BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 22, pp. 4359–4360, 1995

0032-3861/95/$10.00+0.00

Solvent diffusion in poly(ether ether ketone)/poly(ether imide) blends

M. M. Browne, M. Forsyth and A. A. Goodwin*
Department of Materials Engineering, Monash University, Clayton, Vic. 3168, Australia

Solvent uptake in thin, amorphous samples of poly(ether ether ketone), poly(ether imide) and a 50/50 blend has been measured as a function of temperature. Diffusion coefficients, percentage weight increase and apparent activation energies have been calculated. The 50/50 blend shows anomalous diffusion behaviour which may be attributed to specific interactions between the homopolymers and density changes on blending.

(Keywords: poly(ether ether ketone); poly(ether imide); diffusion)

Introduction

High performance thermoplastics are competing against thermosets as matrix materials for composites in lightweight applications as well as against metals in demanding applications[1]. Thermoplastics offer advantages such as high fracture toughness and ease of processing, compared with thermosets. However, in applications which require exposure to corrosive liquids and vapours, the chemical resistance of thermoplastics is of importance. Poly(ether ether ketone) (PEEK) and poly(ether imide) (PEI) are both high performance thermoplastics which, when blended, form a system which is miscible over the whole composition range[2]. PEEK can be processed to a semicrystalline material and thus has excellent chemical resistance, although previous studies on amorphous and semicrystalline PEEK have shown that it absorbs, and is swollen by, a range of solvents which cause plasticization and solvent-induced crystallization[3]. PEI is an amorphous material and therefore has limited chemical resistance. In this work we report on solvent uptake in PEEK and PEI and compare this with solvent uptake in a 50/50 blend of the two polymers. This work is part of an ongoing study of structure/property relationships in miscible polymer blends.

Experimental

Materials. The PEEK used in this study was grade 381 G, supplied by ICI Australia, with $M_w = 73\,000$ and $M_n = 30\,600$ (manufacturer's data). The PEI was Ultem 1000 supplied by GE Plastics. The molecular weights are $M_w = 30\,000$ and $M_n = 12\,000$ (reference 4). A 50/50 blend, calculated as weight percentage, was processed using a Haake Rheocord single-screw extruder at 400°C. Pure PEEK and PEI were also extruded at 400°C and 300°C, respectively. The extruded materials were compression-moulded at 400°C (300°C for PEI) and then quenched into ice/water to form amorphous sheets with thicknesses ranging from 0.2 to 0.4 mm.

Solvent uptake. Rectangular samples, measuring 20 mm by 10 mm, were oven-dried at 90°C for 12 h, weighed, and then fully immersed in sealed jars containing acetone and placed in a controlled-temperature water bath. Samples were removed periodically, blotted dry and weighed on a top-pan balance with a resolution of 10 μg. Acetone was chosen as the diffusing solvent since weight changes during the weighing operation were negligible. Multiple experiments were carried out, until equilibrium was reached, at 25, 35 and 45°C.

Results and discussion

Fick's second law for one-dimensional diffusion relates the change in concentration as a function of time to the change in flux with respect to position, such that:

$$\partial c/\partial t = D\partial^2 c/\partial x^2 \tag{1}$$

where c is concentration, t is time, x is a point along the axis, and D is the diffusion coefficient. The solution of equation (1), for a plane sheet of thickness h, is given by:

$$W_t/W_e = (4D^{1/2}/\pi^{1/2}h)t^{1/2} \tag{2}$$

where W_t is the weight gain at time t and W_e is the equilibrium weight gain. Thus it can be seen that, for Fickian diffusion to occur, the weight gain should be linearly related to the square root of time. The diffusion coefficient can then be determined from the slope of a plot of W_t/W_e against $t^{1/2}$.

