

Diffusion bonding between BPA polycarbonate and poly(butylene terephthalate)

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(Received 24 May 1989; revised 5 October 1989; accepted 5 October 1989)

The diffusion bonding of poly(butylene terephthalate) (PBT) to BPA polycarbonate (BPAPC) has been studied over the temperature range 100–230°C. The studies were carried out on laminates of the two polymers prepared by a novel spray application procedure. Variations in adhesive bond strength with temperature at fixed times and with time at fixed temperatures were determined by means of peel tests. Concurrently, TEM studies of interfacial cross sections were used to monitor the extent of diffusion. The results suggest that adhesion is strongly coupled to the level of solubility between the two resins and is independent of the rate or extent of diffusion once an equilibrium number of interfacial chains has been established. A phenomenological model is presented.

(Keywords: diffusion bonding; poly(butylene terephthalate); BPA polycarbonate)

INTRODUCTION

The adhesion between immiscible and partially miscible polymer pairs is a limiting parameter in various bonding and joining processes (e.g. vibration welding) as well as in the performance of many multiphase blends. In bonds produced at elevated temperatures, interdiffusion is believed to play a major role in building bond strength. The formation of a diffuse interface between dissimilar polymer pairs has been considered by a number of investigators. In the limiting case of zero miscibility, theoretical calculations suggest that partial segmental penetration may produce an interface having a thickness of the order of 50 Å¹. While interfacial regions of this size are difficult to verify experimentally², diffuse interfaces have been observed between polymers with very low levels of miscibility^{3–4}. When such interfaces are viewed in the microscope, they appear as thin bands in which there is a gradient in electron or optical density from one phase to the other. These bands increase in thickness with contact time before reaching a constant value which is dependent on the thermodynamic compatibility but is generally of the order of a few hundred or thousand angstroms⁵. Somewhat thicker interfacial layers of mixed spherulites have been observed in polypropylene/polyethylene laminates annealed at elevated temperatures and crystallized by slow cooling⁶. In fully miscible systems, the interface gradually disappears as complete interdiffusion takes place.

Independent studies of the development of adhesive bond strength between similar (auto-adhesion) and dissimilar polymers appear to be consistent with the development of an interfacial diffusion zone. Most of this work has been carried out on butt welds^{7,8} or lap shear joints^{9,10} of miscible polymers and shows that adhesion rises steadily with welding time. When the pairs are immiscible, significant bond strengths have been observed to develop quickly but adhesion does not improve further

with time¹⁰ as might be expected if the thickness of the diffusion zone reaches a plateau value.

The studies of diffusion bonding between PBT and BPAPC detailed below indicate that, for this partially miscible pair, the relationship between microscopic diffusion processes and macroscopic adhesion may be considerably more subtle than previously believed. The results have led to a new phenomenological model for adhesive bond formation in such systems in which solubility rather than the rate or extent of diffusion is the primary controlling parameter.

EXPERIMENTAL

The PBT and BPAPC used in this study were obtained in the form of commercial moulding resins (Valox 315 and Lexan 141) from the GE Plastics Division. The PBT was moulded into ASTM type D tensile bars on a 28 ton Engel injection moulding machine. The melt temperature was controlled at 250°C and the mould temperature at 55°C. No mould release was employed and the bars were carefully handled with nylon gloves. Examination of the surfaces of randomly selected samples using ESCA showed them to be free of contamination. The near surface crystallinities were determined by X-ray reflection using CuK_α radiation and found to lie in the range 20–25%. (The sampling depth for this technique is approximately 25–50 μm.) Previous analyses of injection moulded PBT parts suggest that their outermost surface crystallinities are, in fact, significantly lower than these values¹¹. The mobile, amorphous character of these surfaces is consistent with the rapid diffusion of PBT into BPAPC described below.

