Influence of morphology on the transport properties of polystyrene/polybutadiene blends. 1. Experimental studies

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Experimental and quantitative image analysis studies are presented to investigate the influence of morphology on the transport of small gaseous penetrants (CO_2, O_2, N_2) in randomly interspersed blends of polystyrene (A) and polybutadiene (B) ranging in volume fractions, ϕ_B, from 0.08 to 0.90. The overall transport process, for the blends, appears non-Fickian even though both pure phases A and B exhibit Fickian behaviour. An explanation of this phenomenon, based solely on morphological effects, is presented. A conclusion of the study is that the different methods usually taken as equivalent, to compute the effective diffusion coefficient from sorption data, can give significantly different results. An examination of the morphology is performed by means of digital image analysis on transmission electron microscopy, *TEM*, micrographs. A significant finding is that, for this system, the maximum intermaterial area density occurs for ϕ_B around 0.15.

(Keywords: morphology; transport; polymer blend; image analysis; sorption)

INTRODUCTION

In this article we explore the relationship between transport and morphology in terms of the diffusion of small molecules (O_2, N_2, CO_2) in mechanically mixed blends of polystyrene and polybutadiene. Of primary interest is the effect of the geometry and topology of each phase on the effective diffusion coefficients of the blends. Also, since the complete three dimensional morphology of a blend is not easily determined by direct two dimensional observations (optical or electron microscopy), due to limitations in contrast methods, sectioning techniques, or the microscope itself, it is useful to determine whether the transport properties of a blend give useful qualitative and/or quantitative morphological information.

In general, it is considered here that small molecules such as O_2, N_2 and CO_2, will diffuse into rubbery or glassy polymers without significantly changing their structure. Thus, it is conceivable that the small molecules may act as 'morphological probes' for the determination of the structure, especially the connectedness, of a polymeric material. One test of this hypothesis is the comparison of morphological information obtained from sorption–desorption experiments with several small molecules in the same polymer blend. The consistency of this information is a check of the hypothesis (but not a validation).

The transport of a penetrant in a polymeric material can be classified into one of three possible modes: Case I or Fickian diffusion, Case II diffusion[1,2] or Super-Case II diffusion[3–5]. Case II diffusion is often seen in vapour and solvent diffusion in rubbery and glassy materials. It is characterized by a swelling front which moves through the material at a constant velocity. This behaviour is thought to occur when the local relaxation time scale of the polymer chains is greater than the diffusion time scale. The velocity of the moving front is determined by the relaxation rate of the polymer chains and, as a consequence, the effective diffusion coefficient of the penetrant (in the Fickian sense) cannot be measured. Super-Case II diffusion is characterized by the presence of both a swelling front moving at constant velocity and a 'Fickian tail' which precedes the front. This phenomenon is thought to occur when the local relaxation time scale of the polymer chains is on the order of the diffusion time scale. In principle, analysis of a sorption experiment will give information on both the relaxation time scale of the polymer molecules and the effective diffusion coefficient of the penetrant. The velocity of the moving front gives information about the relaxation rate, while the 'Fickian tail' gives information on the diffusion coefficient.

In general, the transport of small molecules such as low molecular weight gases (H_2, He, N_2 and O_2) is Fickian, and Henry's law holds for both rubbery and glassy polymers at pressures below approximately 2 atmospheres and at temperatures of approximately 25°C. At pressures above 2 atmospheres significant deviations from both Henry's law and Fick's law are observed[6,7]. Dual-mode sorption models, proposed to account for the deviations, combine Henry and Langmuir isotherms[8–10].

Several studies of transport of low molecular weight gases in polymer blends have been published. The most comprehensive study appears to be the one by Ranby and coworkers[11–14] in which the transport of He, N_2, O_2 and CO_2 was measured in mechanical blends of poly(vinyl chloride) with several rubbery components. The purpose of the work was to determine if transport properties would give information about the miscibility of the blends. However, the data were analysed only in terms of simple linear models and a substantial morphological description was not provided.

Peterson[15] studied the transport properties of blends of polyvinyl acetate (PVAc) with several polymers. In all cases PVAc was the matrix phase. In this study only a few

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compositions were analysed and little morphological information obtained. Masi *et al.*[10] studied the transport of CO_2 in miscible blends of a copolyester with polycarbonate. Three compositions were analysed at penetrant pressures of 1 to 20 atmospheres. Experimental data were compared to predictions of dual-mode sorption models.

Kang *et al.*[16] studied the transport of O_2 and CO_2 in blends of polystyrene (PS) and poly(trimethylsiloxy methacrylate propylsilane) (PTMPS). A limited range of compositions was studied and little morphological information obtained. Experimental data were analysed in terms of a simple linear model which allowed for the presence of 'holes' at the interface of the two phases. The transport properties of blends of these materials with a graft copolymer of PS and PTMPS were also studied. The graft copolymer apparently increased the compatibility of the two pure materials and thus decreased the concentration of 'holes' at the phase interfaces.

Copolymers of polystyrene and polybutadiene[17,18], polyethylene and polypropylene[19], and terpolymers of polyisoprene, polystyrene and poly(vinylbenzyl) dimethylamine[20] have been studied at a few compositions. Substantial morphological descriptions were given; however, transport properties were analysed with only simple linear models and only a few compositions were studied.

