NOTE

History Dependence of Diffusion Coefficients for Glassy Polymer–Penetrant Systems

Diffusion coefficients for glassy polymer–penetrant mixtures are usually regarded as being history-dependent since the diffusivity for a particular system depends on the thermal and concentration history of the system.[1-3] For example, the diffusion coefficient for a system composed of a small amount of penetrant in a glassy polymer depends both on the rate at which the polymer sample is cooled through the transition temperature range and on the extent of isothermal aging at some temperature T_1 below T_g, the glass transition temperature of the polymer. It is usually accepted that the diffusion process in the polymer depends on the free volume in the polymer–penetrant mixture,[1,4] so that an increase in free volume leads to an increase in the diffusion coefficient for the system. As a polymer sample is cooled from some temperature above T_g to some temperature T_1 below T_g, there is a smaller decrease in the polymer specific volume when the polymer is cooled at a faster rate. Hence, more free volume is effectively frozen into the polymer in the nonequilibrium glassy state if the polymer is rapidly quenched rather than cooled slowly. Consequently, for the binary mutual diffusion coefficient D, it follows that

$$D \text{ (rapid cooling)} > D \text{ (slow cooling)} \tag{1}$$

if isothermal aging effects at T_1 are of minor importance. Furthermore, after a polymer has been cooled to T_1, an isothermal aging process will take place at this temperature. Since the volume in the glassy polymer is greater than it would be in an equilibrium liquid state, both the volume and free volume of the polymer will continue to decrease slowly. Therefore,

$$D \text{ (short aging period)} > D \text{ (long aging period)} \tag{2}$$

if the polymer samples are prepared using identical cooling rates.

The objective of this short note is to present data for the polystyrene–methylene bromide system which illustrate the importance of cooling rate and isothermal aging on diffusion coefficients for glassy polymer–penetrant systems.

EXPERIMENTAL

Diffusivity data were collected for the polystyrene–methylene bromide system at 90°C using a step-change sorption experiment carried out on a high-temperature quartz spring sorption balance. The apparatus, experimental procedure, and data analysis are described in detail elsewhere.[5-7] Diffusion coefficients were evaluated at a methylene chloride mass fraction of 0.0055. Glassy polymer samples were prepared by cooling molten polystyrene from 130 to 90°C using two cooling rates: 1 and 10°C/h. After the glassy samples were prepared at 90°C, they were allowed to age isothermally either 16 or 90 h before the sorption experiment was initiated. The data were collected using a commercial polystyrene sample with a weight average molecular weight of 275,000.

RESULTS

The diffusivity data for the polystyrene-methylene chloride system are presented in Table I. Runs 1 and 3 show the effect of cooling rate on diffusivity under conditions where differences in the aging effects should be of secondary importance. The data from these two experiments are in agreement with the anticipated result given by eq. (1). Runs 1 and 2 show the effect of aging time

TABLE I

Diffusion Coefficients for Polystyrene–Methylene Bromide System at 90°C
and Penetrant Mass Fraction of 0.0055

Run no.	Cooling rate (°C/h)	Aging time (h)	$D \times 10^9$ (cm^2/s)
1	10	16	1.25
2	10	90	1.01
3	1	16	0.690

on diffusivity for samples prepared using identical cooling rates. Again, the data are in agreement with the expected result, eq. (2).

The data indicate that substantial differences in D can be caused by the utilization of different cooling rates to prepare glassy polymer samples. This result is similar to the type of results reported by McLoughlin and Tobolsky,[8] who studied the effect of cooling rate on stress relaxation in a glassy polymer. Furthermore, it is evident that significant differences in D are possible if different aging times are utilized for samples prepared using identical cooling rates. The aging effect reported here is similar to the aging data presented by Kapur and Rogers.[3] Clearly, the utilization of different thermal histories in the preparation of polymer samples can lead to significant differences in measured diffusion coefficients. The magnitudes of these differences will of course depend on what combinations of cooling rates and aging times are utilized. At temperatures sufficiently below T_g, aging effects will effectively disappear,[1] but the effect of cooling rate will, of course, still be important.

Consequently, when diffusion coefficients are reported for mixtures of penetrants and glassy polymers, it is important that the precise thermal history (both cooling rates and aging times) of the sample also be reported. Frequently, this is not done, and meaningful comparisons of diffusivity values in glassy polymer–penetrant systems are often not possible.

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