BPAPC/PBT laminates were prepared by spraying a 5% solution of BPAPC in methylene chloride onto the moulded PBT specimens using a small air brush. Using this procedure, uniform coatings approximately 75 μm in

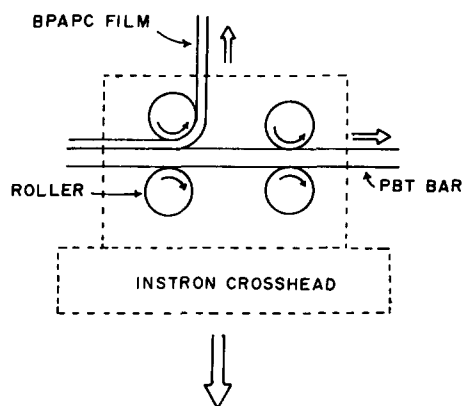


Figure 1 Schematic diagram of jig used for peel tests

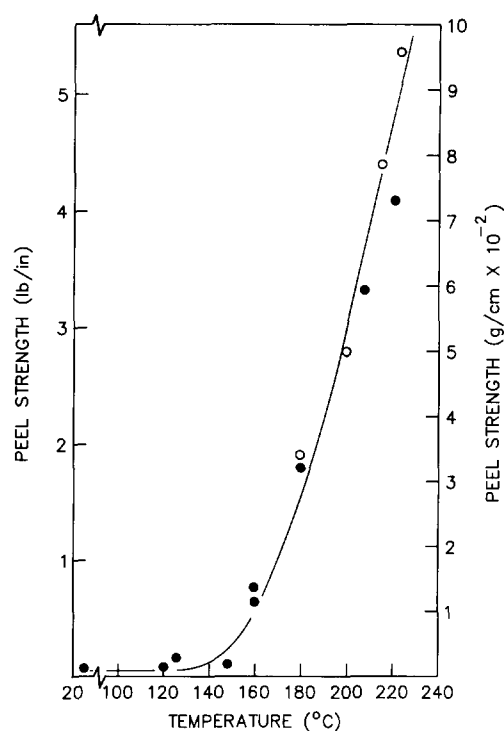


Figure 2 Variation in peel strength with temperature at constant time (10 min) for BPAPC films on PBT. Open circles are interpolated from the isothermal data presented in Figure 3

thickness were obtained in a spraying time of 2 min. Because of high volatility of the spray solvent, the residual concentration in the film was less than 0.1% and no solvent attack on the PBT surface was visible. Drying the laminates for 2 h at 90°C eliminated the last traces of solvent and produced samples having a clear, intact layer of BPAPC.

Annealing was carried out in a circulating hot air oven in which the temperature was controlled to $\pm 1^\circ\text{C}$. The annealed samples were air cooled to room temperature and scribed along their lengths with a razor blade into 5 mm wide strips. The ends of the strips were separated from the PBT substrates to allow attachment of small tabs and the samples were placed in an Instron testing machine equipped with a small jig (Figure 1) for peel strength measurements. The peel tests were carried out at a cross-head rate of 1 inch/min. Because considerable variation was observed in the load/elongation curves during the course of the peel, the reported peel strengths

were calculated by integrating the load traces over the gauge sections of the moulded bars.

Cross-sections of the annealed laminates were examined by transmission electron microscopy. Samples were microtomed at room temperature and stained with RuO_4 to enhance contrast between the PBT and BPAPC phases¹²⁻¹⁴. In the case of partially peeled samples, a thin layer of epoxy was infiltrated between the film and substrate prior to cutting to stabilize the crack tip during cutting. All observations were carried out on a Hitachi H 600 TEM operating at 100 kV.

RESULTS

The variation in peel strength with temperature at constant time (10 min) for the first series of laminates is shown in Figure 2. The unannealed laminates showed very low peel strengths ($< 17.9 \text{ g/cm}$; $< 0.1 \text{ lb/in}$). Low peel strengths continued to be observed up to the BPAPC T_g (150°C). Above this point the adhesion was observed to rise steadily until the highest annealing temperature (230°C) was reached and the BPAPC film could no longer be removed from the substrate ($> 1780 \text{ g/cm}$; $> 10 \text{ lb/in}$).

In a second series of tests, laminated samples were annealed at a series of temperatures for various times ranging from 5 to 40 min. The data are presented in Figure 3. In each case the bond strength was observed to rise rapidly and then become constant with time. The rise in the plateau adhesion values with temperature reproduced the results of the constant time experiments discussed above.

