Transport–morphology relationships in segmented polybutadiene polyurethanes:
2. Analysis

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An analysis of the transport properties in a series of segmented polybutadiene polyurethanes described in Part 1 is presented in terms of the effective medium theory (EMT) and simple transport models involving ordered microstructures. The 75 wt % hard segment (HS) sample is assigned a dispersed morphology of soft segment (SS) spheres in a glassy matrix of hard segment. A lamellar morphology is indicated at 55 wt % HS by all methods of analyses: TEM, SAXS and transport models. Based on sorption studies and the results from SAXS, cylindrical domains of hard segment in a rubbery matrix of soft segment are believed to exist in the dilute range (<40 wt %) of hard segment content. Complex sorption kinetics indicate the inadequacy of Fick's law to describe the transport in copolymer samples of rubbery and glassy materials. Relaxational effects dominate the transport of CO_2 in polybutadiene polyurethanes. In this case, a simple transport model using EMT involving coupled diffusion and relaxation is used to describe the anomalous sorption kinetics.

(Keywords: transport; morphology; sorption; polybutadiene polyurethanes)

INTRODUCTION

Combined transport–morphology studies in copolymers are rare in the literature. The main drawbacks in the existing literature addressing both issues have been the assumption of a particular internal morphology without proof and the application of transport models which are generally not consistent with the actual sample morphology.

In this work we focus on the transport of small molecules (O_2, N_2 and CO_2) in a series of segmented polybutadiene polyurethanes as probes of the underlying domain morphology. As shown in Part 1, the detailed description of domain structures and their connectedness is not completely possible from either TEM or SAXS alone. For example, the phase inversion point cannot be deduced from the electron micrographs. Given these circumstances, transport studies are used as supplements for the elucidation of the morphologies of segmented polyurethanes.

There are several excellent articles in the area of transport properties in polymers available in the literature[1–4]. Other relevant studies focus on blends[5–10], semicrystalline polymers[11] and interpenetrating networks[12,13]. There are a smaller number of studies focussing on copolymers.

A summary of the transport studies in block and segmented copolymers is shown in *Table 1*. The transport is analysed in terms of dilute suspensions of spheres or spheroids. Non-Fickian phenomena dominate the transport of vapours in block copolymers; two-stage and sigmoidal sorption along with film thickness effects are some examples of this behaviour. A concise description of morphologies is given by Barrer[24]. An updated general review is presented by Petropoulos[25]. A review of the transport theories for random composites is given by Sax and Ottino[26]; more recent developments, emphasizing transient studies and renormalization methods are presented by Ottino and Shah[27] and Shah and Ottino[28], respectively.

APPLICATION OF THE EFFECTIVE MEDIUM THEORY

A theory that encompasses some of the physical behaviour observed in the transport of multiphase polymers, especially the change in connectedness as a function of sample composition, is the effective medium theory (EMT). This theory predicts the overall transport properties for randomly inhomogeneous systems and works best when the ratio of the pure component diffusivities is large (>100). It replaces an actual heterogeneous system with an effective homogeneous system that exhibits the same steady state transport properties as the original composite.

Using the value of the pure component properties (diffusivities and solubilities) the overall transport properties (D_{eff}) can be predicted[26]. The model results for the transport of CO_2, O_2 and N_2 for the series of segmented polybutadiene polyurethanes are presented in *Figures 1, 2* and *3*. (Refer to Part 1 for the system description and the experimental results.) The sensitivity of the fitting to the absolute solubility values is also described.

A comparison of the EMT model with the data gives a reasonably good fit with a coordination number equal to 6 with all three permeants. Mechanical property measurements also provide valuable information. A plot of modulus (initial slope from the tensile test measurements) vs. the SS composition is presented in *Figure 4*. At low HS contents this material is a soft rubber, at intermediate compositions the material behaves as a rigid elastomer, and at high HS it becomes a rubber-

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Table 1 Summary of transport studies of gases and vapours in phase-separated polymers (block and segmented) with the corresponding morphology and transport models

