

Interdiffusion in Microlayered Polymer Composites of Polycarbonate and a Copolyester

G. POLLOCK, S. NAZARENKO, A. HILTNER,* and E. BAER

Department of Macromolecular Science and Center for Applied Polymer Research,
Case Western Reserve University, Cleveland, Ohio 44106

SYNOPSIS

The interdiffusion of two miscible polymers, polycarbonate (PC) and a copolyester (KODAR), was studied at temperatures from 200 to 230°C. The two polymers were coextruded as microlayer composites with up to 3713 alternating layers. The microlayer structure provided a large area of intimate contact between the two polymers with minimal mixing. Initially, two glass transition temperatures were observed by DSC that were intermediate between the glass transition temperatures of the pure components. Upon annealing, the glass transition temperatures shifted closer together, reflecting the extent to which interdiffusion had occurred. After no more than 2 h of annealing, a single glass transition temperature was observed. A model was formulated based on Fick's law of diffusion that related the mutual diffusion coefficient, D , to the change in the glass transition temperatures. The model also incorporated an "equivalent" residence time to account for diffusion that occurred during the coextrusion process. It was not necessary to consider the concentration dependence of D to satisfactorily describe the data with this model. For the temperature range from 200 to 230°C, the value of D varied from 4.0×10^{-16} to 1.6×10^{-15} m²/s. The activation energy of interdiffusion was determined to be 95 kJ/mol. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Microlayer composite structures composed of as many as a few thousand layers can be continuously processed with the microlayer coextrusion technology developed by Schrenk and Alfrey.^{1,2} By manipulating the number of layers in the composites, the resulting layer thicknesses can be varied without changing the overall composition. When poly(styrene-co-acrylonitrile), a brittle thermoplastic, is layered with polycarbonate, a ductile thermoplastic, synergistic effects on the mechanical properties are observed as the layer thicknesses are decreased.³⁻⁵ Nanolayered composites of high-density polyethylene and polystyrene have been studied where the polyethylene layer was on the scale of molecular dimensions. The polyethylene lamellae

were observed to display a row nucleated morphology in the extrusion direction.⁶ The coextrusion process requires stringent laminar flow conditions and short processing times. As a result, two miscible polymers can be brought into intimate contact with minimal mixing. This offers a unique opportunity to study the interdiffusion of a miscible polymer pair.

Interdiffusion describes the movement of distinguishable polymer species across an interface or gradient formed by placing the two materials in intimate contact. This process is defined by Fick's law, which relates the flux of species i to the gradient in the concentration of species i . The mutual diffusion coefficient, D , describes the rate of disappearance of the concentration gradient at the interface; it includes both thermodynamic and kinetic factors and is dependent on the composition of the system. Typical diffusivities for polymeric systems are in the range of 10^{-16} to 10^{-10} m²/s.⁷

An unusual opportunity to observe interdiffusion in a bulk material is made possible with the microlayered structures produced by The Dow Chemical

* To whom correspondence should be addressed.

Co.'s coextrusion process. Mixing of two miscible polymers during processing is minimized by the laminar flow conditions, whereas the interfacial area is maximized by making the layers very thin. Because interfacial areas of 1.0 m²/g or higher are achievable, diffusion can be followed by the straightforward technique of DSC and is completed within a reasonable time period. In this study, the glass transition temperatures were obtained by DSC as a function of the annealing time and temperature. Subsequently, the glass transition temperature was directly related to the concentration profile in each layer, which changed as interdiffusion proceeded. This approach was qualitatively described by Keskkula and Paul⁸; the purpose of this work was to quantify their approach.

EXPERIMENTAL

Microlayer composites composed of alternating layers of polycarbonate (PC) and a copolyester (KODAR) were supplied by The Dow Chemical Co. The sheet thickness was about 2.4 mm and the PC was always the outermost layer. The PC was Calibre (trademark, Dow) 22 with a molecular weight of about 30,000. The copolyester was KODAR (trademark, Eastman Kodak Co.) 5445, a copolymer of mainly 1,4-cyclohexane dimethanol and terephthalic acid with a molecular weight of about 50,000. The glass transition temperatures of the PC and the KODAR were 150 and 82°C, respectively, and the KODAR exhibited a melting temperature of 235°C.

Six microlayer samples, PC/KODAR 60/40 (wt/wt) with 657, 1313, 1857, and 3713 layers and 40/60 (wt/wt) with 657 and 1313 layers, were used in this study. The reported compositions were determined from the extruder feed ratios. Sheets of the melt-blended materials, which were prepared in the same process as were the composites, were also supplied in the following compositions: PC/KODAR 0/100, 20/80, 40/60, 60/40, and 100/0 (wt/wt). All samples were dried under vacuum at 75°C for 48 h and stored in a desiccator. The density of the homopolymers and the melt blends was determined according to ASTM 2320.

The transmission optical microscope was used to confirm the number of layers present in the composites and to determine the PC and KODAR layer thicknesses. Sections 0.5 microns thick were microtomed with the RMC MT 6000-XL ultramicrotome and observed under polarized light.

Thermal characterization was performed with the Perkin-Elmer DSC 7 with a dry nitrogen purge. The

temperature was calibrated with two standards, indium and zinc. Specimens weighing about 10 mg were placed in the specimen pans with the layers oriented vertically. The microlayer specimens were heated at a rate of 40°C/min to the annealing temperature and isothermally annealed in the DSC for the appropriate time. After annealing, the specimens were quenched and subsequently scanned at a rate of 10°C/min from 30 to 275°C.

RESULTS

Melt Blends

The density of the melt blends of PC and KODAR is plotted as a function of the PC weight fraction in Figure 1. The densities were additive over the entire composition range, which indicated that any specific interactions between the PC and the KODAR were not strong enough to be manifest as a deviation from additivity. Specific interactions would have resulted in a decrease in the volume.

The glass transition temperature of the melt blends of PC and KODAR is plotted as a function of the PC weight fraction in Figure 2. These blends exhibited a single glass transition temperature intermediate between the pure component glass transitions. The composition dependence of the melt-blend glass transition is best described by the empirical Fox equation:

$$\frac{1}{T_g} = \frac{W_{PC}}{T_{g,PC}^{\circ}} + \frac{(1 - W_{PC})}{T_{g,K}^{\circ}} \quad (1)$$

where W_{PC} is the weight fraction of polycarbonate and $T_{g,PC}^{\circ}$ and $T_{g,K}^{\circ}$ are the homopolymer glass transition temperatures of the PC and KODAR, respectively. In strongly interacting systems, the glass transition temperatures are observed to display a marked deviation from conventional behavior as predicted by either the Fox equation or the Wood equation.⁹ The composition dependence of both density and glass transition temperature is consistent with a weakly interacting system.