Examination of the PBT/BPAPC interfaces of the original laminates by TEM showed no indication of interdiffusion down to a resolution limit of 50 Å. In samples annealed at elevated temperatures, however, crystalline fibrils of PBT could be observed growing into the BPAPC. The fibrils were first observed at annealing temperatures above 205°C and annealing times in excess of 10 min. The length of the fibrils was found to increase steadily with annealing temperature at constant time and with annealing time at constant temperature. A typical series of micrographs taken of samples annealed at 216°C for 5, 10, 20 and 40 min is shown in Figure 4. Under isothermal conditions, the average fibril length was found to vary linearly with time^{1/2} as indicated by the plots in Figure 5. Such behaviour is expected for a diffusion controlled process.

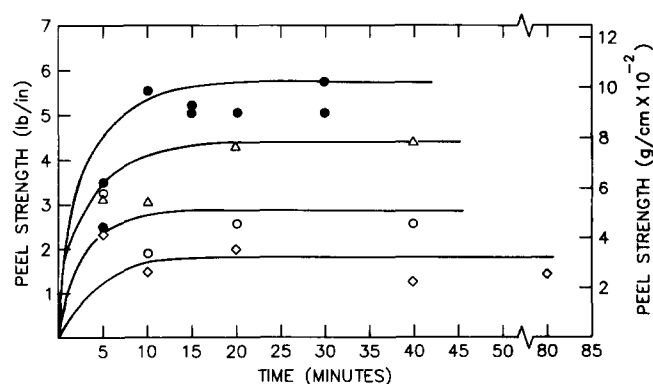


Figure 3 Variation in peel strength with time at fixed annealing temperatures for BPAPC films on PBT. \diamond , 180°C; \circ , 200°C; \triangle , 215°C; \bullet , 222°C

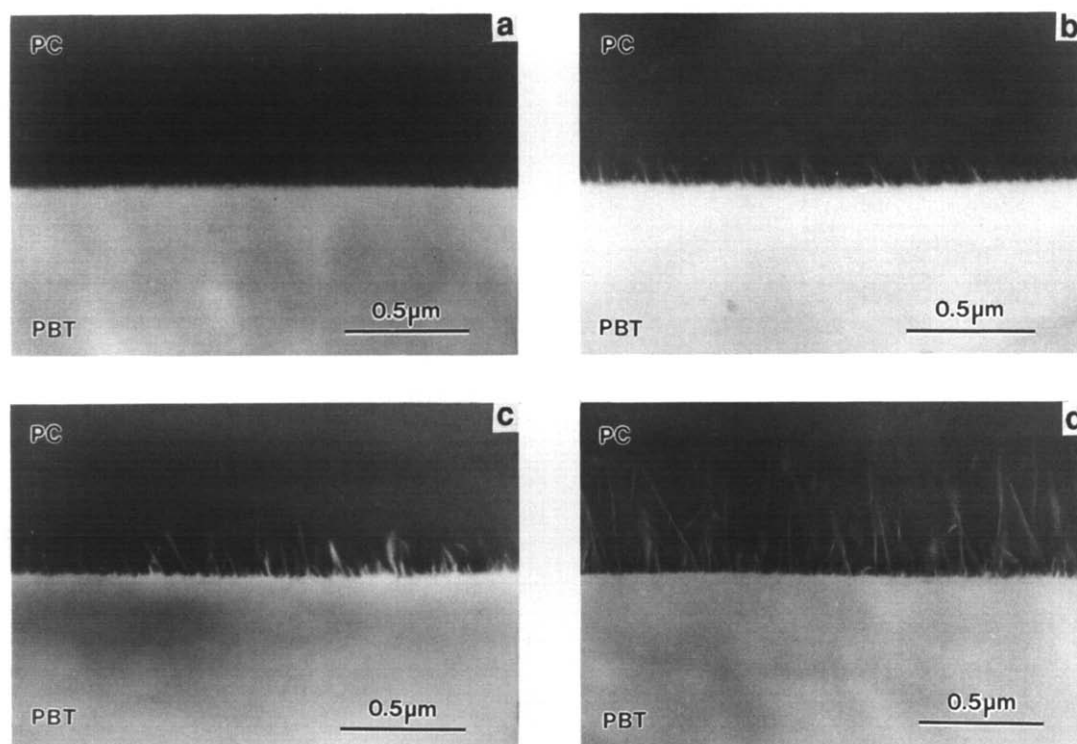


Figure 4 TEM photographs of PBT/BPAPC cross-sections stained with RuO_4 taken from samples annealed at 216°C for (a) 5 min; (b) 10 min; (c) 20 min; (d) 40 min. The steady growth of PBT fibrils into the BPAPC phase is evident

