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Effect of Antiplasticization on Gas Sorption and Transport. III. Free Volume Interpretation

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Synopsis

Previous papers have shown that antiplasticization of polysulfone and poly(phenylene oxide) by low molecular weight diluents is accompanied by substantial reductions in permeability to gases like helium, carbon dioxide, and methane because of reduced mobility in the glass. These effects are not explained even qualitatively by the extent of volume contraction on mixing for these mixtures. However, as shown here, a simple free volume treatment provides an excellent correlation of these effects. Free volume was computed from measured specific volume and an estimate of the volume at the absolute zero of temperature of the material from a group contribution method. Application of this approach to the mechanical stiffening associated with antiplasticization is suggested. The basis and limitations of this analysis are discussed.

INTRODUCTION

In the first two papers of this series,^{1,2} antiplasticization responses³⁻¹⁷ caused by the addition of low molecular weight diluents to polysulfone and poly(phenylene oxide) were described. In addition to the usually observed stiffening effect, it was found that incorporation of such diluents dramatically reduces the rate at which gases permeate these polymers in agreement with limited results reported previously.^{16,17} Although these diluents do decrease the extent of gas solubility, it is clear that the major effect on gas permeability is a reduction in mobility for migration of gas molecules in the glassy matrix consistent with a diminished rate of main chain motions believed to accompany antiplasticization.¹⁶ Neither the stiffening effect nor the reduction in gas permeability correlated even qualitatively with the observed nonadditivity of volume for these mixtures. Since both properties are related to the free volume of the polymer system, this seems somewhat surprising at first sight. However, as shown here, simple observation of volume nonadditivity does not fully indicate the changes in free volume of a mixture. Accounting for the free volume of the diluent in addition to the nonadditivity of volume on mixing does give a satisfactory correlation of the transport and mechanical behavior as described here.

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BACKGROUND

The intuitive notion of free volume is widely used in discussions of polymer properties,^{5,18-21} particularly those related to mobility or transport behavior with strong roots in the pioneering work of Hildebrand²² and Doolittle.^{23,24} Numerous models have appeared in the literature^{25,26} relating diffusional phenomena to free volume, most of which employ the theoretical framework developed by Cohen and Turnbull.²⁷ Generally, the theory predicts that quantities related to mobility vary exponentially with the reciprocal of free volume. A major limitation to the quantitative use of free volume theories is the lack of a sound operational definition of free volume or a means to measure it experimentally.^{15,28,29} Here we adopt the following simplistic definition of specific free volume:

$$\hat{V}_F = \hat{V} - \hat{V}_0 \quad (1)$$

where \hat{V} is the experimentally observed specific volume and \hat{V}_0 is an estimate of the specific volume at the absolute zero of temperature. A group contribution approach to the latter is used.

Lee³⁰ has employed a similar definition rather successfully for empirically correlating gas permeability of a wide range of polymers. His approach to \hat{V}_0 was to compute the van der Waals specific volume, \hat{V}_w , of the polymer from group contributions and to equate

$$\hat{V}_0 = 1.3\hat{V}_w \quad (2)$$

as suggested by Bondi.¹⁵ For a given gas, rather good correlations of the permeabilities for various polymers were obtained using

$$P = Ae^{-B/(\hat{V} - \hat{V}_0)} \quad (3)$$

where A and B are constants for each gas type. Such an approach implies that the solubility portion of the permeability coefficient does not vary much from polymer to polymer.

In what follows we will use this rather simple approach with one exception. The method of relating \hat{V}_0 to the van der Waals volume given by eq. (2) is empirical and somewhat arbitrary. Sugden³¹ has estimated \hat{V}_0 directly for a large number of compounds and developed a set of group contributions that represent these results rather well. We will use this method since it is simpler and more direct. We have also used the Bondi approach as Lee did, and these results are described fully elsewhere.³² Values for \hat{V}_0 obtained by the Sugden method are somewhat larger than those by the Bondi method as seen in Table I. However, the subsequent correlations obtained are qualitatively the same for each method; although, the Sugden approach gives slightly better quantitative correlations as described later.