In this article we study, experimentally, the transport–morphology relationships of randomly interspersed polystyrene/polybutadiene blends in terms of O_2, N_2 and CO_2 for a wide composition range; qualitative and quantitative descriptions of the morphology at each composition are given. In a second article[21] we discuss the modelling of the experimental data presented here.

In general, the experiments which are discussed here apply to diffusion of small molecules in glassy and rubbery polymer blends at approximately room temperature and at sub-atmospheric and atmospheric pressures. Henry's law and Fick's law are used to analyse experimental data.

The polymeric materials used are polybutadiene and polystyrene. These materials are immiscible[18,22,23]. Due to their immiscible nature, their blends are expected to exhibit two phases with each phase being similar to the pure components (i.e. similar mechanical, thermodynamic and transport properties). The interface between the phases is assumed to be very small and the boundary effects negligible. In this case the transport properties of the composite (effective permeability) lie between two values, those of the pure component materials. In contrast, miscible polymer blends are often homogeneous at a length scale on the order of molecular dimensions and may exhibit synergistic behaviour[24].

EXPERIMENTAL MATERIALS

Blends of polystyrene and polybutadiene were prepared by intensive mechanical mixing, using a Banbury mixer. Precisely weighed amounts of the two pure components (in the form of pellets) were simultaneously added to the Banbury mixer (model A.A.514 S.B., C. W. Brabender Inc.) and mixed at 30 rpm for 20 min at 160°C. It was noticed that after approximately 3 min of mixing, the blended material became opaque, indicating that the pure components had been reduced in size to the order of one micron[25]. The blends produced were 8, 15.8, 23, 31.2, 51.6, 76 and 90 volume per cent polybutadiene.

The resultant material was removed from the mixer and sections of the order of 1 cm^3 were cut. These sections were compression moulded into discs 20 mm in diameter and 1 mm thick. The moulding was performed under vacuum, 0.05 mm Hg, at a temperature of 140°C. Portions of these thin discs were used in the sorption apparatus to determine effective diffusion coefficients and effective solubility coefficients.

The polystyrene used was 'as received' Lustrex (Monsanto) with $M_w = 250\,000$, $T_g = 90°C$ and $\rho = 1.05$ g cm^{-3} at 25°C. The polybutadiene was Diene 35 NFA/AC, an alkyl lithium polymerized polybutadiene made by Firestone Synthetic Rubber and Latex Company, with $M_w = 182\,000$, $T_g = -96°C$, and $\rho = 0.90$ g cm^{-3} at 25°C.

These components were chosen because of the large difference in effective diffusion coefficients for small molecules (about two orders of magnitude) and due to the presence of a well-known contrasting method for morphological studies, OsO_4 staining[26].

DETERMINATION OF THE MORPHOLOGY OF PS/PB POLYMER BLENDS

Electron microscopy

The morphology of the polymer blends was investigated by transmission electron microscopy in a JOEL 100CX electron microscope. Small sections of material were cut from the sample discs and sectioned using a Richter ultramicrotome at −110°C with a glass knife (the 90% PB sample was cut with a diamond knife). Sections obtained were estimated to be 500–1000 Å thick. The thin sections were then stained with osmium tetroxide. The specimens were placed on a glass slide and suspended over a 0.5% aqueous solution of osmium tetroxide in a tightly closed glass vessel for approximately 3.5 h.

Morphological description

A qualitative description of the morphology of the blends may be obtained by visual inspection of the micrographs obtained by transmission electron microscopy. *Figures 1*, *2*, *3* and *4* are representative of the structures in each blend. In these micrographs, the dark phase is polybutadiene and the white phase is polystyrene. These micrographs seem to indicate that polystyrene is the continuous phase and polybutadiene the discontinuous phase over the range of volume fractions below 15.8 vol% polybutadiene. Above 31.2 vol% polybutadiene, the polybutadiene seems continuous and the polystyrene seems discontinuous. This indicates that a 'phase inversion' occurs somewhere between 15.8 and 31.2 vol% polybutadiene. However, we must keep in mind that the micrographs are two dimensional projections of a three dimensional structure. Thus, a bicontinuous structure, if one exists, will not be detected by a single micrograph or several micrographs. Indeed, the only way to determine the bicontinuous nature of a composite is by careful analysis of serial sections. Due to the small sample sizes used in microtoming and transmission electron microscopy, this procedure is extremely difficult and was not performed in these studies.

The geometrical description of the dispersed phase in the blends is quite complicated. Qualitatively, at volume fractions of polybutadiene less than 0.2, the polybutadiene domains are highly elongated structures of complex

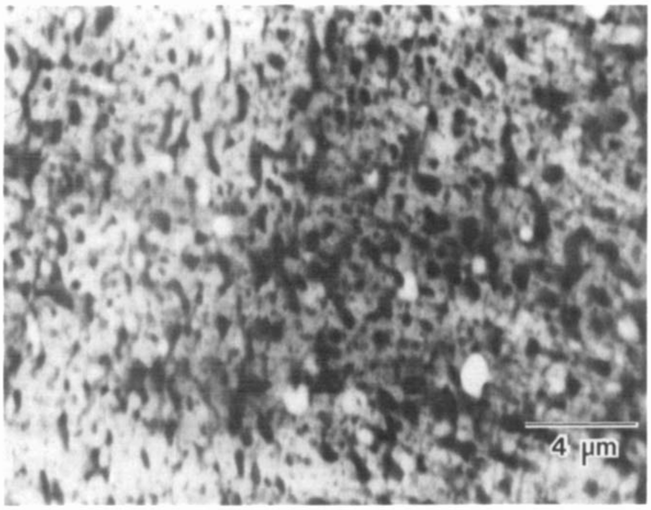

Figure 1 Typical *TEM* micrograph of a mechanical blend of polystyrene and polybutadiene. Volume fraction of polybutadiene is 0.158