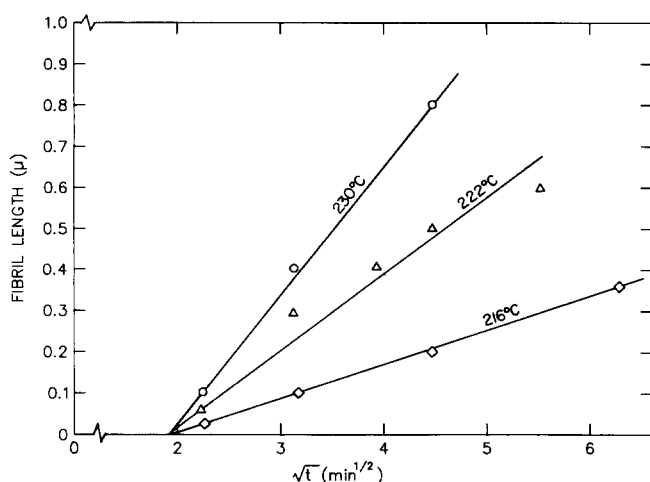


Figure 5 Variation in PBT fibril length with $t^{1/2}$ for samples annealed at (◇) 216°C , (△) 222°C , and (○) 230°C

The micrographs provided no indication of back diffusion of BPAPC into the PBT phase although some movement of this kind must occur. The large difference in the T_g values of the two resins (45°C vs. 150°C) suggests, however, that PBT is the faster moving species and that the diffusion process is dominated by the movement of these chains into BPAPC. This view is consistent with observations of the mutual diffusion of polystyrene ($T_g = 100^\circ\text{C}$) and poly(2,6-dimethyl-1,4-phenylene oxide) ($T_g = 215^\circ\text{C}$) in which the diffusion process is controlled by the movement of polystyrene¹⁵.

In order to determine if the fibrillar growth occurred in the course of annealing or developed as the samples were cooled, a series of samples was annealed at a fixed temperature and time (230°C , 10 min) and then quenched

at various rates. One sample was cooled in air at ambient temperature, a second was immersed in ice water (0°C), and a third was immersed in a mixture of dry ice and ethanol (-78.5°C). Micrographs of the three samples are shown in Figure 6. The steady decrease in fibril length and density at the higher quench rates provides strong evidence that they form as a result of crystallization and phase separation of PBT from the BPAPC during cooling. This process has been documented previously for PBT/BPAPC melt blends¹²⁻¹⁴. The persistence of these growths even at very high cooling rates demonstrates that the process occurs extremely rapidly.

DISCUSSION

The foregoing experiments provide convincing evidence that PBT fibril growth occurs as the result of crystallization of PBT chains which have diffused into the BPAPC film upon annealing. The fibrils appear to be nucleated at the interface and grow into the BPAPC phase in a manner that is consistent with the concentration gradient that is expected to form during this process. The linear variation in fibril length with $t^{1/2}$ suggests that the maximum extent of fibril growth mirrors the extent of diffusion although PBT crystallization is expected to terminate at some limiting concentration, c^* , greater than zero. If c^* is constant at a given temperature, it can be shown that a $t^{1/2}$ dependence is preserved using Crank's analysis of diffusion in composite media¹⁶. For the situation where the diffusion constant in one region is D_1 and that in an adjacent region is D_2 , the concentration of the diffusing species in region 2 as a function of the distance (x) and time (t) is given as:

$$c(x, t) = c_\infty \operatorname{erfc} \left(\frac{x}{2(D_2 t)^{1/2}} \right) \quad (1)$$