For the present application we must address the estimation of \hat{V}_0 for mixtures. Since we are basically using this quantity as a measure of "occupied" volume, we assume as done previously³³ that it is an additive function of the

TABLE I
Estimates for \hat{V}_0 Using Group Contribution Methods

Name	Abbreviation	\hat{V}_0 (cm ³ /g)	
		Sugden	Bondi
Polysulfone	PSF	0.708	0.678
Poly(phenylene oxide)	PPO	0.773	0.750
Polystyrene	PS	0.836	0.785
Poly(methyl methacrylate)	PMMA	0.755	0.729
Polycarbonate	PC	0.773	0.694
Tetramethyl bisphenol-A polycarbonate	MPC	0.787	0.757
Poly(vinyl chloride)	PVC	0.666	0.595
Poly(vinyl benzoate)	PVB	0.728	0.685
Polyethersulfone	PES	0.694	0.616
Tricresyl phosphate	TCP	0.744	0.695
4,4'-Dichlorodiphenyl sulfone	DDS	0.629	0.593
N-phenyl-2-naphthylamine	PNA	0.794	0.743
Kronitex 50	Kronitex 50	0.774	0.688
Di-2-ethylhexyl phthalate	DOP	0.885	0.814
Dioctyl sebacate	DOS	0.945	0.862

mixture, i.e.,

$$\hat{V}_0 = (\hat{V}_0)_d w + (\hat{V}_0)_p (1 - w) \quad (4)$$

where subscripts d and p refer to diluent and polymer, respectively, and w is the weight fraction of diluent in the mixture. Since the excess specific volume, as defined previously,¹ is

$$\Delta\hat{V}_e = \hat{V} - [\hat{V}_d w + \hat{V}_p (1 - w)] \quad (5)$$

then it is easy to see that the free volume of the mixture is

$$\hat{V}_F = \hat{V} - \hat{V}_0 = [(\hat{V} - \hat{V}_0)_d w + (\hat{V} - \hat{V}_0)_p (1 - w)] + \Delta\hat{V}_e \quad (6)$$

CALCULATED FREE VOLUME FOR MIXTURES

The scheme outlined above was used to estimate the free volumes for mixtures of polysulfone, PSF, and poly(phenylene oxide), PPO, with the various diluents employed in the previous papers.^{1,2} The results are shown in Figures 1 and 2. According to eq. (6), the dashed line connecting values of the free volume of the pure components is the result expected if simple volume additivity occurs, whereas the deviation from this ideal is the excess volume of mixing. A major factor affecting the behavior of the mixtures is the free volume of the diluent relative to that of the pure polymer.

As may be seen in Figure 1, the free volumes of the diluents used in the polysulfone study, as calculated by this approach, stand in the order TCP > DDS > PNA, with TCP being the only one with a larger free volume than polysulfone. The extents of deviation from volume additivity, or excess

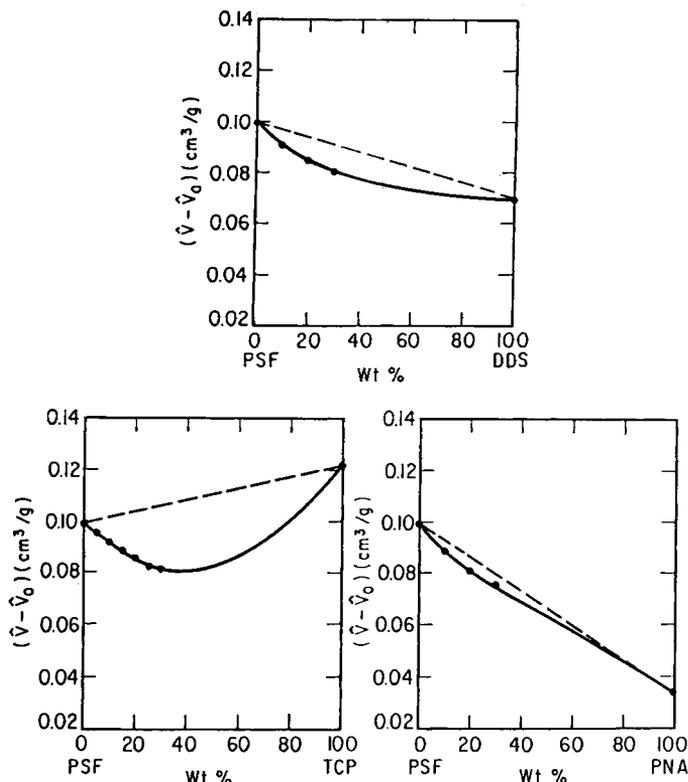


Fig. 1. Free volume of mixtures of polysulfone with various diluents calculated from experimental specific volumes at 30°C and the Sguden method to estimate \bar{V}_0 .