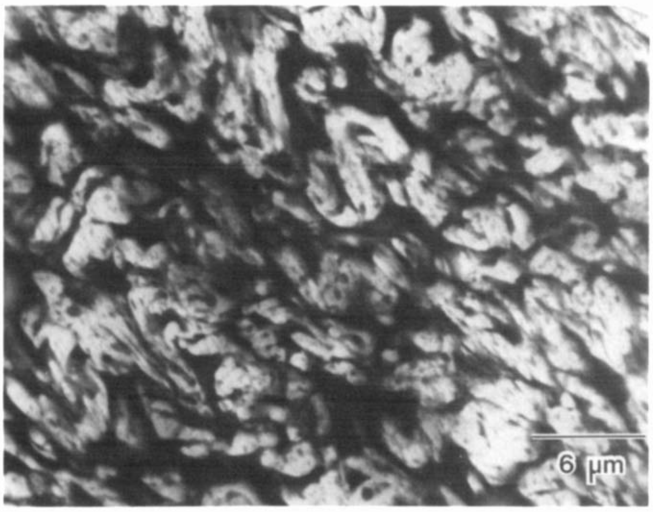

Figure 2 Typical *TEM* micrograph of a mechanical blend of polystyrene and polybutadiene. Volume fraction of polybutadiene is 0.312

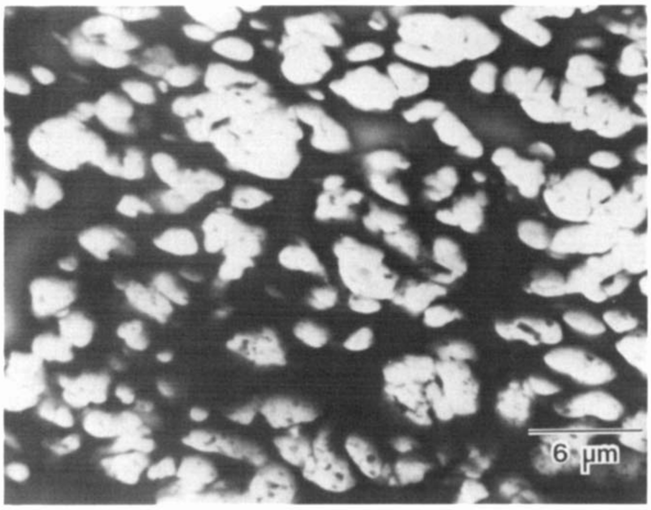

Figure 3 Typical *TEM* micrograph of a mechanical blend of polystyrene and polybutadiene. Volume fraction of polybutadiene is 0.516

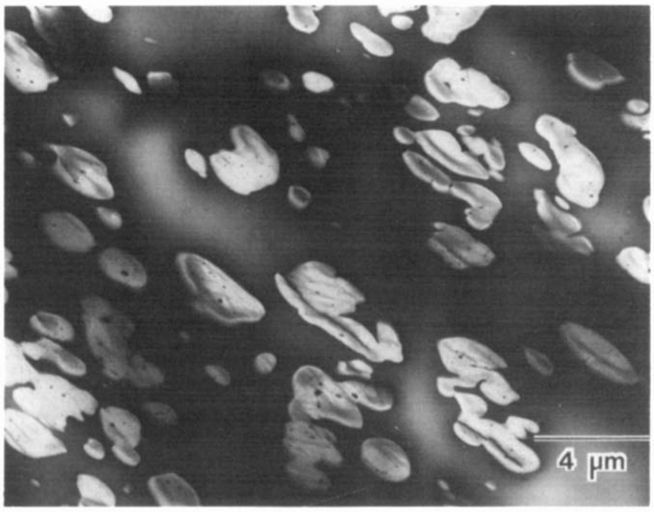

Figure 4 Typical *TEM* micrograph of a mechanical blend of polystyrene and polybutadiene. Volume fraction of polybutadiene is 0.760

nature. At high volume fractions of polybutadiene, the polystyrene domains are roughly ellipsoidal with the degree of convexity decreasing with increasing content of polybutadiene. At volume fractions of polybutadiene above 0.75, the polystyrene domains are particles of fairly regular shape, roughly equivalent to ellipsoids.

Digital image analysis

Often micrographs obtained from electron microscopy studies are analysed by visual inspection only. However, our visual perception is quite limited as human beings are unable to visually detect greater than two point correlations and orientation of objects with less than 20% orientation[27,28]. More reliable information and a greater variety of information may be obtained from numerical studies of micrographs. Recent advances in the field of digital image analysis and large scale computation have now made this possible[28].