Microlayer Composites

The microlayer composites contained weld lines about 7 microns thick, which resulted from layer multiplication during the coextrusion process. The 657- and 1857-layered composites had 7 weld lines, and the 1313- and 3713-layered composites, 15 weld lines. Away from the weld lines, the layers were very

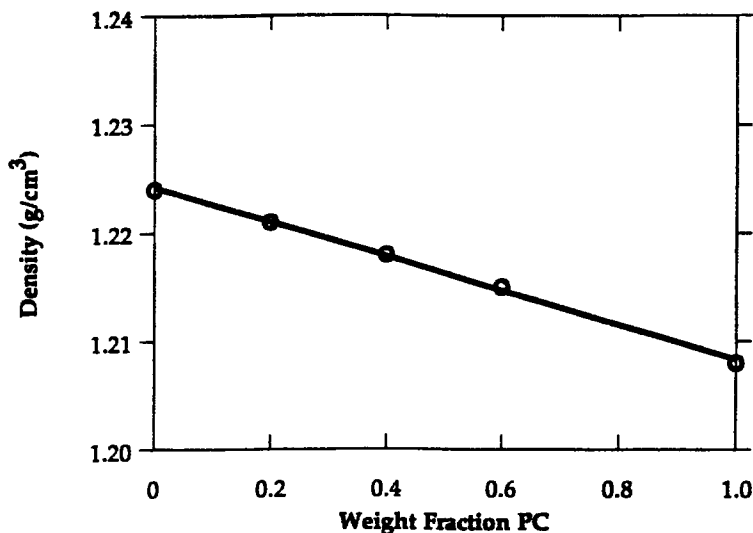


Figure 1 Density of PC/KODAR melt blends as a function of PC weight fraction.

uniform in thickness as shown by the optical micrograph of the PC/KODAR 60/40 (wt/wt) composite viewed under polarized light in Figure 3. The light-colored layers were KODAR, and the dark layers, PC. The layer thicknesses of the PC and KODAR in this composite determined from optical micrographs were 3.1 ± 0.3 and 2.2 ± 0.4 microns, respectively, as shown in Table I. The large standard deviation arose from variations in the thickness of layers close to the weld lines. This affected less than 10% of the material; uniformity in most of the layers was within 0.1 micron. The layer thicknesses were

also calculated from the composition, obtained from the extruder feed ratios, and the number of layers. The calculated values were in good agreement with the layer thicknesses determined from direct observation in the optical microscope as shown by the comparison in Table I. Values of layer thickness obtained by direct observation were used in the analysis.

A series of thermograms of the glass transition region, 70 to 160°C, in Figure 4 shows the effect of annealing the PC/KODAR 60/40 (wt/wt) composite with 657 layers at 200°C. When the heat flow

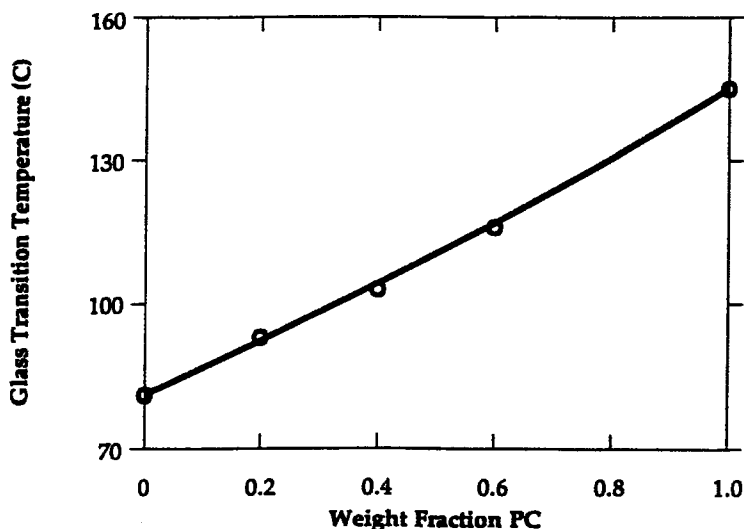


Figure 2 Glass transition temperature of PC/KODAR melt blends as a function of PC weight fraction. The solid line was calculated from eq. (1).

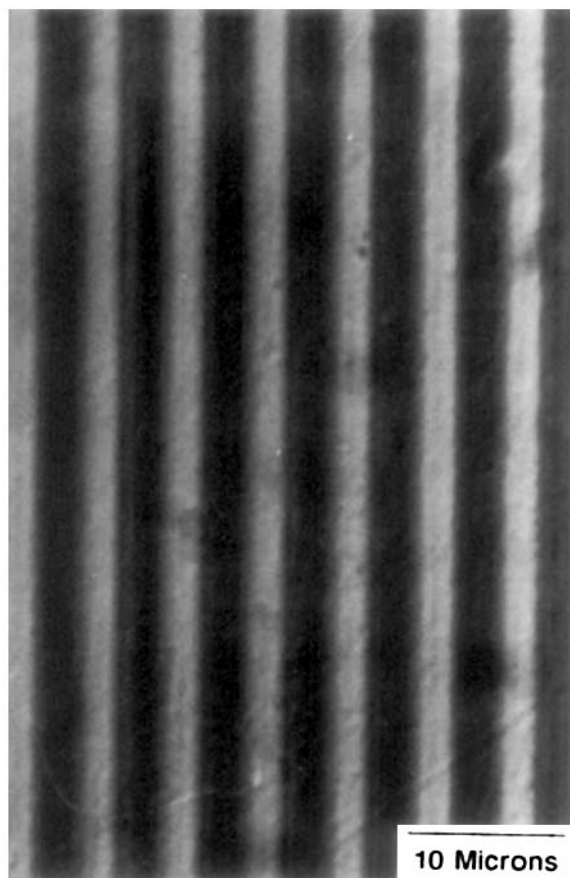


Figure 3 Optical micrograph of the PC/KODAR 60/40 composite with 657 layers.

was plotted vs. temperature, the glass transition appeared as a step change in the specific heat capacity. On either side of the glass transition, the thermal response was characterized by a linear base line. The glass transition temperature was defined as the point half-way between the two linear base lines. The breadth of the transition was taken as the temperature interval defined by the intersection of the base

lines with the tangent to the curve at the glass transition temperature, as shown in Figure 5. The transition breadths are indicated in the figures by vertical bars. Upon annealing at 200°C, the glass transitions broadened and shifted toward one another. After 1 h of annealing, a single, broad glass transition was observed that sharpened upon further annealing. After 4 h of annealing at 200°C, a single, sharp glass transition was observed at the same temperature as the glass transition of the melt blend of that composition. After annealing 48 h, the single, sharp glass transition had increased by 3°C.