volumes, with polysulfone stand in exactly the same order, i.e., TCP > DDS > PNA, as noted previously.¹ The absolute free volume of the diluent, in this case, dominates the free volume of the mixture, such that the effectiveness for reducing free volume of polysulfone stands in the order PNA > DDS > TCP, which agrees with the ranking of antiplasticization response.¹

On the other hand, TCP and its close structural relative, Kronitex 50, have lower free volumes than poly(phenylene oxide), whereas DOS is about the same as PPO. The value for DOP lies between those for DOS and TCP. Although the departure from volume additivity decreases in the order DOS > DOP > TCP as mentioned previously,² the effectiveness in reducing free volume of poly(phenylene oxide) lies in the order TCP > DOP > DOS, which also agrees with the ranking of antiplasticization response. Thus, it is qualitatively clear that excess volume of mixing is only a part of the issue in antiplasticization and that the absolute volume of the diluent free volume must also be considered. The next two sections quantify the correlations with free volume.

CORRELATION OF TRANSPORT BEHAVIOR

Strictly speaking, the free volume treatments mentioned earlier only consider mobility, whereas the permeability coefficient is a product of thermo-

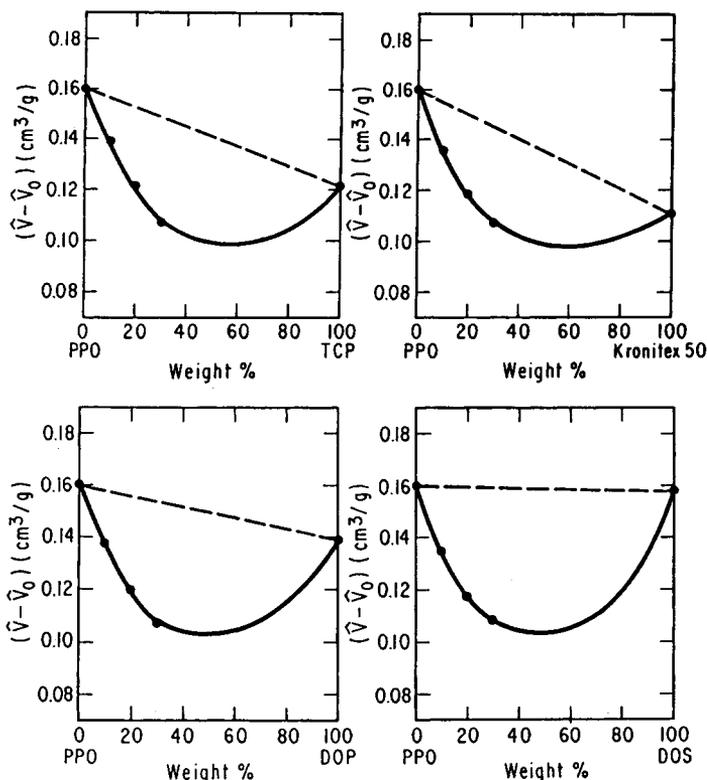


Fig. 2. Free volume of mixtures of poly(phenylene oxide) with various diluents as described in Figure 1.

dynamic and transport terms. To separate the permeability into its thermodynamic, or solubility, and its mobility, or diffusion coefficient, parts require information about the penetrant sorption isotherm. For the systems of interest here, this information has only been obtained for CO_2 , so it is the only penetrant that can be examined in this way. To obtain a simple model-independent measure of the CO_2 diffusion coefficient, we arbitrarily selected a pressure of 10 atm and computed an average effective diffusion coefficient, \bar{D} , from the permeability at a 10 atm driving pressure and the amount of gas sorbed by the polymer at 10 atm, C , i.e.,

$$\bar{D} = \frac{P \cdot p_2}{C} \text{ at } p_2 = 10 \text{ atm} \quad (7)$$

Values of \bar{D} for CO_2 in poly(phenylene oxide) (PPO), polystyrene (PS), polycarbonate (PC) and for polysulfone (PSF) were computed from measured P and C with the results plotted as a function of the free volume computed from experimental density and the \hat{V}_0 using Sugden's method as the solid points shown in Figure 3. As expected from Lee's analysis, a reasonably good straight line correlation of these points is obtained for the coordinates employed in Figure 3. The open circles represent similar calculations for mixtures of PPO and PSF with the various diluents employed in the previous papers.^{1,2}