The micrographs obtained from electron microscopy studies were digitized using an Optronics Colormation Mark II Digital Scanner. The Mark II is a rotating-drum type scanning/plotting device which offers high positional accuracy and very accurate light intensity discrimination. The apparatus is controlled by a companion Wang minicomputer and is configured to output to magnetic tape. This system is owned and operated by the University of Massachusetts/Amherst Remote Sensing Center. The resolution of the scanner may be varied from 12.5 to 200 microns. In essence, the scanner separates a picture into small squares (pixels) of a size specified by the operator, then averages the intensity of transmitted light through that square (for a negative micrograph) and assigns a corresponding location in a two dimensional array an interger value between 0 and 255. The value assigned is normalized with reference to the intensity of 100% transmission of light. The maximum number of pixels that a standard 4″ × 5″ negative micrograph can be separated into is approximately 8×10^7.

The size at which the operator digitizes the micrograph is one of several important factors. The digitizing process can be looked upon as a transfer function. This transfer function has an associated error which should be minimized. In principle, the minimum error occurs when the size of the pixels is infinitesimally small. However, as with most large scale computing problems, the cost of computing increases non-linearly with the size of the two dimensional array. Thus, an optimum size must be chosen which minimizes both the loss of information and the cost.

For the micrographs obtained in these studies (which were taken at magnifications of 3300× to 8600×), the pixel size was set at 100 by 100 microns (thus the smallest domains, such as in *Figure 1*, were represented by at least 40 pixels, and the average size of the two dimensional arrays created upon digitization of the micrographs was 650×900).

A major problem in analysing a digitized image is the determination of the range of intensities corresponding to each of the phases present in the original image. This is the only other point at which the judgement of the operator may influence the quantities determined in the forthcoming calculations. Three methods may be used: first, determination of the range of intensities of each phase on a point by point basis; second, the same but on a line by line basis, in which a line is passed through several adjoining phases and the intensity along that line is plotted *versus* distance (this method helps to identify phase boundaries). Third, analysis of the histogram of frequency *versus* intensity for the entire two-dimensional array. However, due to gradients in staining agent and thickness in the samples, the histogram may exhibit a single maximum, due to overlapping of the intensity distribution for each phase. In the micrographs obtained for the polybutadiene and polystyrene blends the range of intensities characteristic of each material was determined using all three methods. Filtering, in Fourier space, of high frequency components (noise) and low frequency components (large scale gradients) was also used. It was noted that analysis of the histogram of intensities was usually ineffective.

Once the range of intensities for each phase has been determined, the average size of each phase ($\bar{l}_i$), the interfacial area density (a_v), the degree of linear orientation (Ω_{lin}), and the volume fractions (ϕ_i) can be calculated[28–30]. Software, compatible with the digital image analysis system, was developed to calculate these quantities. The area fractions of each phase on an image were calculated by summing the number of pixels with intensities in the range assigned to each phase. The volume fractions for a random composite are identical to the area fractions. The interfacial area density was calculated by placing random test lines on the image and counting the intersections of test lines with interfaces per unit length of test line (P_L). The fundamental equation of stereology, $a_v = 2P_L$[29], can then be used to calculate a_v.The average phase size was determined from the average intercept length of each phase with random test lines. The degree of linear orientation was determined by measuring P_L for a set of parallel test lines placed at various angles on the image. The degree of linear orientation quantifies the amount of anisotropy in the image; here we use the definition given by Underwood[29]. In this case the degree of linear orientation varies from 0, for an isotropic system, to 1.0 for a completely ordered system (i.e. parallel lamellae). The results of these calculations are given in *Table 1*. The results for Ω_{lin} should be interpreted with care, since they depend on the size of the picture analysed.

Table 1 Quantitative information obtained from *TEM* micrographs

Material	Size of image (μm × μm)	Area fraction of polybutadiene	a_v (m^{-1})	$\bar{l}_{PB}$ (m)	$\bar{l}_{PS}$ (m)	Ω_{lin}
8.0% PB	13.0×14.5	0.078	3.1E6	1.0E-7	12.0E-7	0.267
15.84% PB	13.1×15.2	0.17	4.0E6	19.E-7	8.1E-7	0.114
23.0% PB	13.2×18.7	0.28	3.6E6	3.5E-7	7.6E-7	0.063
31.2% PB	20.5×27.2	0.30	2.5E6	4.8E-7	1.1E-6	0.235
51.6% PB	27.6×19.4	0.66	1.9E6	1.4E-6	7.0E-7	0.212
76.0% PB	19.1×27.9	0.74	1.5E6	2.0E-6	7.6E-7	0.130

The area fractions of polybutadiene computed from the images agree quite well with the volume fractions computed from the relative weights of the constituents in the blends. This indicates that the sections examined are representative of the sample (i.e. the structure is roughly isotropic and homogeneous at the length scale of the micrograph, which is approximately 20 microns). More accurate estimates would be obtained if several arbitrary micrographs of the same sample were analysed; however, cost constraints made this prohibitive.

The interfacial area density is plotted *versus* the volume fraction of polybutadiene in *Figure 5*. This curve is highly skewed toward the low volume fractions of poly butadiene. The maximum occurs for $\phi_B \approx 0.15$. Random filling of two phases on a regular or irregular tessellation produces a curve of a_v *versus* volume fraction which is symmetric about the volume fraction 0.5. This clearly indicates that the system studied here cannot be modelled by random filling of a fixed tessellation[31] over the entire range of volume fractions.