The glass transitions of the PC/KODAR 60/40 composite with 657 layers are plotted as a function of the annealing time in Figure 6. The initial glass transition temperatures of the composite and the glass transition temperatures of the pure components and the melt blend are included for comparison. Before annealing, the composite exhibited two glass transitions but these were intermediate between the transition temperatures of the pure components, which suggested that some degree of interdiffusion had occurred during the coextrusion process. Upon annealing, the glass transitions simultaneously broadened and shifted closer together, until after 1 h of annealing, a single broad transition was observed. Further annealing for 4 h served to sharpen the single transition with no change in temperature.

It is known that KODAR crystallizes slowly at elevated temperatures. Since crystallization would have affected the diffusion process, thermograms were always taken to a temperature well above the 220 to 240°C range where KODAR melts. No crystallinity was detectable by DSC in the starting microlayer material, nor was a KODAR melting peak observed in the annealed materials until the annealing time reached 6 h. Since only 4 h of annealing at 200°C was sufficient to produce a single glass transition in the composite, it was concluded that

Table I Microlayer Composite Layer Thicknesses

PC/K (Wt/Wt)	No. Layers	Layer Thickness Calculated		Layer Thickness Measured	
		L_{PC} (μm)	L_K (μm)	L_{PC} (μm)	L_K (μm)
60/40	657	3.7	2.6	3.1	2.2
	1313	1.9	1.3	1.7	1.2
	1857	1.4	0.9	1.3	0.9
	3713	0.9	0.6	1.1	0.8
40/60	657	2.9	3.8	2.6	3.3
	1313	1.2	2.0	1.0	1.6

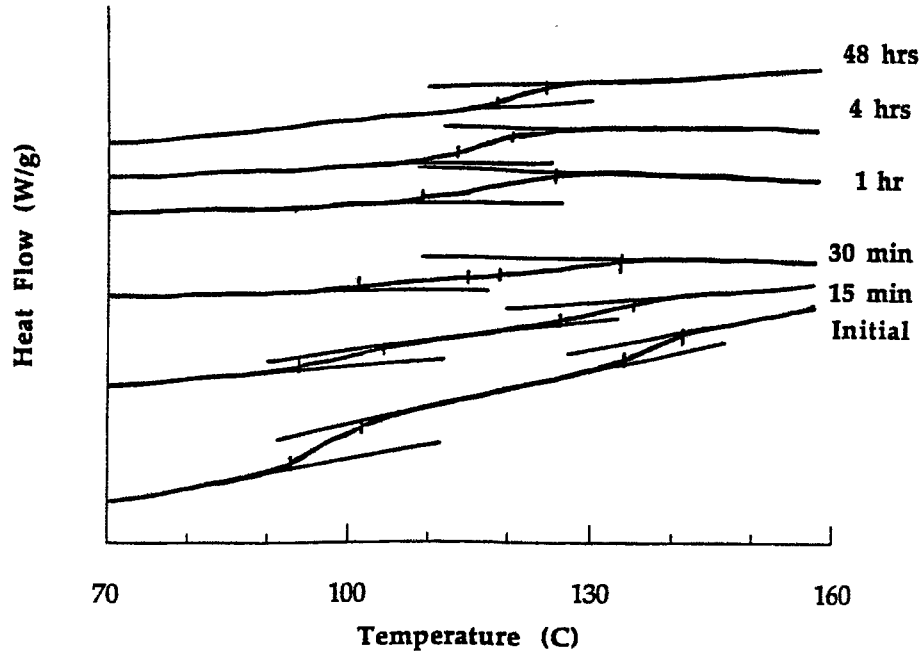


Figure 4 A series of DSC thermograms of the glass transition region for the PC/KODAR 60/40 composite with 657 layers annealed at 200°C.

interdiffusion was much faster than crystallization at this temperature. Thus, mixing of the two components was complete before crystallization began, with the result that any subsequent crystallization occurred from the homogeneous blend. Some crystallization after 6 h of annealing accounted for the slight increase in the glass transition temperature between 4 and 48 h of annealing since crystallization of KODAR caused the amorphous phase to become richer in PC.

DISCUSSION

Derivation of the Diffusion Model

The change in the composition profile through the microlayer composite as the composite is annealed is illustrated schematically in Figure 7. Ideally, the coextrusion process imparts a sharp boundary between the layers with no intermixing. When the composite is heated above the glass transition tem-

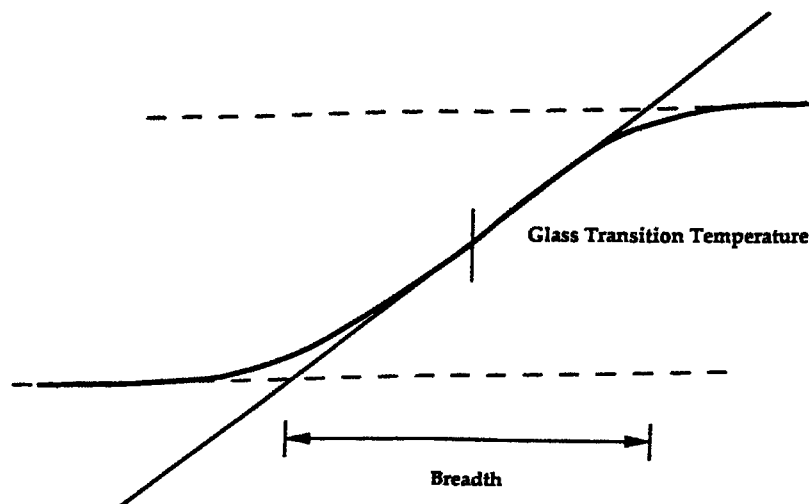


Figure 5 Schematic diagram of the DSC glass transition with the transition temperature and transition breadth defined.