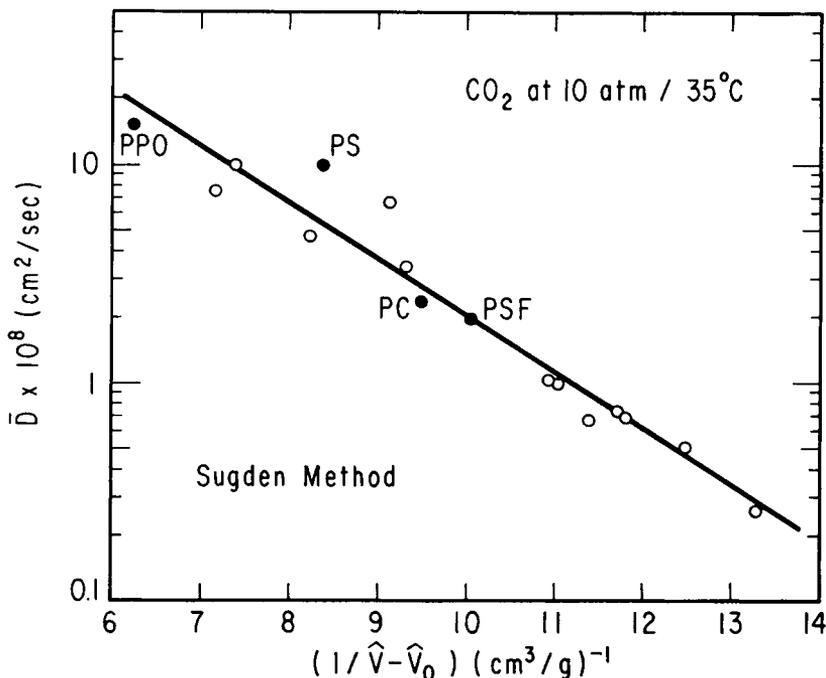


Fig. 3. Correlation of average diffusion coefficient of CO_2 at 35°C in various pure polymers (solid points) and mixtures of PSF and PPO with diluents (open points) with free volume.

The data for the mixtures fit very well the correlation established by the pure polymers, indicating that the free volume as computed from eq. (6) accounts fully for the effects of antiplasticization on the CO_2 diffusion coefficient. Mixture points such as those for high concentrations of DOS in PPO, where significant upturn in permeability versus diluent concentration occurred, have been omitted from this plot for reasons that will be given later.

Since solubility effects do not vary as much from polymer to polymer as mobility does, one is somewhat justified in attempting similar free volume correlations of the composite permeability parameter as did Lee.³⁰ Our results for helium, carbon dioxide, and methane are shown in Figures 4, 5, and 6, respectively. Some additional pure polymers have been included to expand the basis for the correlation and these include MPC (tetramethyl bisphenol-A polycarbonate),³⁴ PVB [poly(vinyl benzoate)],³⁵ PES (polyethersulfone),³² PMMA [poly(methyl methacrylate)],³⁶ PVC [poly(vinyl chloride)],³⁷ and PC (polycarbonate).³⁸ In general the correlations for these pure polymers are quite good. In a few cases there are rather significant deviations that may stem from a variety of causes that will not be enumerated here. The open points correspond to data for mixtures of PPO and PSF with diluents.^{1,2} It is quite clear that the mixture results are well correlated by the same relationships that approximately represent the pure polymer data. Thus, this simple free volume approach gives a satisfying unification of the effects of antiplasticization on gas permeability behavior. To the level of correlation shown here, solubility considerations are evidently of secondary importance.