Ref.	System	Morphology/permeants	Transport model
14	MDI/BDO (HS) PTMA SS	30 wt% HS spheres of HS N_2, O_2, Ar, He, H_2	Higuchi's model
16	PSX/PSF	21–76 wt% PSF spheres O_2, N_2	Maxwell's model
20	SBS	26 vol% PS cylinders PS	Michael–Bixler's model
	SB	37 vol% PS lamellae inert gases	
17	MDI/BDO (HS) PTMA, PTMEG (SS)	30–47 wt% HS domains O_2, H_2, CO_2	Mobility restrictions
22	SBS	27.7 wt% PS cylinders PS cyclohexane vapours	Sigmoidal sorption
21	SBS	26 vol% PS cylinders PS	Two-stage sorption Thickness anomalies
	SB	37 vol% PS lamellae n-hexane vapours	
18	MDI/BDO (HS) PTMO (SS)	48.6 wt% HS glassy HS domains ODCBZ vapours	Diffusion–relaxation
23	SBS	29.3 wt% PS lamellae	Non-Fickian sorption
	SB	5–85 wt% PS cyclohexane vapours	

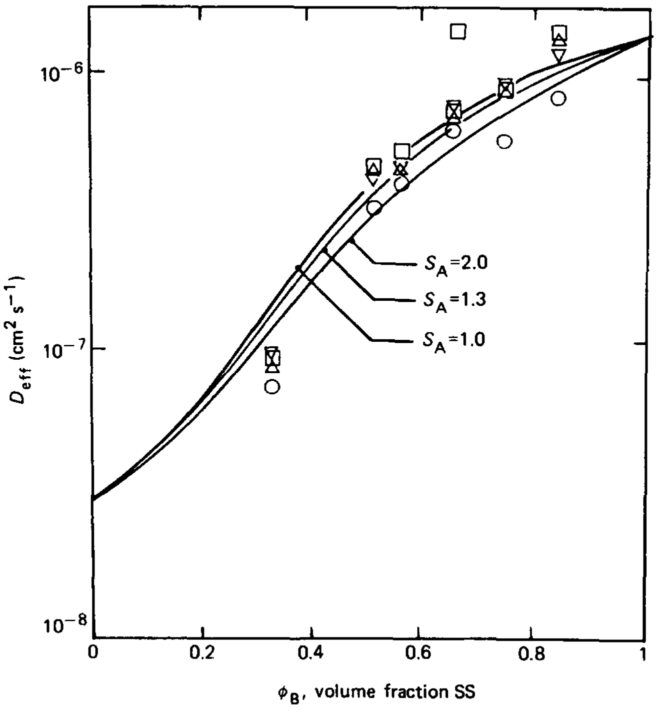

Figure 1 Application of the effective medium theory (EMT) to the transport properties of CO_2 polybutadiene polyurethanes for three solubilities in the A phase (S_A) (S_B=1.00 cc(STP)/cc.atm)

toughened plastic. Phase inversion from the mechanical (*Figure 4*) and transport data appears to occur about 55 vol% of soft segment.

Even though one can represent the transport properties of segmented polyurethanes by EMT, caution is advised. Structural complexities in this class of copolymers limit the straightforward application of the theory. The results from the solubility measurements suggest interaction between the permeant and the microphases. The possible presence of a significant interfacial region and/or

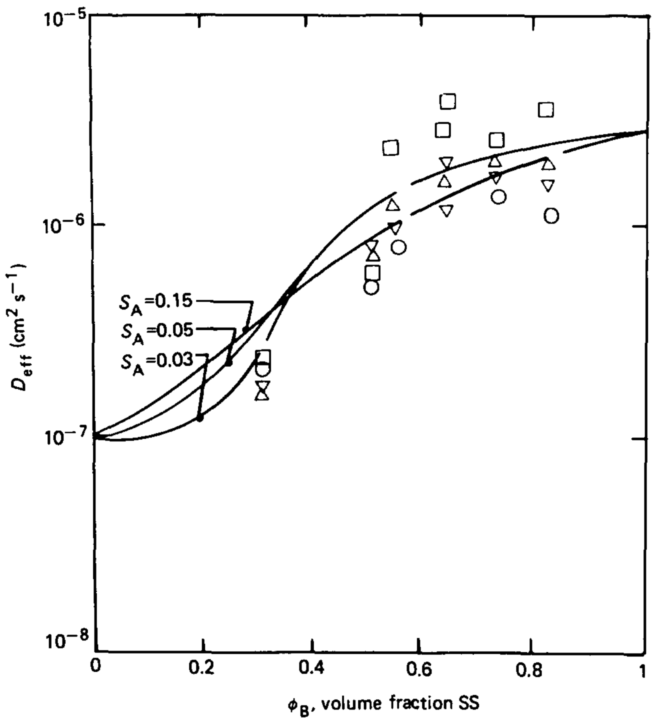

Figure 2 Application of the effective medium theory (EMT) to the transport properties of O_2 in polybutadiene polyurethanes for three solubilities in the A phase (S_A) (S_B=0.050 cc(STP)/cc.atm)

