB}}}{\partial r}\right] \tag{3}$$

with the boundary and initial conditions:

$$C_{\mathrm{PB}} = C_{\mathrm{S}} \text{ at } r = R \text{ and any } t \quad \text{and} \quad C_{\mathrm{PB}} = 0 \text{ at } t = 0 \text{ and } r > R \tag{4}$$

where C_{PB} is the relative PB weight fraction, C_{S} is the PB weight fraction at the droplet surface, and R is the droplet radius. The analytical solution of the diffusion eqs 1 and 2 assumes the form[14]

$$\frac{C_{\mathrm{PB}}(r,t)}{C_{\mathrm{S}}} = \frac{R}{r}\,\mathrm{erfc}\left[\frac{r-R}{2\sqrt{Dt}}\right] \tag{5}$$

Equation 5 contains only D as a material parameter, which should be considered as an apparent diffusion coefficient when applied to polymer blends where mass transport is molecular weight dependent. This model successfully describes the experimental data, as can be seen in Figure 3, where the solid line represents a fitting of the measured $C_{\mathrm{PB}}(t)$ values with eq 5, obtained by leaving C_{S} and D as free parameters. This fitting provides a diffusion coefficient of $D = (0.68 \pm 0.05) \times 10^{-11}$ cm^2/s. Similar diffusion coefficients values were obtained from the $C_{\mathrm{PB}}(t)$ fits at different distances from the droplet interface.

Further insight into the diffusion coefficient can be gained by analyzing the $C_{\mathrm{PB}}(r - R)$ profiles at different times. Figure 4A shows the progressive decreasing of $C_{\mathrm{PB}}(r - R)$ with penetration into the PDMS sample for some selected times (2, 20, and 45 h). A quantitative analysis of these trends can be again obtained by fitting the experimental data with the $C_{\mathrm{PB}}(r - R)$ expression of eq 5. The diffusion coefficients D, resulting from each fit, are presented in Figure 4B, where it is evident a decreasing of this parameter with the observation time, starting from $D = (3.19 \pm 0.16) \times 10^{-11}$ cm^2/s (at $t_1 = 2$ h) down to $D = (0.53 \pm 0.02) \times 10^{-11}$ cm^2/s (at $t_2 = 45$ h). This behavior suggests a PB diffusion process which is selective with respect to molecular weight. In fact, the higher is the molecular weight of PB polymer chains, the slower is their diffusion into the PDMS continuous phase. We have used a phenomenological exponential law given by

$$D(t) = (D_0 - D_\infty)\mathrm{e}^{-t/\tau} + D_\infty \tag{6}$$

to fit the data of Figure 4B. In eq 6 τ is a decay time, while D_0 and D_∞ represent the diffusion coefficients at the starting time ($t = 0$) and at the quasi steady-state regime (due to slowing down of the diffusion process with increasing molecular weight), respectively. From the fitting parameters ($\tau = 2.8 \pm 0.2h$, $D_0 = (4.0 \pm 0.5) \times 10^{-11}$ cm^2/s, and $D_\infty = (0.59 \pm 0.04) \times 10^{-11}$ cm^2/s) it is possible to calculate the time-average diffusion coefficient:

$$\langle D \rangle = \frac{1}{T}\int_0^T D(t)\,\mathrm{d}t \approx \frac{D_\infty T + (D_0 - D_\infty)\tau}{T} \tag{7}$$

where T is the observation time (~45 h in our experiment). From eq 7 we get $\langle D \rangle = (0.8 \pm 0.1) \times 10^{-11}$ cm^2/s, which is consistent with the diffusion coefficient $D = (0.68 \pm 0.05) \times 10^{-11}$ cm^2/s estimated from the $C_{\mathrm{PB}}(t)$ behavior of Figure 3, which takes into account the whole molecular weight distribution characterizing the polydispersed PB polymer.

In conclusion, we have applied Raman microscopy to study diffusion in a polymer blend by a droplet-based system. Data analysis by Fick's law shows that the diffusion coefficient at a given distance from the droplet surface is a decreasing function of time, in agreement with a molecular-weight-dependent selective diffusion process. In principle, this technique could be used to get information on the molecular weight distribution of the diffusing polymer provided that data pertaining its molecular configuration in the continuous phase are available.

Acknowledgment. G. Rusciano acknowledges CNISM (Consorzio Nazionale Interuniversitario per le Scienze Fisiche della Materia) for her research fellowship. S. Guido acknowledges COST action P21 "The physics of droplets". The authors thank Prof. G. Marrucci for the critical reading of the manuscript.

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MA800866M