An explanation of this behaviour lies in the analysis of the pure component properties at the mixing conditions. At the mixing temperature (160°C) the viscosity of polybutadiene is much less than that of polystyrene. Due to this difference in viscosities, the polybutadiene may act as a lubricant between the high viscosity polystyrene domains. Thus, at relatively low volume fractions of polybutadiene, thin sheets of polybutadiene coat the polystyrene domains. This behaviour produces continuous domains of polybutadiene at relatively low volume fractions. The typical cluster of polybutadiene is ramified whereas the typical cluster of polystyrene is rounded. Thus, the maximum in the interfacial area density occurs at relatively low volume fractions of polybutadiene, as seen in *Figure 5*.

The degree of linear orientation of polybutadiene in each of these micrographs varies from 0.1 to 0.2. A truly random isotropic system should have a degree of linear orientation equal to zero. However, due to the low glass

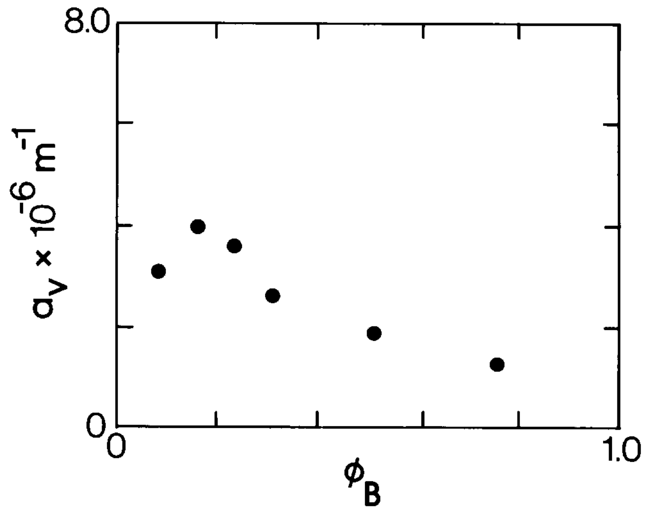

Figure 5 Intermaterial area density (i.e. perimeter of contact between materials per unit area) computed from *TEM* micrographs of the blends. ϕ_B is the volume fraction of component B, polybutadiene

transition temperature of polybutadiene, the microtoming technique may be responsible for a significant amount of the linear orientation of the polybutadiene phase (i.e. as the knife cuts through the polybutadiene domains it may deform them, due to the rubbery nature of polybutadiene). Microtoming at −110°C limits this phenomenon but the extent of the limitation has not been explored.

Sorption measurements

The measurement of effective diffusion coefficients and effective solubility coefficients for CO_2, O_2 and N_2, were carried out using a constant pressure sorption apparatus. The apparatus consists of a gas inlet system, a Cahn model-2000 electrobalance, and a continuous chart recorder (Houston Instruments Omniscribe Recorder model D217-15AQ). Sorption and desorption experiments were run at approximately 25°C and from subatmospheric to atmospheric pressures. This apparatus was based on designs by Berens[32] and Peterson[15].

Calculation of effective transport parameters from sorption and desorption experiments have been described by Berens[32] and Felder and Huvard[33]. In all, there are four classical methods of calculating the effective diffusion coefficient from the weight *versus* time curve for a sorption or desorption experiment. These are: *Initial slope method*, *Half-time method*, *Limiting slope method* and the *Moment method*. The comparison of values obtained by each method affords new insight into the transport process. In all four methods the effective solubility coefficient is determined in the same manner (i.e. from the equilibrium, $t \to \infty$, weight gain or loss).

The transport properties of the pure components were first determined in order to assess whether the transport of these gases obeyed Fick's law and Henry's law. Dimensionless mass *versus* time curves obtained from sorption and desorption experiments were nearly superimposable (see *Figure 6*) for all permeants and for both pure components. Also, the effective diffusion coefficients determined from each of the four methods were consistent, within experimental error (less than 15%). These two criteria[33] indicate that transport of CO_2, O_2 and N_2 in polystyrene and polybutadiene at pressures less than one atmosphere and at approximately 25°C is Fickian and the effective diffusion coefficient is independent of the concentration of the penetrant.

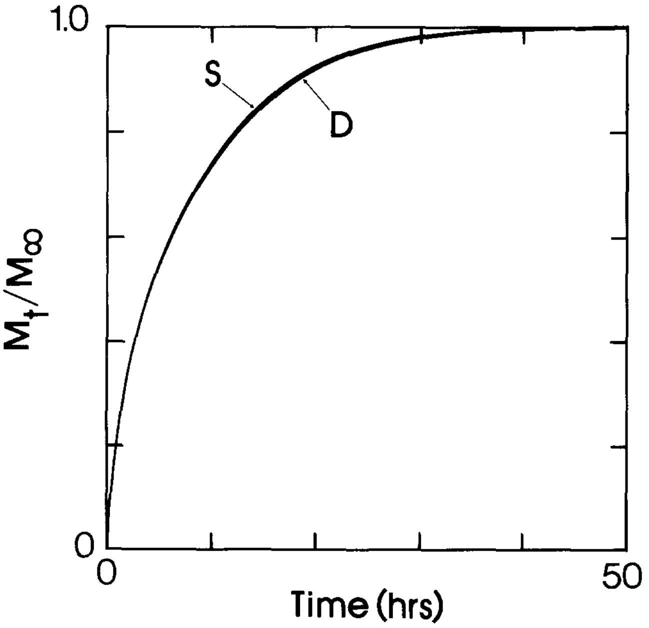

Figure 6 Comparison of sorption and desorption curves for CO_2 diffusion in polystyrene at 25°C. M_t is the weight of sorbed or desorbed penetrant at time t. M_∞ is the equilibrium weight of sorbed or desorbed penetrant (i.e. initial weight of sample minus final weight of sample). S—sorption curve. D—desorption curve