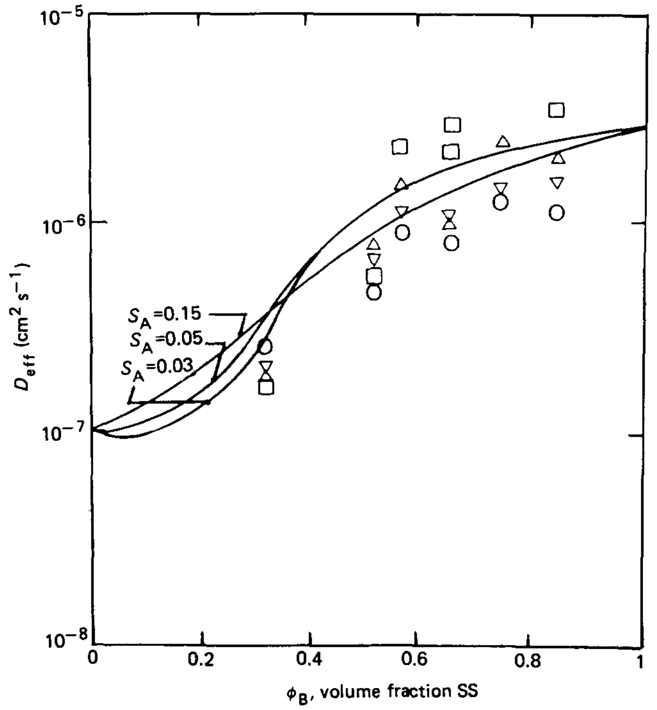

Figure 3 Application of the effective medium theory (EMT) to the transport properties of N_2 in polybutadiene polyurethanes for three solubilities in the A phase (S_A) (S_B=0.15 cc(STP)/cc.atm)

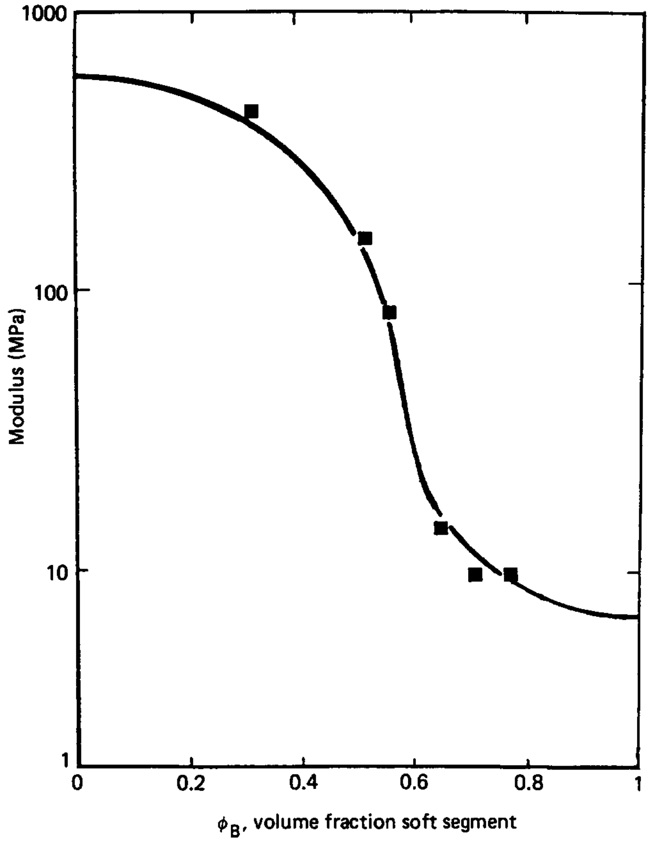

Figure 4 Modulus as a function of the volume fraction of the soft segment in PBD polyurethanes