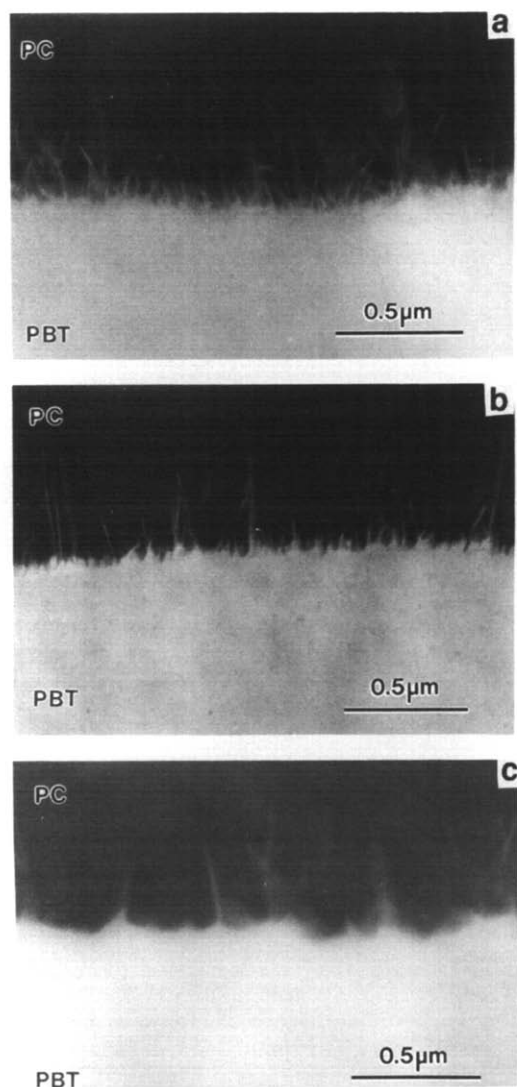


Figure 6 TEM photographs of PBT/BPAPC cross-sections stained with RuO₄ taken from samples annealed for 10 min at 230°C and cooled in (a) air; (b) ice water; and (c) ethanol/dry ice

where

$$c_{\infty} = \frac{k}{1 + k(D_2/D_1)^{1/2}}$$

and

$$k = c_2/c_1$$

Here c_1 and D_1 and c_2 and D_2 are the limiting equilibrium concentrations and diffusion coefficients of PBT in the PBT-rich and BPAPC-rich phases, respectively. Substituting the threshold concentration for fibril growth, c^* , into equation (1)

$$\frac{c^*}{c_{\infty}} = \operatorname{erfc}\left(\frac{S}{2(D_2t)^{1/2}}\right) \quad (2)$$

where S is the maximum fibril length at c^* . Rewriting

$$\frac{S}{2(D_2t)^{1/2}} = \operatorname{erfc}^{-1}\left(\frac{c^*}{c_{\infty}}\right)$$

or

$$S = \underbrace{2\operatorname{erfc}^{-1}\left(\frac{c^*}{c_{\infty}}\right)}_n D_2^{1/2} t^{1/2} \quad (3)$$

Thus the maximum extent of fibril growth is expected to be linear with $t^{1/2}$. Equation (3) shows that the maximum fibril length depends on $D_2^{1/2}$, $t^{1/2}$, and n so that a simple evaluation of D_2 is precluded from the present study. Values for n^2D_2 obtained from the data in Figure 5 are listed in Table 1. Comparison of these numbers with diffusion coefficients measured for other polymers⁵ shows that they are somewhat low as expected from the foregoing analysis.

Having established that a PBT diffusion zone forms in BPAPC and continues to advance with time at constant temperature and temperature at constant time, it is unexpected that the interfacial adhesion rises with temperature under isochronal conditions but becomes constant with time under isothermal conditions. The behaviour is best explained in terms of the partial miscibility of the two resins. Since the more mobile phase (PBT) is the primary diffusant, it is useful to model the process in terms of PBT chains moving into a BPAPC continuum.

At the start of the isothermal annealing experiment, PBT molecules begin to migrate across the phase boundary. The number of chains which can be accommodated in the BPAPC layer adjacent to the interface is limited by the solubility of PBT in BPAPC. From earlier studies of melt blends prepared at higher temperatures, it is estimated that this fraction is ~10% by weight¹⁷. Those chains which become entangled in both phases produce the observed initial rise in adhesion. With time, the first PBT chains move deeper into the BPAPC following Fickian kinetics and are replaced by new chains moving across the interface. Because the solubility constraints must still be satisfied, however, the concentration of PBT chains in the growing diffusion zone, and, more particularly, those extending across the interface, does not increase appreciably. Because it is these chains which control adhesion, the bond strength necessarily becomes constant with time. When the temperature is raised, the solubility of PBT in BPAPC rises, the number of interfacial chains increases, and the adhesion climbs to a new plateau value. This process is shown schematically in Figure 7.