Sorption and desorption experiments were also done on the polymer blends. Values of the effective solubility coefficients (S_{eff}) and the effective diffusion coefficients (D_{eff}) determined by the three methods for the polymer blends are given in *Table 2*. Calculations from the moment method are not included, as these values were indistinguishable from values computed from the half-time method. The sorption curves cannot be fitted with a constant value for the effective diffusion coefficient. In general, the effective diffusion coefficient determined from the initial slope method is greater than the values obtained from the half-time and limiting slope methods, and the values obtained from the half-time method are greater than values obtained by the limiting slope method (with the exception of the two cases underlined in *Table 2*). The experimental error in these values is less than ±15%.

The classical explanation for this phenomenon is that the diffusion coefficient is dependent on the concentration

Table 2 Experimental data for blends of polystyrene and polybutadiene

		D_{eff} (cm^2 s^{-1})			S_{eff}
Material	Penetrant	Initial slope method	Half time method	Limiting slope method	(cm$^3_{stp}$/g atm)
Polystyrene	CO_2	4.8E-8	4.7E-8	5.3E-8	1.9
	O_2	1.2E-7	1.2E-7	1.3E-7	0.165
	N_2	4.2E-8	5.0E-8	4.6E-8	0.090
Polybutadiene	CO_2	3.6E-6	3.1E-6	2.9E-6	0.78
	O_2	4.5E-6	4.6E-6	4.3E-6	0.078
	N_2	3.0E-6	3.3E-6	3.7E-6	0.04
8.0%PB/ 92.0%PS	CO_2	6.4E-8	6.1E-8	5.7E-8	1.60
	O_2	1.6E-7	1.5E-7	1.3E-7	0.14
	N_2	7.0E-8	6.0E-8	5.0E-8	0.087
15.84%PB/ 84.16%PS	CO_2	1.1E-7	8.3E-8	5.6E-8	1.62
	O_2	4.0E-7	2.2E-7	1.0E-7	0.149
	N_2	1.8E-7	1.6E-7	6.5E-8	0.11
23.0%PB/ 77.0%PS	CO_2	2.4E-7	2.2E-7	1.9E-7	1.50
	O_2	4.4E-7	3.2E-7	3.4E-7	0.13
	N_2	2.7E-7	1.7E-7	1.5E-7	0.07
31.2%PB/ 68.8%PS	CO_2	4.8E-7	4.2E-7	3.6E-7	1.48
	O_2	6.0E-7	4.8E-7	4.1E-7	0.135
	N_2	1.1E-6	6.3E-7	4.2E-7	0.091
51.6%PB/ 48.4%PS	CO_2	8.4E-7	7.8E-7	5.9E-7	1.47
	O_2	1.5E-6	1.2E-6	1.1E-6	0.145
	N_2	9.0E-7	9.0E-7	5.1E-7	0.075
76.0%PB/ 24.0%PS	CP_2	2.4E-6	1.5E-6	2.0E-6	1.14
	O_2	3.3E-6	2.1E-6	2.5E-6	0.114
	N_2	2.5E-6	1.7E-6	1.6E-6	0.065
90.0%PB/ 10.0%PS	CO_2	3.7E-6	3.2E-6	3.1E-6	1.02
	O_2	3.2E-6	2.9E-6	2.9E-6	0.11
	N_2	3.4E-6	2.2E-6	2.2E-6	0.053

of the penetrant (decreasing with increasing concentration). However, experiments on the pure components indicated that the effective diffusion coefficient was independent of the concentration of the penetrant. In this work we put forward the idea that these effects might be due solely to morphological effects. An alternative explanation might be based on the properties of the mixing region between the two phases. However, this region is expected to be quite small (on the order of tens of Angstroms).

Interestingly, at low volume fractions of polybutadiene the value of D_{eff} computed from the limiting-slope method is very close to the value of D_{eff} for pure polystyrene (see *Figures 7*, *8* and *9*); while at high volume fractions of polybutadiene, the value of D_{eff} computed from the initial-slope method is close to the value of D_{eff} for pure polybutadiene. As noted in the qualitative morphological description, the polystyrene is continuous at low volume fractions of polybutadiene, while the polybutadiene is continuous at high volume fractions of polybutadiene. Analysis of these data[21] indicates that the more conductive material (polybutadiene) exerts a disproportionate influence on the transport during the initial part of the experiment and the polystyrene does the same during the later stages of the experiment. However, the difference between the values tends to decrease with increasing volume fraction of the more conductive component (polybutadiene).