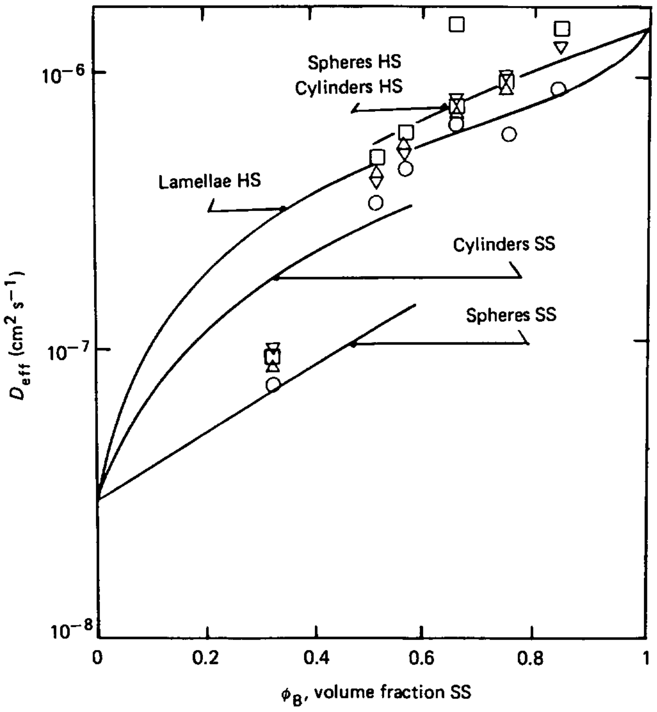

Figure 5 Morphological predictions from models with ordered microstructures and disordered macrostructures for the transport of CO_2 in polybutadiene polyurethanes ($S_A = 1.25$, $S_B = 1.4$ cc/(STP)/cc.atm)

incomplete phase separation are also not taken into account in the EMT model.

Another simple model is based on the presence of locally ordered microstructures (lamellar, cylindrical, etc.) which are disordered on large scales[26]. The predictions of such models for our polyurethane system are shown in *Figures 5* to *10*; small changes in solubility values are shown for each penetrant (CO_2, *Figures 5* and *6*; O_2, *Figures 7* and *8*; and N_2, *Figures 9* and *10*). The behaviour of all three permeants is consistent with the presence of equivalent domain structures, although more scattering is found in the results with N_2 and O_2 due to experimental uncertainties. A transition from a dispersed HS domain morphology to a continuous glassy HS phase occurs between 50 and 75% HS. Spheres of SS in a HS matrix are predicted at 75 wt% HS, followed by a

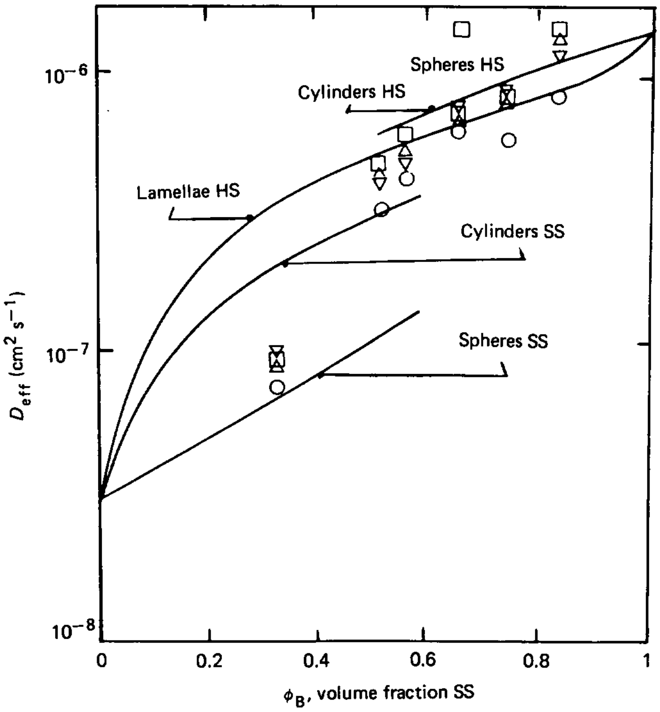

Figure 6 Morphological predictions from models with ordered microstructures and disordered macrostructures for the transport of CO_2 in polybutadiene polyurethanes ($S_A = S_B = 1.00$ cc(STP)/cc.atm)