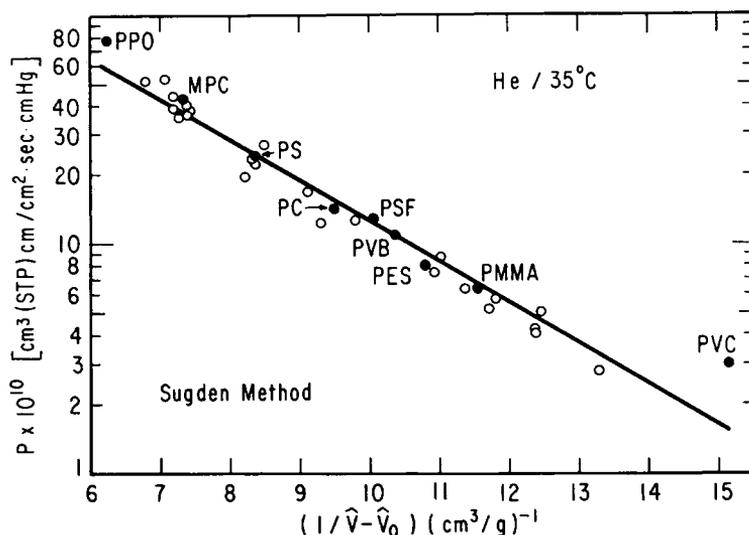


Fig. 4. Permeability-free volume correlation for helium at 35°C. Pure polymers (●), mixtures (○).

Table II lists the values of the parameters A and B in eq. (3) obtained for each gas by statistically fitting the data in Figures 4–6 to this equation. Values obtained for A and B , when the method by Bondi was used to estimate the free volume, are also shown in Table II. A statistical correlation coefficient was also computed in each case to give a measure of the quality of the fit. Based on this measure, the fits obtained using the Sugden method

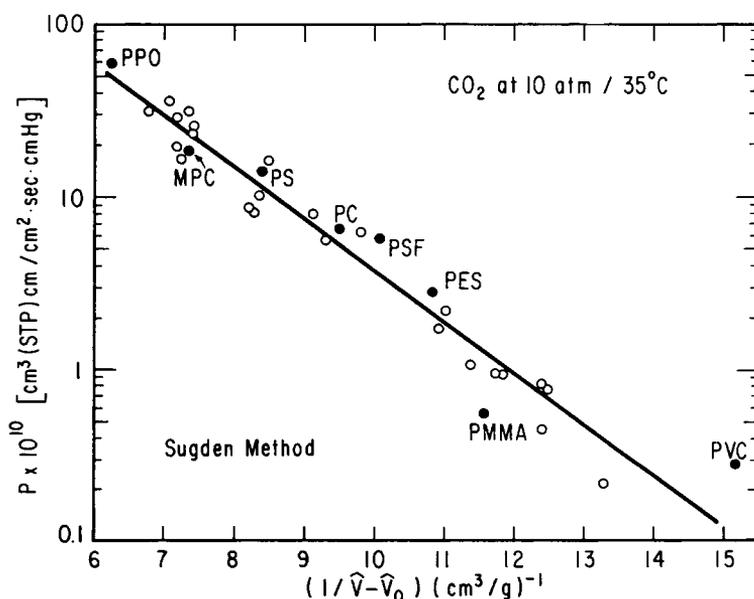


Fig. 5. Permeability-free volume correlation for carbon dioxide at 35°C. Pure polymer (●), mixtures (○).