This phenomenon may be explained with the help of the qualitative description of the morphology and concepts embedded in percolation theory[34,35]. At any given composition a finite amount of each material is present at the sample boundaries (i.e. in a finite sample the accessible volume fraction of both materials may be non-zero at any composition). The presence of the more conductive

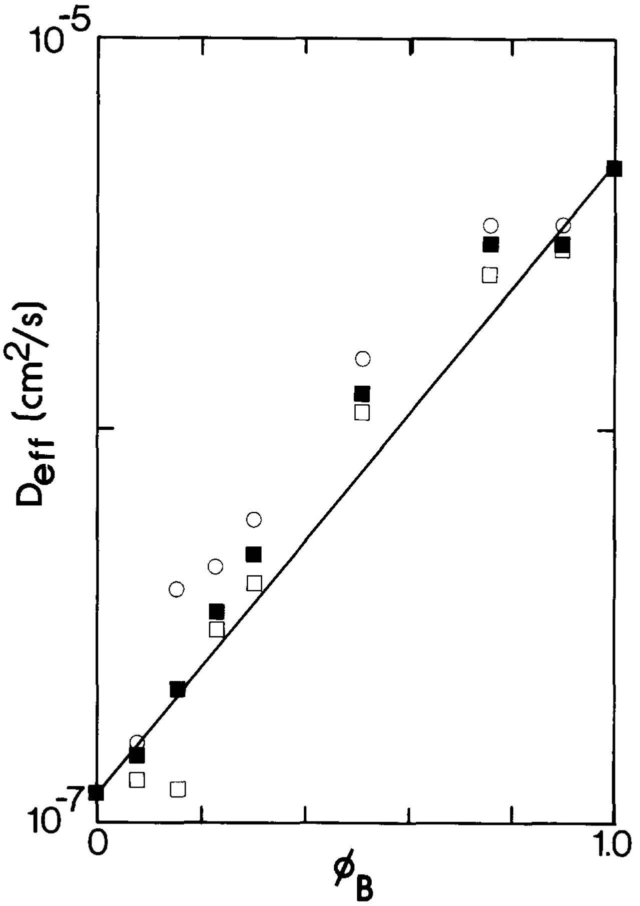

Figure 8 Comparison of diffusion coefficients determined by initial-slope method (○), limiting-slope method (□), and half-time method (■) with predictions of a simple logarithmic average. Data correspond to O_2 diffusion in PS/PB blends at 25°C

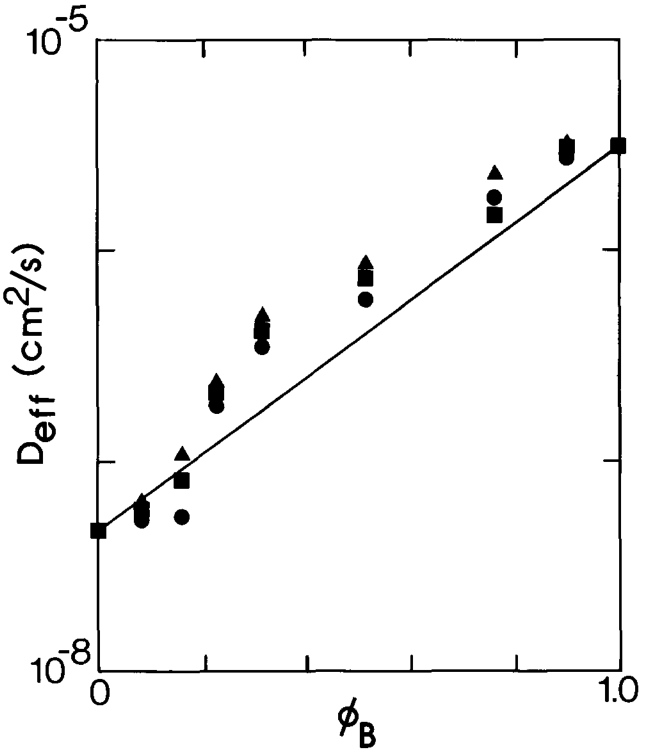

Figure 7 Comparison of diffusion coefficients determined by initial-slope method (▲), limiting-slope method (●), and half-time method (■) with predictions of simple logarithmic average. Data correspond to CO_2 diffusion in PS/PB blends at 25°C

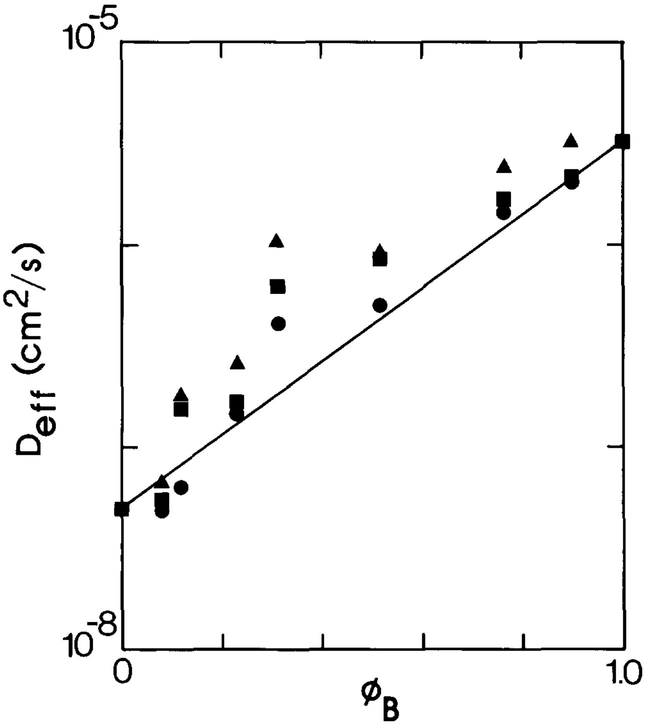

Figure 9 Comparison of diffusion coefficients determined by initial-slope method (▲), limiting-slope method (●), and half-time method (■) with predictions of a simple logarithmic average. Data correspond to N_2 diffusion in PS/PB blends at 25°C