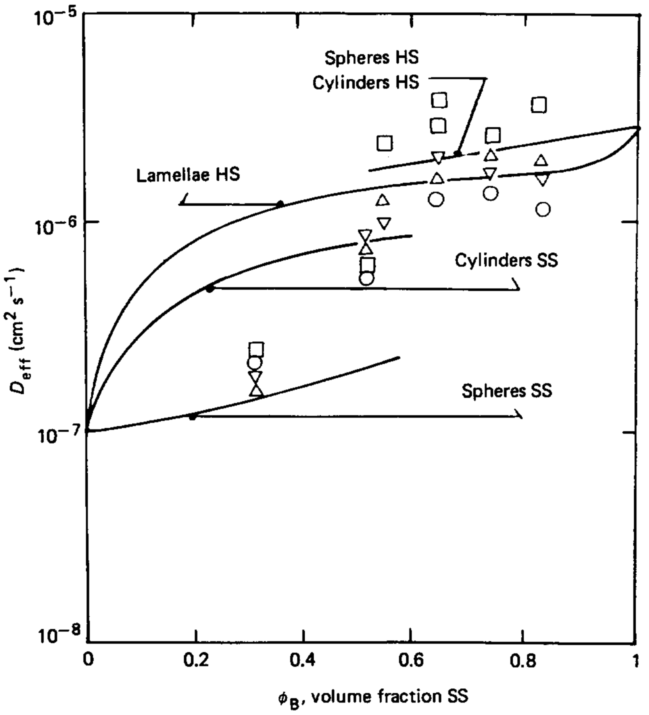

Figure 7 Morphological predictions from models with ordered microstructures and disordered macrostructures for the transport of O_2 in polybutadiene polyurethanes ($S_A = 0.05$, $S_B = 0.15$ cc(STP)/cc.atm)

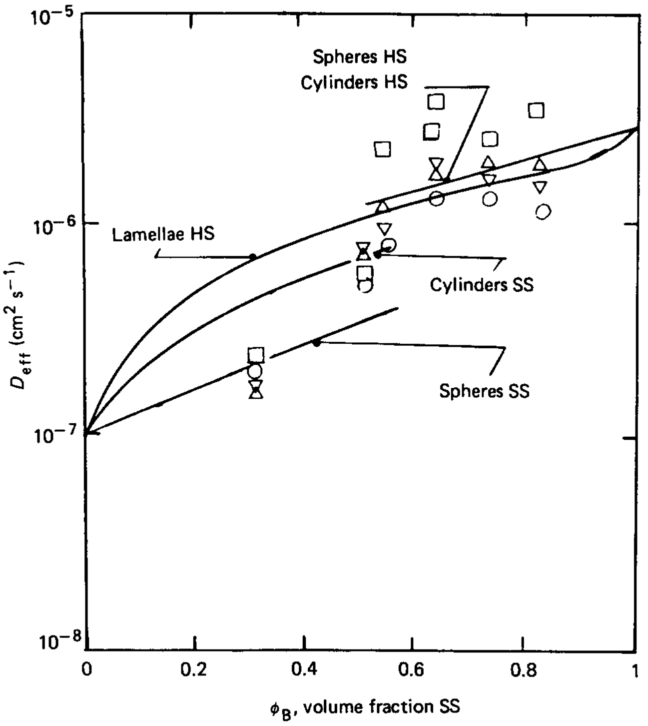

Figure 8 Morphological predictions from models with ordered microstructures and disordered macrostructures for the transport of O_2 in polybutadiene polyurethanes ($S_A = S_B = 1.00$ cc(STP)/cc.atm)

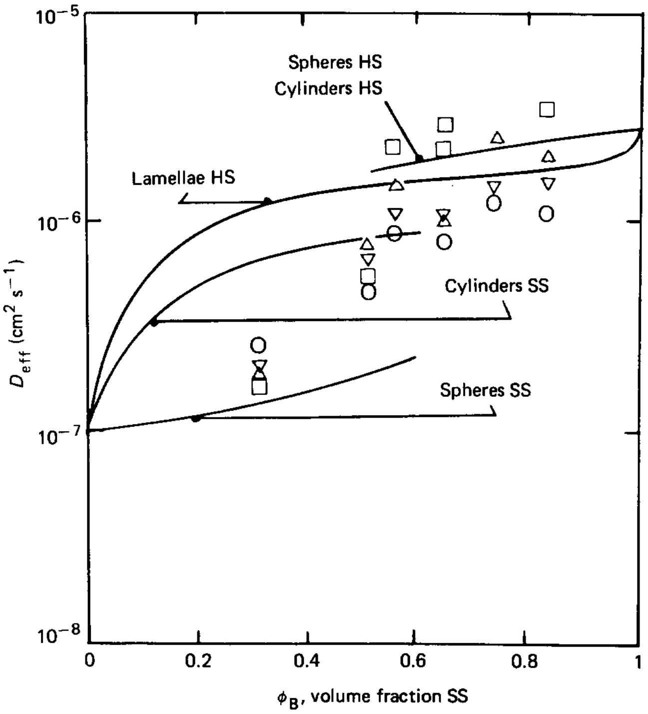

Figure 9 Morphological predictions from models with ordered microstructures and disordered macrostructures for the transport of N_2 in polybutadiene polyurethanes ($S_A = 0.05$, $S_B = 0.15$ cc(STP)/cc.atm)