The most significant feature of this model is the fact that essentially all of the bond strength is established during the first stages of diffusion and that the level of adhesion is fixed at a given temperature by the number of chains traversing the interface once this initial diffusion has occurred. This number is controlled only by the local solubility and not by the diffusion kinetics or the size of the diffusion zone. TEM studies of cross-sections cut from partially peeled samples support this hypothesis. In samples showing both large and small diffusion zones, the debonding line is coincident with the original interface and the PBT fibrils remain embedded in the BPAPC film (see Figure 8).

The model is also consistent with the mathematical treatment of the diffusion process given above. The

Table 1 Calculated n^2D_2 for PBT in BPAPC

Temperature (°C)	n^2D_2 (cm ² /s)
216	3.0×10^{-13}
222	1.3×10^{-12}
230	4.1×10^{-12}

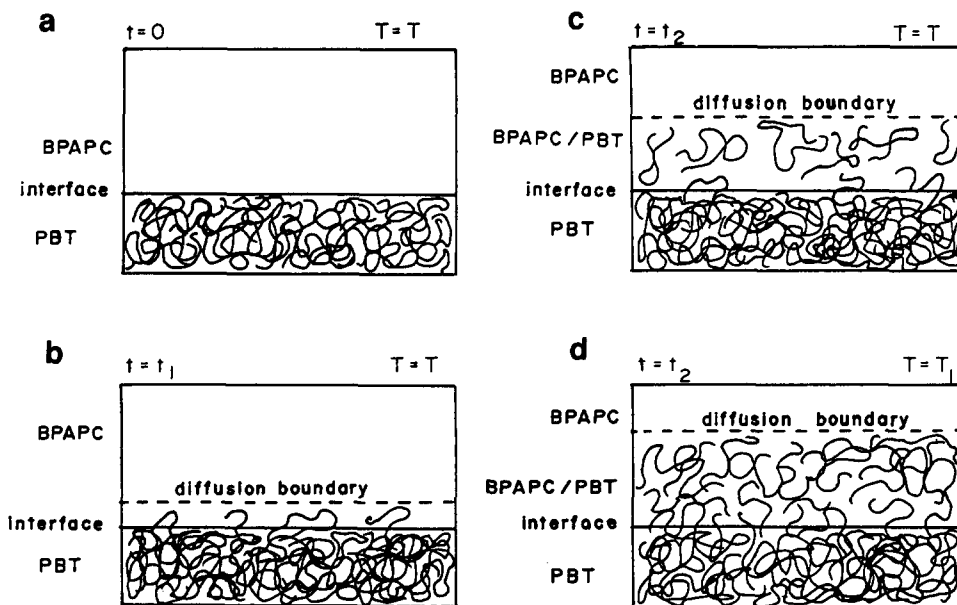


Figure 7 Schematic diagram showing primary features of PBT/BPAPC thermal bonding: (a) At time zero ($t=0$) no diffusion has taken place. (b) At time t_1 interfacial migration of PBT has occurred producing adhesion. (c) At time $t_2 (>t_1)$ a diffusion zone is formed but the number of 'interfacial' chains remains constant. (d) At time t_2 and temperature $T_1 (>T)$, the number of 'interfacial' chains has increased producing higher adhesion than in case (c)

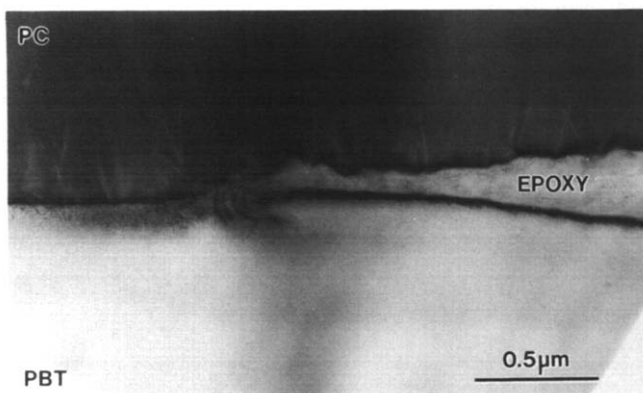


Figure 8 TEM photograph of crack tip cross section from partially peeled PBT/BPAPC laminate showing the fracture running along the original interface and the crystalline PBT fibrils embedded in the BPAPC/PBT diffusion zone. The crack tip was infiltrated with epoxy and the sample was stained with RuO₄