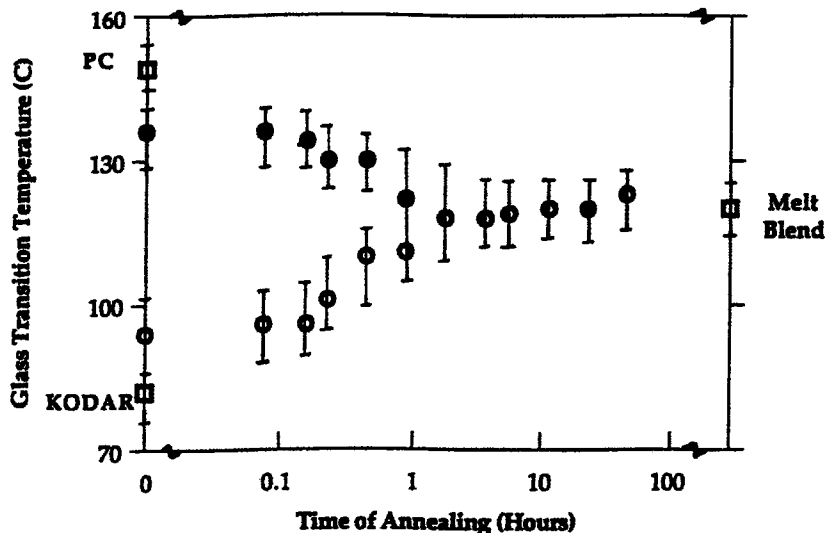


Figure 6 The glass transition temperatures and breadths of the PC/KODAR 60/40 composite with 657 layers as a function of the annealing time at 200°C.

peratures of both components, the polymers have sufficient mobility for interdiffusion to occur. The extent of interdiffusion depends upon the magnitude of the mutual diffusion coefficient and the annealing time. The composition profile changes as diffusion proceeds until, at some time that depends on the thickness of the layers, a constant composition is achieved.

To analyze the interdiffusion process, an interdiffusion element is defined as one-half of a PC layer

together with one-half of the adjacent KODAR layer and the interface. Only one-half of each layer is required due to the symmetry of the microlayered structure. The situation is equivalent to a diffusion couple of finite thickness.¹⁰ The uniformity of the layers ensures that the interdiffusion element is representative of the entire microlayer structure, whereas the large number of layers in the composites allows end effects to be neglected.

Several assumptions were introduced to simplify

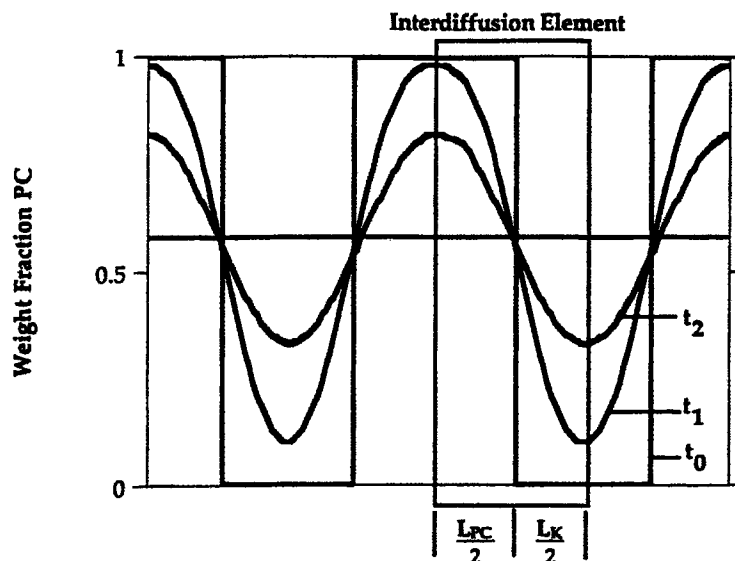


Figure 7 Schematic diagram of the change in the composition profile during annealing. The interdiffusion element is defined as one-half of a PC layer together with one-half of the adjacent KODAR layer and the interface.

the analysis. The mutual diffusion coefficient D for this polymer pair is assumed to be constant, i.e., independent of composition, and a function of temperature only. Furthermore, the position of the interface between the diffusing species is assumed to be fixed. These assumptions are equivalent to the case of a weakly interacting polymer pair, $\chi \cong 0$. Furthermore, these assumptions imply that the polymers have similar degrees of polymerization within the short chain limit, $N_A \cong N_B < N_e$, where N_e is the number of segments between entanglements, and have equivalent chain segment mobilities.¹¹

The concentration profile is obtained from Fick's equation for the case of one dimensional, nonsteady-state diffusion:

$$\frac{\partial W_i}{\partial t} = D \frac{\partial^2 W_i}{\partial x^2} \quad (2)$$

where W_i is the weight fraction of species i ; t , time; x , position; and D , the mutual diffusion coefficient. The initial conditions for an interdiffusion element with a sharp interface are

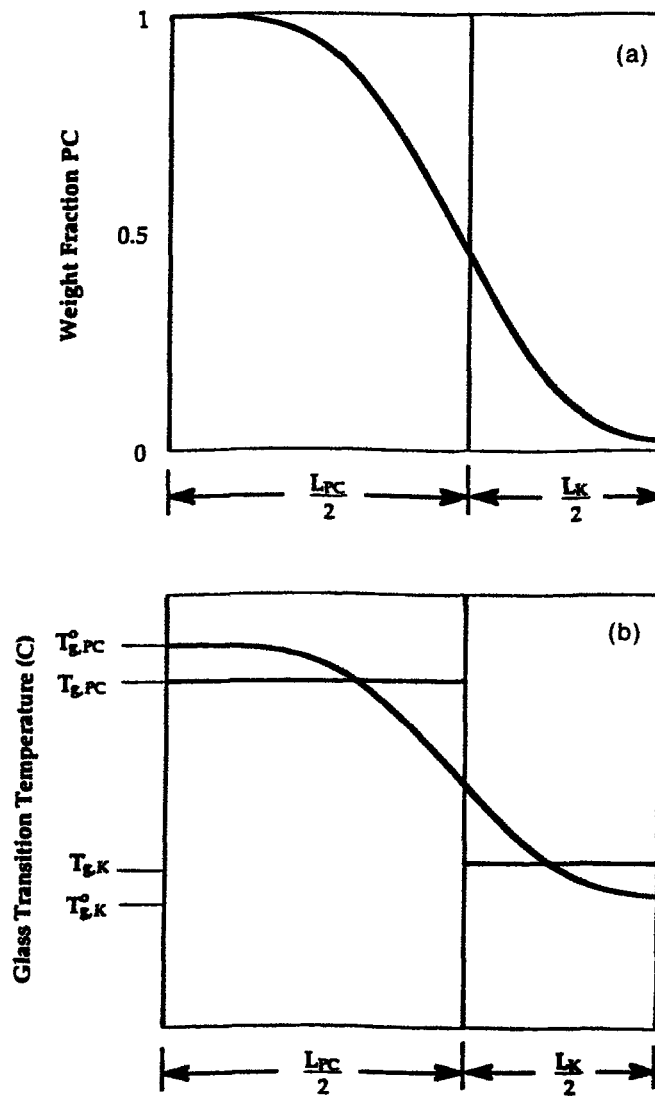


Figure 8 (a) The composition profile through the interdiffusion element calculated from eq. (5) for the PC/KODAR 60/40 composite with 657 layers using arbitrary values of D and t . (b) The corresponding variation in the glass transition temperature calculated from eq. (6) with the average glass transition temperature calculated for each layer.