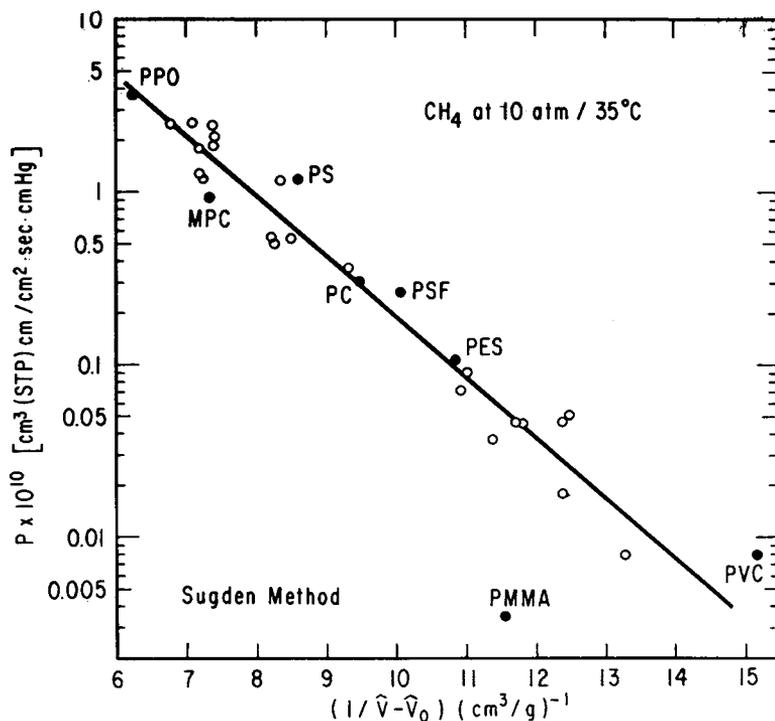


Fig. 6. Permeability-free volume correlation for methane at 35°C. Pure polymers (●), mixtures (○).

were substantially better than those based on free volume from the Bondi method, which is the reason a preference for the former was stated previously.

CORRELATION OF MECHANICAL BEHAVIOR

Intuitively, the stiffening effect associated with antiplasticization^{1,2} may also be related to the loss in free volume. To quantify this we plot the storage modulus of mixtures of PSF and PPO with diluents reported earlier, for an arbitrary low temperature, versus free volume on simple arithmetic coordi-

TABLE II
Parameters for Permeability—Free Volume Correlation

Method for estimating \hat{V}_0	Gas	A^a $\left[\frac{\text{cm}^3 (\text{STP}) \cdot \text{cm}}{\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}} \right]$	B^a (g/cm ³)	Correlation coefficient
Sugden	He	7.60×10^{-8}	0.409	0.981
	CO ₂	3.74×10^{-7}	0.690	0.974
	CH ₄	6.18×10^{-8}	0.808	0.942
Bondi	He	3.86×10^{-6}	0.780	0.923
	CO ₂	6.56×10^{-6}	1.333	0.929
	CH ₄	2.17×10^{-6}	1.589	0.915

^aCoefficients *A* and *B* in eq. (3).

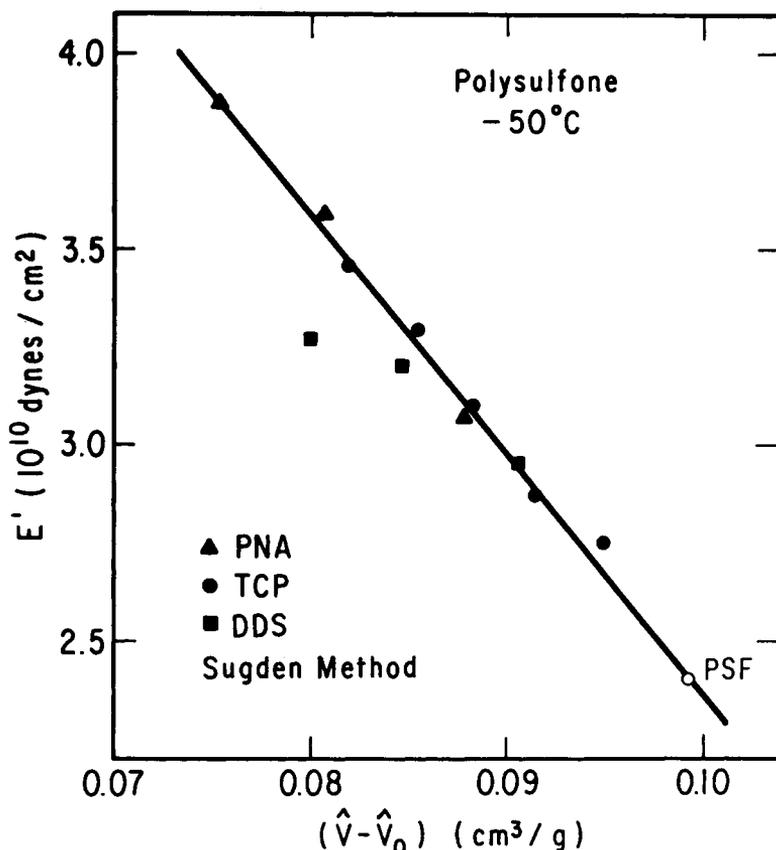


Fig. 7. Correlation of the storage modulus at -50°C for polysulfone-diluent mixtures with free volume at 30°C . Open point is value for pure polysulfone. Frequency = 110 Hz.

nates in Figures 7 and 8. A remarkably good correlation is seen in Figure 7 for polysulfone mixtures, whereas a similar trend is seen in Figure 8 for PPO, although the correlation is not as good quantitatively for the latter as for the former.