Figure 1 shown the weight uptake with $t^{1/2}$ for samples of PEEK, PEI and a 50/50 blend, at 25°C. Care was taken to ensure that the samples were of equal thickness as the slope of such plots has been shown to be dependent on sample thickness[5]. The curves exhibit marked upward curvature with only the initial slope being linear, and this region was used in the calculations of D. The upward curvature has been attributed to plasticization of PEEK by the ingressing solvent and a subsequent change in the mobility of the polymer molecules[5]. From *Figure 1* we can also see that the normalized weight uptake for the blend falls significantly below that of the homopolymers and that equilibrium is reached at longer times. With regard to

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*To whom correspondence should be addressed

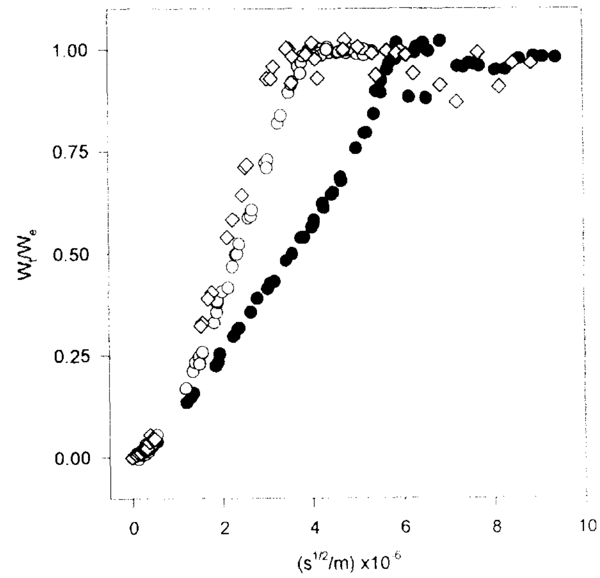

Figure 1 Normalized weight uptake at 25°C for PEI (◇), PEEK (O) and a 50/50 blend (●)

the homopolymers, the upward curvature for PEI is slightly greater than that for PEEK, although equilibrium is reached at approximately the same time. As equilibrium is approached, maxima in the weight uptake of acetone are observed. This has been observed in other polymer/solvent systems in which it arises as a consequence of solvent-induced crystallization[6]. As the crystals grow, excess solvent is expelled and desorbs from the polymer, reducing the equilibrium value of weight uptake. This effect is most apparent in systems in which rapid sorption of the solvent occurs relative to the crystallization rate. With regard to the materials studied here, this phenomenon requires further investigation.

Table 1 lists the calculated diffusion coefficients and weight increase at equilibrium for PEEK, PEI and the blend at 25, 35 and 45°C. At 25 and 35°C the diffusion coefficients for PEEK and PEI are identical, within experimental error, whereas at 45°C diffusion into PEEK is much more rapid. The diffusion coefficient for the blend is below that of both homopolymers at 25°C, but is similar to that of PEI at 45°C. The percentage weight increase for PEEK decreases slightly with increasing temperature and is in good agreement with a recent study of acetone diffusion in PEEK[6]. Both PEI and the blend absorb a greater percentage of acetone, compared with PEEK. Only at 45°C is the weight increase for the blend intermediate between that of the homopolymers. The temperature dependence of the diffusion coefficient was used, through an Arrhenius plot of log D against $1/T$, to calculate an apparent activation energy for diffusion. Values of approximately 135±35, 40±10 and 65±10 kJ/mol^{-1} were found for PEEK, PEI and the 50/50 blend, respectively. For linear additivity a value closer to 90 kJ mol^{-1} for the blend would be expected.

Table 1 Temperature dependence of the diffusion coefficient and weight increase for PEEK, PEI and 50/50 blend

Temperature (°C)	Sample	Diffusion coefficient (10^{15}ms$^{-1/2}$)	Weight increase (%)
25	PEEK	3.4±1.0	14.2±0.1
	50/50 blend	1.2±0.2	20.7±0.4
	PEI	2.4±0.6	18.8±0.4
35	PEEK	8.4±3.4	13.1±0.2
	50/50 blend	-	20.2±0.2
	PEI	5.2±0.6	17.6±0.4
45	PEEK	100±30	12.1±0.2
	50/50 blend	6.2±1.5	16.9±0.3
	PEI	6.8±0.5	19.4±0.4

Conclusions

The diffusion of acetone into the 50/50 blend of PEEK and PEI is anomalous in that values of both the diffusion coefficient and apparent activation energy are not intermediate between the homopolymers but show a negative deviation from linearity, whereas at 25 and 35°C the percentage weight increase exhibits a positive deviation. These trends may arise from changes in chain mobility in the blend due to the weak specific interactions between PEEK and PEI that are known to occur[4], or from density changes on blending, which would also affect the diffusion behaviour. These factors require further investigation and we are currently studying the morphology and relaxation behaviour of PEEK/PEI blends before and after exposure to solvent.

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