lamellar morphology at 55 wt% HS, and cylinders or spheres of HS in the dilute range of HS content. Anisotropic domains (cylinders) of HS were suggested by SAXS of the same samples[29,30].

THE DIFFUSION–RELAXATION MODEL

Non-Fickian behaviour is frequently observed for the diffusion of organic vapours and liquids in glassy polymers[31–34]. A useful classification of non-Fickian behaviour was proposed by Alfrey *et al.*[35] by considering the relative rates of diffusion and relaxation. A criterion for the prediction of whether or not transport is diffusion or relaxation controlled is the diffusional Deborah number[36] which is defined as the ratio of a characteristic mean relaxation time to a characteristic diffusion time.

Unfortunately, there is not a single mathematical model which successfully predicts all the experimental deviations from Fick's Law observed in the transport of gases and vapours in polymers[37,38]. Models have been proposed by Berens[39] and Berens and Hopfenberg[19]; they have been extended by Joshi and Astarita[40] and recently reviewed by Astarita and Nicolais[41]. These empirical models describe the mass uptake in glassy materials as due to a combination of (a) Fickian and (b) relaxation components.

When the transfer of heat or mass into polymers involves structural changes in which there are rearrangements of the polymer segments, the kinetics of these changes can be coupled to the transport process. Experimental evidence for this situation is presented by Bagley and Long[42] and Long and Richman[43] for the transport of acetone into cellulose acetate films. A two-stage behaviour suggests a gradual change in the material taking place on a much longer time scale than diffusion.

In our case the two-stage behaviour is most noticeable with CO_2. Hence our modelling efforts will concentrate on this permeant. A simple model to interpret the observed anomalous behaviour in the transport of CO_2 in segmented polybutadiene polyurethanes can be developed on the basis of the model proposed by Joshi and Astarita[40] to study copolymers of glassy and rubbery components. A time dependent surface concentration proportional to the amount of glassy material exposed at the interface is used as the boundary condition. The diffusional contributions are based on EMT, while relaxational parameters are obtained from the fitting of the model to the glassy component (HS).

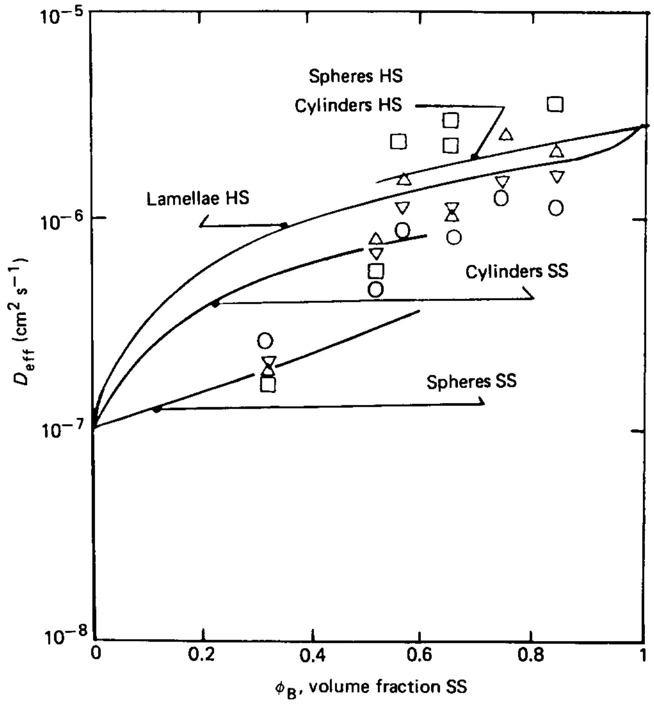

Figure 10 Morphological predictions from models with ordered microstructures and disordered macrostructures for the transport of N_2 in polybutadiene polyurethanes ($S_A = 0.10$, $S_B = 0.15$ cc(STP)/cc.atm)

The extent of coupling between diffusion and relaxation is given by the parameter ϕ_e, the ratio of the effective diffusion time (θ_D) to the relaxation time (θ_R) in the glassy material:

$$\phi_e=\left(\frac{\theta_D}{\theta_R}\right)^{1/2}=\left(\frac{L^2}{4D_e\theta_R}\right)^{1/2} \tag{1}$$

where $L/2$ is the sample half-thickness, and D_e is the effective diffusion coefficient predicted from the EMT.