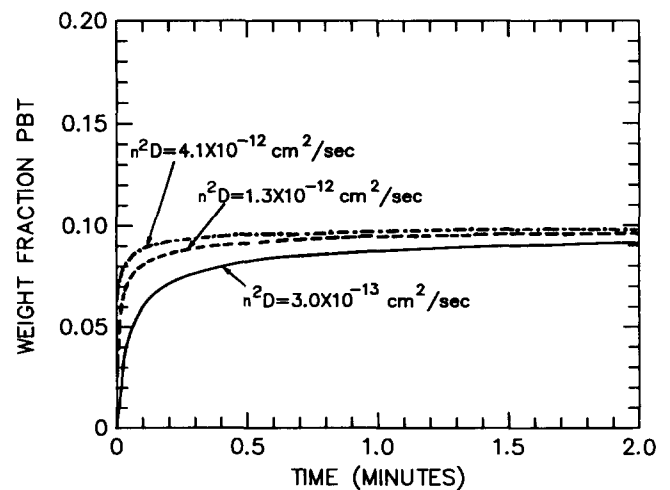


Figure 9 Plot showing the PBT concentration in the BPAPC/PBT mixed phase 100 Å from the interface as a function of time. The profiles were calculated using equation (1) and the values in Table 1

time-dependent concentration profile for PBT in BPAPC adjacent to the interface can be calculated for various values of n^2D_2 using the values in Table 1. The results at a distance of 100 Å are shown in Figure 9 for the case in which the equilibrium solubility of PBT in BPAPC is 10% by weight. The distance was chosen to approximate a typical radius of gyration since chains within this zone have a reasonable probability of being entangled in both phases. The concentration is seen to rise rapidly in the first minute and then to remain almost constant with time as predicted by the model. The calculated rise is sharper than that observed experimentally (Figure 3). This discrepancy is thought to arise from time required for the experimental samples to reach thermal equilibrium. The thermal lag time may be estimated from the diffusion curves in Figure 5 which extrapolate to a 'zero' time of 3.6 min. Thus the data in Figure 3 should correctly be displaced to the left by this time lag producing a rise in

adhesion with time whose shape very closely mirrors that calculated using equation (3).

CONCLUSIONS

The current studies provide a number of new insights into the thermal bonding of PBT and BPAPC. Bonds are produced only above the glass transition temperature of both resins. Adhesion rises primarily as the result of the migration of amorphous PBT chains into the BPAPC to produce tie molecules spanning the interface. The level of adhesion is dictated by the number of chains participating in this process and is governed by the solubility of PBT in BPAPC at a given temperature. Thus the adhesion rises with temperature but rapidly reaches a constant value with time at a given temperature. The

shape of the isothermal adhesion/time curves is well approximated by a simple diffusion calculation of PBT chain concentrations in the BPAPC phase adjacent to the interface.

During both isochronal and isothermal experiments PBT continues to diffuse into BPAPC although after the initial penetration the size of the diffusion zone is unrelated to the bond strength. Recrystallization of PBT from the diffusion zone during cooling provides a convenient morphological 'tag' for following the diffusion process. It seems likely that the maximum fibril length parallels but lags behind the diffusion front because crystallization terminates below some critical concentration c^* . It can be shown that the observed variation in fibril length with $t^{1/2}$ is expected under such conditions.

Comparison of our results with published data which also show that the adhesion between immiscible polymers remains constant with time at a fixed temperature¹⁰ suggests that the model which has been advanced in this work may apply broadly in partially miscible systems. When miscibility rises to the point where a homogeneous concentration gradient is established in the interfacial region, it is expected that the size of the diffusion zone may become a more important determinant of bond strength.

ACKNOWLEDGEMENTS

The authors are indebted to J. Caraher for moulding the

tensile bars used in this study, and to M. Garbaskas for X-ray crystallinity measurements.

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