$$W_{PC} = 1 \quad \text{for} \quad 0 \leq x \leq \frac{L_{PC}}{2} \quad (3a)$$

$$W_{PC} = 0 \quad \text{for} \quad \frac{L_{PC}}{2} < x \leq \frac{(L_{PC} + L_K)}{2} \quad (3b)$$

From the symmetry of the composite, the composition gradient at both boundaries of the interdiffusion element is equal to zero:

$$\left(\frac{\partial W_{PC}}{\partial x}\right)_{x=0} = \left(\frac{\partial W_{PC}}{\partial x}\right)_{x=L_{PC}+L_K/2} = 0 \quad (4)$$

The partial differential eq. (2) can then be solved by the method of separation of variables,¹² which results in

$$W_{PC}(x, t) = \frac{L_{PC}}{L_{PC} + L_K} + \sum_{n=1}^{\infty} \frac{2}{n\pi} \sin\left(\frac{\pi n L_{PC}}{L_{PC} + L_K}\right) \times \cos\left(\frac{2n\pi x}{L_{PC} + L_K}\right) \exp\left(\frac{-4n^2\pi^2 Dt}{(L_{PC} + L_K)^2}\right) \quad (5)$$

Equation (5) is not a closed solution of eq. (2), but converges rapidly.

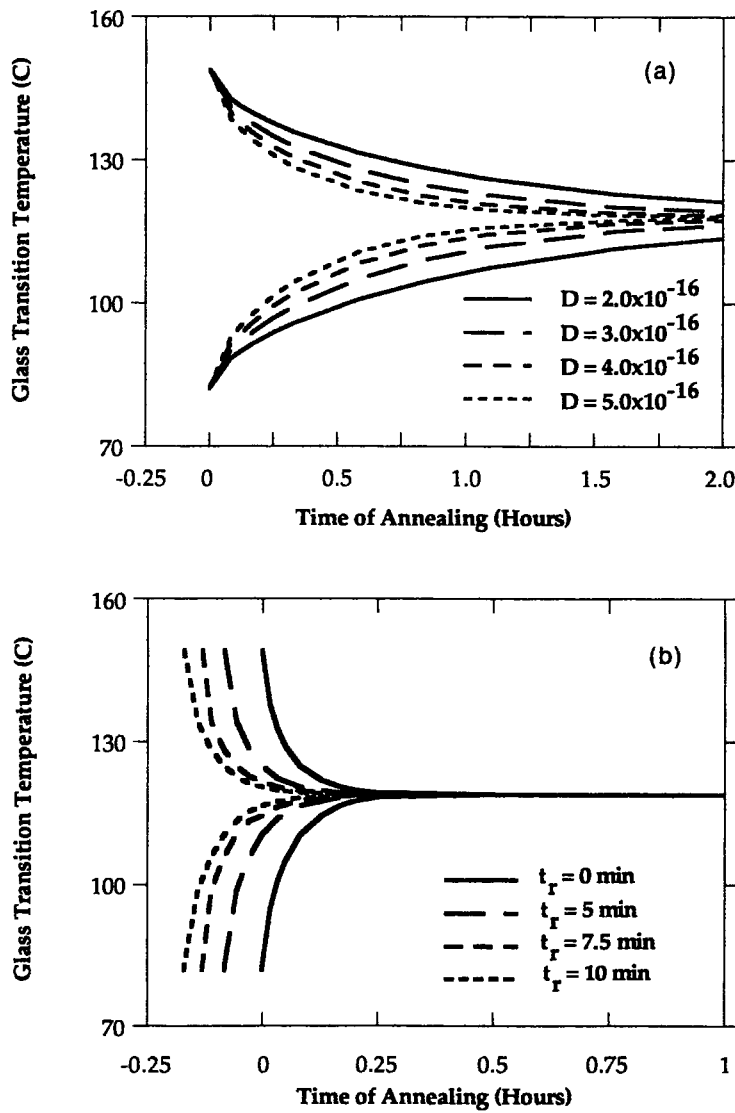


Figure 9 Sensitivity of the calculated average glass transition temperature to the mutual diffusion coefficient, D , and the residence time, t_r . (a) Effect of D on the PC/KODAR 60/40 composite with 657 layers; (b) effect of t_r on the PC/KODAR 60/40 composite with 3713 layers.

The composition profile of the PC/KODAR 60/40 composite with 657 layers calculated from eq. (5) using arbitrary values of D and t is plotted in Figure 8(a). An accuracy of 0.001% was achieved with $n = 15$. The composition profile was converted to a profile of the glass transition temperature through the interdiffusion element by substituting eq. (5) into the Fox equation:

$$\frac{1}{T_{g,PC}(x,t)} = \frac{W_{PC}(x,t)}{T_{g,PC}^0} + \frac{(1 - W_{PC}(x,t))}{T_{g,K}^0} \quad (6)$$

The glass transition temperature profile in Figure 8(b) was calculated from eq. (6) for the composition profile in Figure 8(a). An average glass transition temperature for each of the half-layers of the inter-

