Coupling between flow and diffusion at polymer/polymer interfaces: large amplitude oscillatory shear experiments

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Abstract Coupling between flow and diffusion at symmetric polymer/polymer interfaces has been investigated. Polystyrene/polystyrene sandwich assemblies were subjected to large-amplitude oscillatory shear (LAOS) using a sliding-plate rheometer (SPR) and the stress was monitored as a function of time. The results were treated using a new model combining Wagner’s model with the theory of Doi and Edwards. The model explicitly expresses the influence of the strain and stress amplitudes frequency and time on the self-diffusion process. The apparent self-diffusion coefficient was found to increase with welding time, in agreement with our previous results obtained using small-amplitude oscillatory shear measurements. However, it was found in the present case that the self-diffusion coefficient depends strongly on the strain and stress amplitudes and frequency, and its steady state value was found to be larger than that determined from small-amplitude oscillatory shear measurements. It appears that the large strain oscillatory shear field continuously increases the density of chain ends at the interface and thus increases the flux of mass transport.

Key words Diffusion · Interface · LAOS · Integral models

Introduction

In our previous work (Bousmina et al. 1998; Qiu and Bousmina 1999, 2000; Vaudreuil et al. 2000) we have shown that rheometry can be a useful tool for monitoring the diffusion process at polymer/polymer interfaces. In particular, we have shown that by measuring the complex shear modulus of a sandwich type assembly with time, it is possible to determine the diffusion coefficient at both symmetric and non-symmetric polymer/polymer interfaces. The conversion of the complex modulus to the diffusion coefficient was carried out using two new molecular models allowing for the determination of both self and mutual diffusion coefficients for symmetric and non-symmetric systems, respectively. The modeling was based on the reptation concept applied to particular problem of interfaces (de Gennes 1971; Doi and Edwards 1986). Our previous work also includes mechanical modeling based on fluxes across the interface (Vaudreuil et al. 2000). However, in our previous work we limited our treatment to small-amplitude oscillatory shear flow where the diffusion process affects the flow and its signature was reflected in the variation of the dynamic moduli of the sandwich type assembly with time, but the flow did not affect the dynamics of the chains during their excursion across the interface. This approach allowed us to establish only a semi-coupling between flow and the diffusion process.

In present paper we consider the full coupling between flow and diffusion by performing large amplitude oscillatory shear (LAOS) measurements using a sliding-plate rheometer (SPR) (Giacomin et al. 1989; Demarquette and Dealy 1992) developed at McGill University. In the present case, we have mutual effects: the diffusion affects the flow and conversely the flow affects the diffusion process.

Such experiments are conducted on a polystyrene/polystyrene sandwich type assembly and the measured self-diffusion coefficient is compared to that determined using small-amplitude oscillatory shear measurements.
and the results of the literature obtained by various authors under quiescent conditions using classical spectroscopic techniques.

**Experimental method**

The polystyrene used in this work is a commercial polymer, PS 667, obtained from Dow Chemical Inc. Its weight-average molecular weight and polydispersity index measured by GPC are $M_w = 352,900$ and $M_w/M_n = 1.63$. Its glass transition temperature is $100 \, ^\circ\text{C}$ as measured by DSC. Rectangular samples 150 mm in length, 30 mm in width and 0.5 mm in thickness were prepared for rheological testing by compression molding at 200 °C using well-cleaned and polished molds in order to ensure intimate contact at the interface. Granules of polystyrene were dried under vacuum for at least 48 h and were molded under fixed conditions in order to minimize sample-to-sample variation. Fifteen sandwich samples were used for relaxation experiments and were prepared by bringing two plaques with smooth surfaces into intimate contact and placing them in an oven under vacuum at 115 °C for various welding times before being sheared in the sliding-plate rheometer (SPR). This rheometer eliminates edge effects by use of a shear stress transducer and allows measurements at large deformation rates and total strains (Giacomin et al. 1989; Demarquette and Dealy 1992).

The samples for large-amplitude oscillatory shear measurements were also obtained by compression molding and then were annealed at 85 °C under vacuum for one week to eliminate eventual surface inhomogeneity and allow relaxation of the eventual oriented chains at the surface resulting from compression in the mold. First plaque was placed on the stationary plate, and the second plaque was mounted on the top of it and well aligned, as shown in Fig. 1. The plates were previously heated and maintained at a constant temperature of 115 °C. Sample loading must be fast and carefully executed to avoid a decrease of the plate temperature. A period of 30 min was allowed for thermal equilibrium after the loading of the samples before starting the deformation. The shear stress was measured as a function of time at a fixed frequency. The data were collected every 10 min for the first 2 h and every 1 h thereafter. For each frequency, the data were obtained on six different fresh samples and were reported on the same figure.

![Fig. 1 Sandwich sample set-up for rheological testing in sliding plate rheometer (SPR) under large amplitude oscillatory shear flow](image)

**Experimental results**

Figure 2 shows the shear stress vs time after a step strain for samples with various welding times. Two features can be noticed: (i) the sandwich samples with longer welding times relax more slowly than those with shorter welding times; (ii) the magnitude of the shear stress increases with welding time. This can be easily understood in terms of chain diffusion at the interface. As time passes, more and more chains cross the interface and penetrate the other side, creating entanglements and a dense network at the interphase. The initially sharp and weak interface disappears and it is gradually replaced by a stronger interphase. This result is in qualitative agreement with our previous work (Qiu and Bousmina 1999) where the elastic modulus of the multilayer samples was found to increase with welding time before reaching a steady state plateau.

Figures 3 and 4 are plots of shear stress amplitude vs welding time at frequencies of 0.01 and 1 Hz. The shear stress variation with time at a frequency of 0.01 Hz is qualitatively similar to that observed in the linear viscoelastic region (Qiu and Bousmina 1999, 2000). However, at the higher frequency of 1 Hz, the shear stress amplitude varies with time in a nearly linear fashion and increases with frequency at a given welding time.

To explain these data and to infer from them a diffusion coefficient that describes the chain dynamics we use the Wagner and tube model. The resulting

![Fig. 2 Shear stress relaxation vs time for samples obtained at different welding times](image)