The parameter m_e is the ratio of the residual driving force to the driving force for ordinary diffusion:

$$m_e=\frac{C_1^*-C_{10}}{C_1^*-C_0}=\frac{mS_A\phi_A}{S_A\phi_A+S_B\phi_B} \tag{2}$$

C_1^* is the equilibrium concentration at time infinity, C_0 is the initial concentration, and C_{10} is the instantaneous concentration established at the interface at the beginning of the experiment. The parameters m_e and θ_R are calculated from the fitting of the model to the pure hard segment copolymer sample, i.e. all the parameters can be obtained from the experimental data at $\phi_A=1$ and $\phi_B=0$.

Values of ϕ_e and m_e were calculated for each copolymer sample. A list of the parameter values for the transport of CO_2 in polybutadiene polyurethanes is shown in *Table 2*. From the fitting of the model to the hard segment sample, a characteristic relaxation time (θ_R) of 320 h and a value of $m_e=0.90$ was obtained. This value of m_e represents an initial mass uptake of 10% of the equilibrium M_∞. The model predictions are summarized in *Figure 11* where W is the dimensionless mass uptake. Increasing the hard segment content results in an apparent reduction in solubility for a short time experiment. This is in agreement with our experimental solubility values. The increased solubility in the glassy materials was computed in a long term experiment in the hard segment sample (Part 1). The appearance of a second stage is predicted to occur at approximately 5 h. Since our typical experiment was between 1 to 4 h the appearance of a second stage was observed in long term runs only.

Table 2 Effective transport properties of CO_2 in segmented polybutadiene polyurethanes using a model with EMT-relaxation ($D_A=3.00\times10^{-8}\,\text{cm}^2\,\text{s}^{-1}$, $D_B=1.34\times10^{-6}\,\text{cm}^2\,\text{s}^{-1}$, $S_A/S_B=1.20$)

ϕ_B	$\phi_e=\left(\frac{\theta_D}{\theta_R}\right)^{1/2}$	$m_e=\frac{mS_A\phi_A}{S_A\phi_A+S_A\phi_B}$	D_{eff} (cm^2 s^{-1})[a]	D_{model} (cm^2 s^{-1})[b] (with relaxation)
0.85	0.026	0.16	1.04×10^{-6}	9.99×10^{-7}
0.72	0.039	0.28	7.72×10^{-7}	7.39×10^{-7}
0.66	0.040	0.38	6.56×10^{-7}	6.27×10^{-7}
0.63	0.042	0.37	6.00×10^{-7}	5.71×10^{-7}
0.56	0.042	0.44	4.74×10^{-7}	4.52×10^{-7}
0.52	0.034	0.47	4.05×10^{-7}	3.86×10^{-7}
0.30	0.053	0.66	1.17×10^{-7}	1.08×10^{-7}

[a] Calculated from the EMT with D_A from the initial slope desorption experiment

[b] Calculated from the half-time method

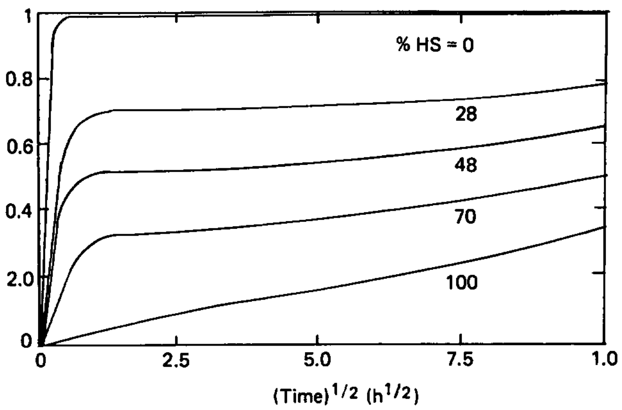

Figure 11 EMT-relaxation model predictions for the transport of CO_2 in a series of polybutadiene polyurethanes