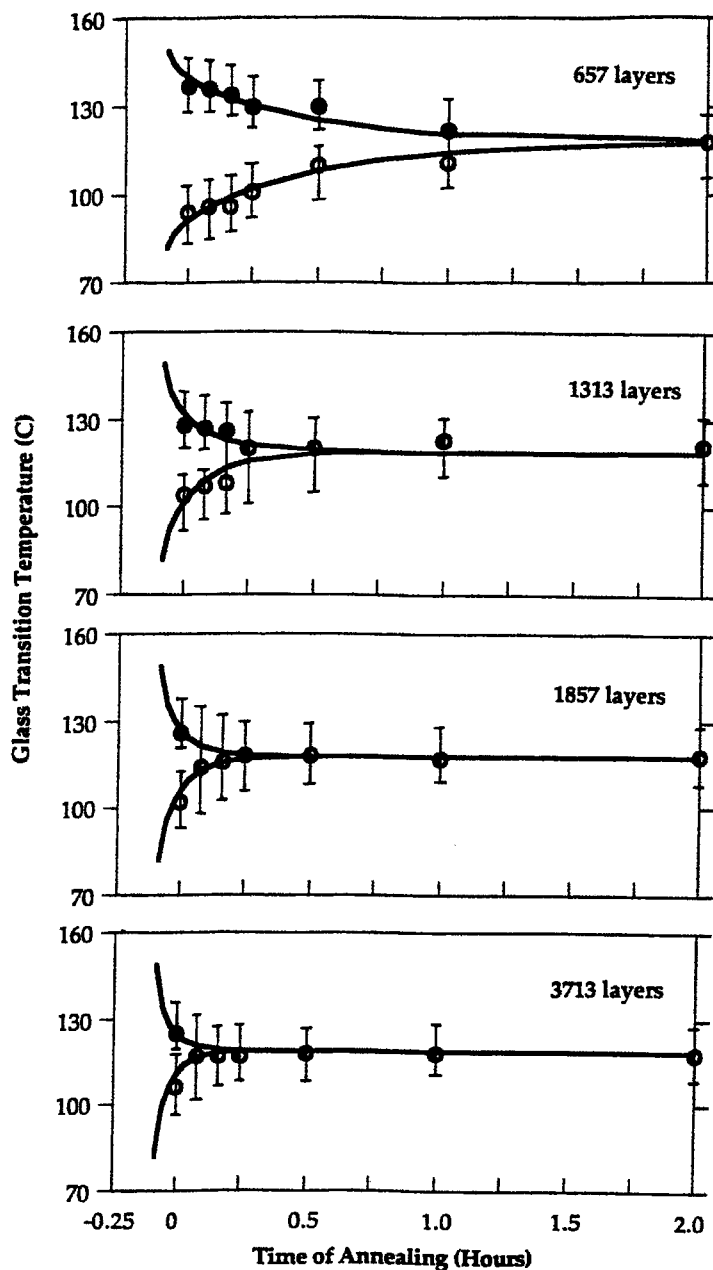


Figure 10 Observed glass transition temperature for the PC/KODAR 60/40 composites annealed at 200°C compared with the calculated average glass transition temperature calculated with $D = 4.0 \times 10^{-16} \text{ m}^2/\text{s}$ and $t_r = 5 \text{ min}$.

diffusion element was obtained by summing the glass transition profile at 0.05 micron intervals and dividing by the number of intervals. The average glass transition temperature calculated for each of the half-layers is included in Figure 8(b) as a horizontal line. The calculated average glass transition temperatures were subsequently compared with the glass transition temperatures obtained experimentally.

Comparison of Model and Data

The sensitivity of the calculation to *D* is shown in Figure 9(a) for the PC/KODAR 60/40 composite with 657 layers. Increasing *D* increased the rate at which the glass transition temperatures converged to a single transition temperature. A fitting proce-

dure was used to obtain the value of *D* that best described the experimental data. Data from the composite with the thickest layers, which required the longest annealing time for complete mixing, were used to determine the best value of *D*.

The diffusion model requires that the initial glass transition temperatures of the two layers be equal to the glass transition temperatures of the pure components. Since this was not the case, and the initial glass transition temperatures were intermediate between the glass transition temperatures of the pure components, the mixing that occurred during coextrusion was accommodated by introducing an "equivalent" residence time, *t_r*. Nominally, the composite was extruded at approximately 260°C with a residence time in the extruder on the order

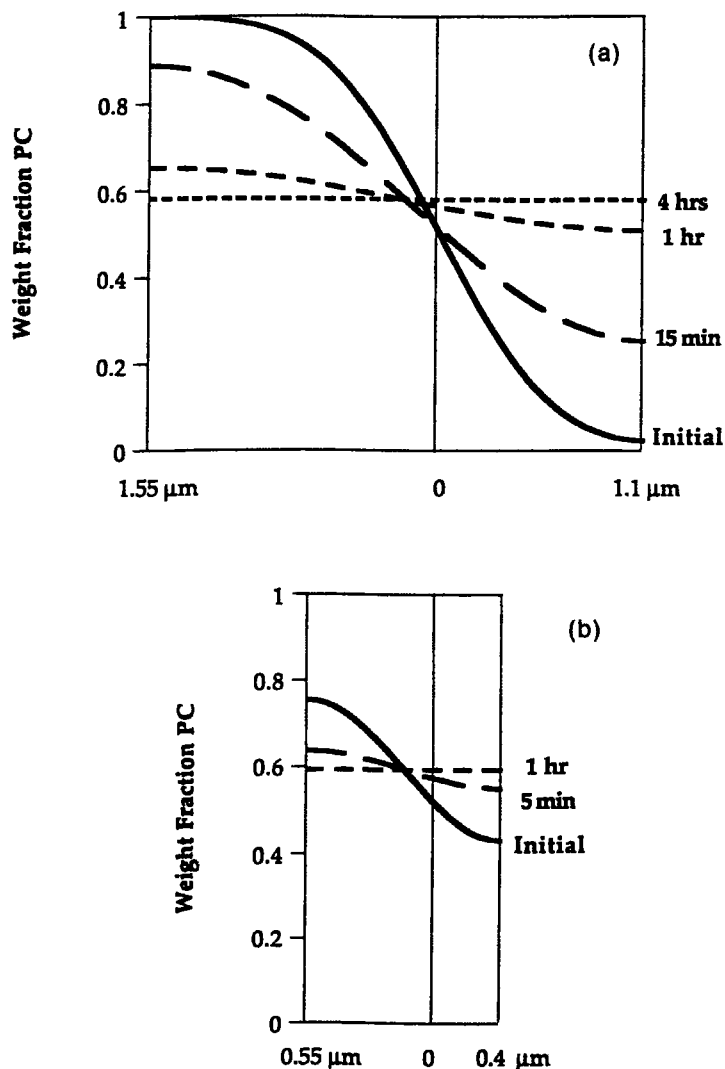


Figure 11 Composition profiles for the PC/KODAR 60/40 composites calculated from eq. (5) with $D = 4.0 \times 10^{-16} \text{ m}^2/\text{s}$ and $t_r = 5 \text{ min}$. (a) 657 layers; (b) 3713 layers.

of 5–10 min; however, the actual time–temperature history experienced by the composite during coextrusion was not known well enough to include explicitly in the model. Instead, an “equivalent” residence time was defined as the time at 200°C, which resulted in the same amount of interdiffusion as did the coextrusion process.