material leads to a relatively rapid weight increase during the initial portion of the experiment. Thus the effective diffusion coefficient computed by the initial-slope method is larger than that computed from the half-time method. As the experiment proceeds the rate of weight increase achieves a state more nearly representative of the entire morphology of the sample. Near the end of the experiment, domains of the more conductive phase are near equilibrium while domains of the less conductive phase are still sorbing a significant amount of the penetrant. Thus, the weight increase with time near the end of the experiment is relatively slow, leading to an effective diffusion coefficient computed from the limiting-slope method which is less than that computed from the half-time method. This effect will be more pronounced for components with a greater difference between diffusion coefficients and when the length scales of the domains are of the same order of magnitude (i.e. effect is dependent on time scales for diffusion). Large differences in the solubility of the penetrant in the pure components may mask this effect.

This indicates that one should be careful in reporting an effective diffusion coefficient for a polymer blend, or any other composite medium including semi-crystalline and filled polymer systems. In these instances the choice of the value of the effective diffusion coefficient should depend on the stage of the sorption process in which one is interested, with the method used corresponding to the stage of interest (i.e. initial-slope for the beginning of the sorption experiment, limiting-slope for the later stages of the experiment). Numerical studies on random cellular media[35] have shown similar behaviour, and also indicate that sorption and permeation experiments do not always give consistent information.

The consistency of information obtained from different permeant molecules may be assessed by comparing the dimensionless diffusion coefficient ratio ($D_{\mathrm{eff}}/D_{\mathrm{B}}$) for each penetrant at each volume fraction of the blend. *Figure 10* illustrates this comparison. The proximity of the data indicate that the different penetrant molecules may see the same general structure. Thus, comparison of model predictions for each of the penetrant molecules is a practical method of determining the limitations and accuracy of the models. Also, differences in the effective diffusion coefficients, as computed by the various methods, *are qualitatively similar for all three penetrants. Figures 7, 8* and *9* show the variations in D_{eff} with the volume fraction in polybutadiene. The solid line corresponds to the classical logarithmic volumetric average computed from the pure component values and the volume fractions ($\ln D_{\mathrm{eff}} = \phi_{\mathrm{A}} \ln D_{\mathrm{A}} + \phi_{\mathrm{B}} \ln D_{\mathrm{B}}$). Obviously this estimation method for D_{eff} is inadequate. A rigorous modelling of the experimental data is given in an accompanying article[21].

CONCLUSIONS

We have presented an extensive experimental study of diffusion of small molecules in a mechanically mixed polymer blend. In addition to measuring the effective transport properties, a qualitative and quantitative description of the morphology aided by electron microscopy and quantitative image analysis was given. Although mixing was expected to produce nearly chaotic interpersions, the morphological parameters exhibited significant deviations from values expected for random systems.

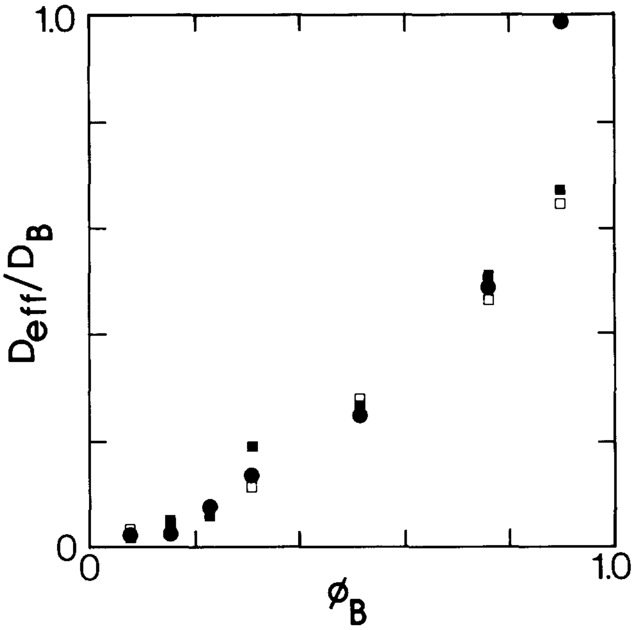

Figure 10 Dimensionless diffusion coefficient ratio for the series of PS/PB blends studied in this work. (■) CO_2 is penetrant, (□) O_2 is penetrant, (●) N_2 is penetrant. D_{B} is the diffusion coefficient for component B, polybutadiene

The morphology of a blend is dependent on the processing conditions and thermodynamics. For these blends, the deviation from a perfectly random system is most likely due to the widely different viscosities of the two components at the processing temperature. It has been suggested that the less viscous phase, polybutadiene, acts as a lubricant between particles of the more viscous phase, polystyrene, during mixing. This behaviour leads to a highly elongated and connected polybutadiene structure at low volume fractions of polybutadiene. This conjecture is supported by the results report here. However, rigorous morphological descriptions of the three-dimensional structures cannot be given, due to the limitations of analysis of two-dimensional projections.

The transport of these small penetrant molecules in the blends appeared to be time dependent, in our case the effective diffusion coefficients decreased as the sorption or desorption experiment proceeded. This behaviour was not seen in the pure components. An explanation of this phenomenon was given based solely on morphological effects, using concepts embedded in percolation theory. However, explanations based on interfacial effects, although conceivable, have not been studied here.

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