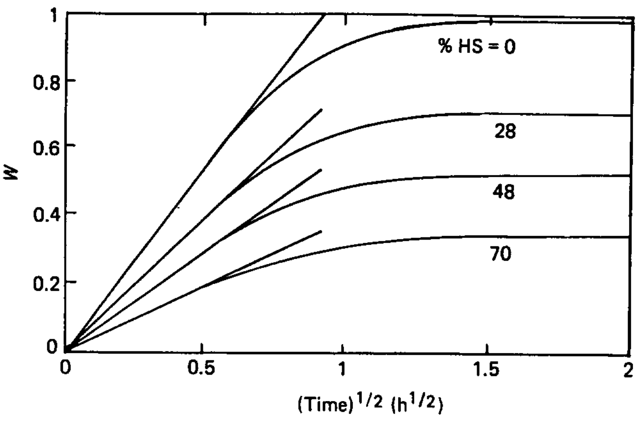

Figure 12 EMT-relaxation model predictions for the transport of CO_2 in a series of polybutadiene polyurethanes as a function of time ($t=\tau/\theta_D$)

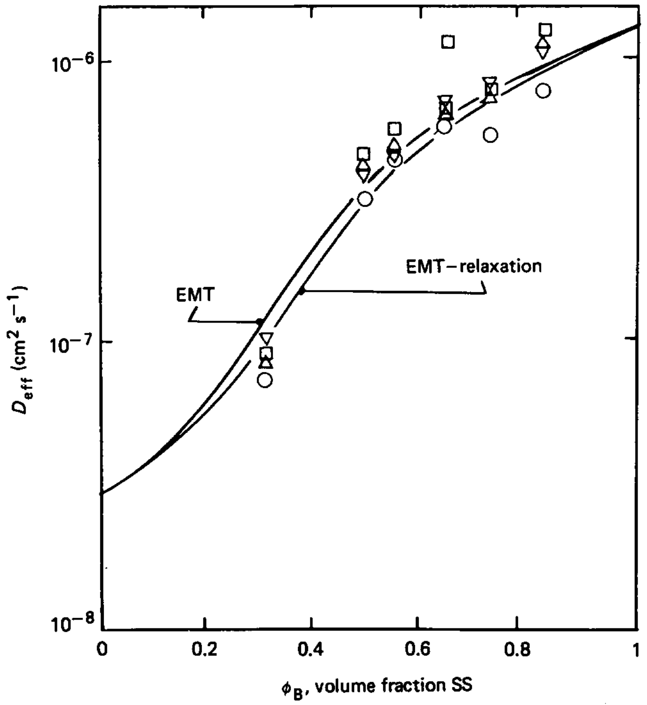

Figure 13 Comparison of the experimental results with the EMT and the EMT-relaxation model for the transport of CO_2 in polybutadiene polyurethanes

The initial stages of sorption predicted from our model can be considered approximately Fickian (*Figure 12*) up to $t/\theta_D\approx4$. Hence, the diffusion coefficient (D_{model}) was computed from the half-time method, using the first plateau as M_∞. This method and the initial slope method were used in the determination of our experimental diffusion coefficients.

A summary of the model predictions (EMT-relaxation) is given in *Figure 13*, along with the experimental results and the predictions from EMT. From the values of the model parameters ($\phi_e\ll1$), it is predicted that the transport of CO_2 in polybutadiene polyurethanes is dominated by relaxation in the hard segment phase.

CONCLUSION

The transport properties of O_2, N_2 and CO_2 in segmented polybutadiene polyurethanes (described in Part 1) were used as probes of the domain morphology. Model predictions using the effective medium theory and simple models involving ordered microstructures predict a spectrum of phase separated morphologies as a function of sample composition. Spheres of soft segment in a glassy matrix of hard segment (75 wt% HS), lamellar morphology at 55 wt% HS and cylindrical or spherical domains of hard segment in a rubbery matrix below 50 wt% HS. These morphological predictions are partly corroborated by the results of SAXS and TEM (Part 1) and the mechanical properties.

A simple transport model involving coupled diffusion and relaxation was used in the interpretation of the experimental results. Relaxation-controlled kinetics dominated the transport of CO_2 in glassy polyurethanes, while diffusion dominated the transport in the rubbery samples. The anomalous behaviour exhibited by the glassy materials was ascribed to the presence of a time-dependent boundary condition as a result of the hard segment material present at the surface.

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