The sensitivity of the calculation to the residence time is shown in Figure 9(b) for the PC/KODAR 60/40 composite with 3713 layers. This composite had the thinnest layers and complete mixing occurred in the shortest time. As a result, the data for this composite were not very sensitive to D , but were very sensitive to the residence time.

Initial values of D and t_r were obtained independently by fitting data from the 657- and 3713-layered

composites, respectively, and then D was adjusted slightly to obtain the best fit of the 657-layered composite with the residence time included in the calculation. The standard deviation of the theory from the experimental data did not exceed 2.5°C, which was within the experimental error of the glass transition measurement. The calculated glass transition curves are compared with the experimental data from the four PC/KODAR 60/40 composites in Figure 10. Values of $D = 4.0 \times 10^{-16} \text{ m}^2/\text{s}$ and $t_r = 5 \text{ min}$ were used.

The magnitude of D is in line with values of the mutual diffusion coefficient reported for other miscible polymer pairs. For example, D for a poly(vinyl chloride)/poly(*e*-caprolactone) pair in the temperature range 70–110°C is on the order of 10^{-14} to

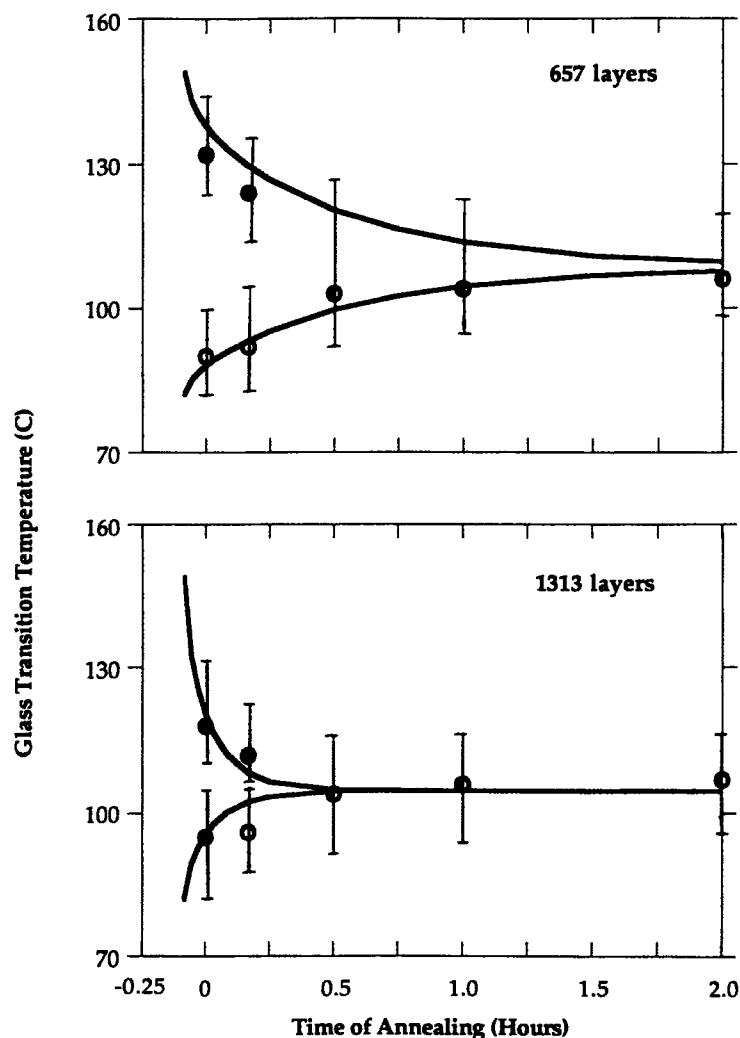


Figure 12 Observed glass transition temperatures for the PC/KODAR 40/60 composites annealed at 200°C compared with the calculated average glass transition temperature calculated with $D = 4.0 \times 10^{-16} \text{ m}^2/\text{s}$ and $t_r = 5 \text{ min}$.

10^{-15} m²/s.¹³ In the polystyrene/poly(dimethylphenylene ether) system, D is in the range of 10^{-12} to 10^{-15} m²/s for the temperature range of 180–260°C.¹⁴

The values of D and t_r obtained by fitting were used to calculate the composition profiles for the PC/KODAR 60/40 composites with 657 and 3713 layers at several annealing times. The initial composition profiles in Figure 11 (a) and (b) correspond

to the equivalent residence time of 5 min. The effect of the residence time was strongly related to the thickness of the layers. When the layers were relatively thick, the residence time had a large effect on the composition only in the region near the interface, whereas for the 3713-layered composite, the residence time alone was sufficient to produce almost complete mixing of the two polymers.

The same values of D and t_r were used to calculate

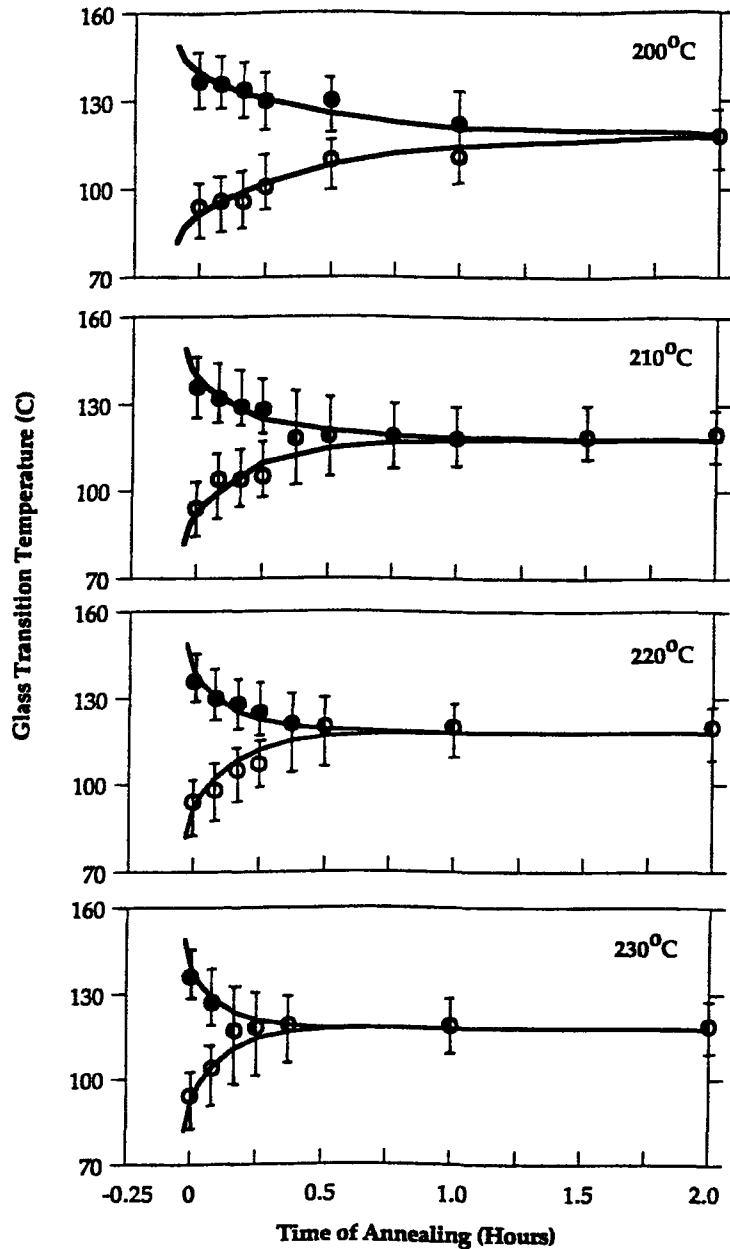


Figure 13 Observed glass transition temperatures for the PC/KODAR 60/40 composite with 657 layers annealed at four temperatures between 200 and 230°C compared with the calculated average glass transition temperatures.

Table II Diffusion Model Parameters

Annealing Temperature (°C)	D (m ² /s)	t_r (min)
200	4.0×10^{-16}	5.00
210	8.0×10^{-16}	2.67
220	1.2×10^{-15}	1.67
230	1.6×10^{-15}	1.25

the glass transition curves for the PC/KODAR 40/60 composites with 657 and 1313 layers. Comparison of the data in Figure 12 showed that these values also satisfactorily described the 40/60 composites.

Activation Energy Determination

Interdiffusion was examined in the temperature range from 200 to 230°C. Below 200°C, interdiffusion was slow enough that crystallization of KODAR occurred concurrently with diffusion. At higher temperatures, there was concern that transreaction would complicate the results¹⁵; the choice of 230°C as the highest temperature was based on a report that no evidence of the ester-carbonate interchange reaction was found after prolonged processing of PC and KODAR at this temperature.¹⁶ The glass transition temperatures of the PC/KODAR 60/40 composite with 657 layers annealed at four temperatures, 200, 210, 220, and 230°C, are compared in Figure 13. The shorter time required for convergence to a single glass transition as the annealing temperature was increased reflected the increase in D .

To fit the glass transition data for temperatures above 200°C, only D was varied independently. The other parameter needed for fitting the data, the "equivalent" residence time, t_r , described the initial state of the composite by representing the interdiffusion that occurred during processing. To produce the same initial state when D was varied, it was necessary to determine a new "equivalent" residence time, which was the time required at the new temperature to achieve the same amount of interdiffusion that occurred in 5 min at 200°C. This was done by choosing a value of D , calculating t_r , then adjusting D and recalculating t_r until the best fit was obtained. The values of D and the corresponding residence times for the four temperatures are given in Table II. The glass transition curves calculated with these values are included in Figure 13.

The diffusion coefficient is plotted in Figure 14; the correlation coefficient for the linear plot is 0.98. The value of 95.0 kJ/mol obtained for the activation energy is on the same order of magnitude as values for other miscible polymer pairs reported in the literature. The poly(vinyl chloride)/poly(ϵ -caprolactone) system is reported to have an activation energy of 49 kJ/mol in the temperature range from 70 to 110°C.¹³ The activation energy of the polystyrene/poly(dimethylphenylene ether) miscible system reportedly varies between 60 and 104 kJ/mol in the temperature range from 180 to 260°C.¹⁴

CONCLUSIONS

The creation of a large interfacial area with minimal mixing by microlayer coextrusion made it possible

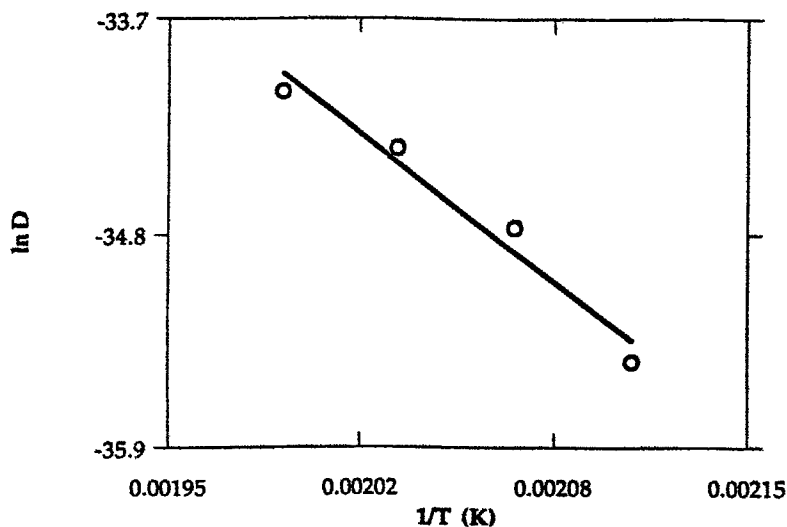


Figure 14 Temperature dependence of the mutual diffusion coefficient, D .

to study the interdiffusion of a weakly interacting miscible polymer pair: polycarbonate and KODAR copolyester. Characterization of the glass transition behavior as a function of annealing time at temperatures between 200 and 230°C led to the following conclusions:

1. The two glass transitions observed initially were intermediate between the glass transition temperatures of the pure homopolymers. With annealing time, the glass transitions shifted closer together until a single glass transition was observed.
2. The symmetry of the microlayer composite made it possible to model the composition profile through the layer thickness by application of Fick's equation for one dimensional, nonsteady-state diffusion. When the Fox equation was used to relate composition to the glass transition temperature, it was possible to predict the average glass transition temperature in each layer.
3. A good fit of the experimental data was obtained without considering the composition dependence of the mutual diffusion coefficient, D . In the temperature range from 200 to 230°C, the value of D varied from 4.0×10^{-16} to 1.6×10^{-15} m²/s, and the activation energy of interdiffusion was determined to be 95 kJ/mol. These values are comparable to those reported in the literature for other miscible polymer pairs.

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