Note that in these plots we are attempting to relate mechanical behavior at -50°C for PSF and -100°C for PPO to free volume at 30°C . This has obvious problems, but there is no alternative since volumetric data at these low temperatures are not available, and at 30°C the mechanical behavior is already influenced to a serious degree by the lowering of T_g by the diluents. Our point here is simply that to a certain degree the mechanical stiffening effect associated with antiplasticization can be understood in terms of the same type of free volume analysis successfully used for transport behavior.

It is interesting to note that the slopes in Figures 7 and 8 differ by a factor of 2.5–4. A reduction in free volume for PPO systems causes less increase in modulus than for PSF systems even though the comparison is made at a higher temperature for PSF than for PPO. Thus, we may say that PPO is less prone to mechanical antiplasticization than PSF. One might speculate that this propensity is related to the fact that PSF has a much more pronounced

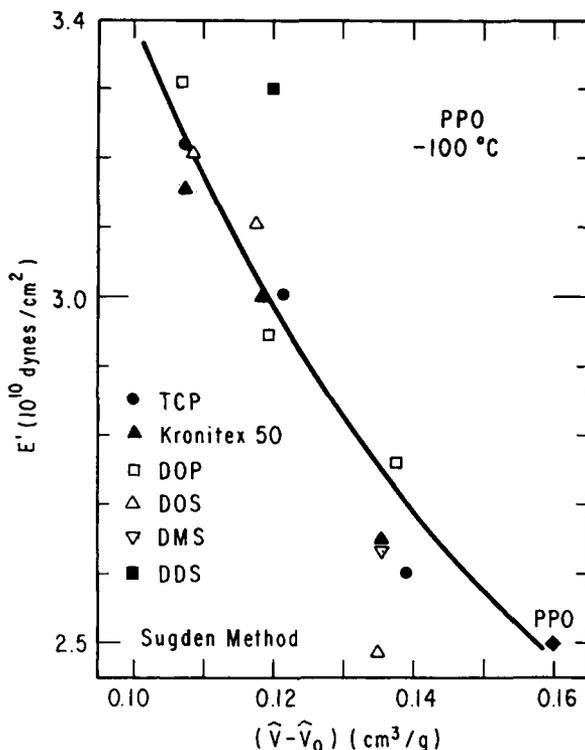


Fig. 8. Correlation of the storage modulus at -100°C for poly(phenylene oxide)-diluent mixtures with free volume at 30°C . Point for pure PPO is labelled. Frequency = 110 Hz.

sub- T_g relaxation mechanism than does PPO. Addition of diluents greatly suppresses the sub- T_g relaxation peak of PSF,¹ whereas certain diluents seem to create low temperature relaxation mechanisms in PPO.²

SUMMARY

A simple free volume approach has been used successfully to correlate, and to this extent explain, the reduction in gas permeability that occurs when certain diluents are added to polysulfone and poly(phenylene oxide). These diluents cause a reduction in mixture-free volume that leads to a decrease in penetrant mobility in the glassy mixture. The solubility of the gas in the polymer is also changed, but this is of lesser importance. The free volume was calculated from the observed specific volume and an estimated occupied volume obtained from group contribution schemes intended to give the specific volume at absolute zero of temperature. The occupied volume for mixtures was assumed to be a simple additive contribution from each component. The group contribution scheme developed by Sugden seems to be somewhat better for this purpose than the one suggested by Bondi and used by Lee. On the other hand excess volume of mixing alone does not explain the observed results of antiplasticization, since it fails to account for the influence of the absolute free volume of the diluent. Based on these results, the most effective antiplasticizer for any given polymer should be the one having the

lowest free volume that is miscible with the polymer. However, unusually large volume contractions on mixing could override this simple prescription although no case of this was observed here.

The present approach offers no attempt to explain or to rationalize the magnitude of the excess volume of mixing observed. Presumably this is a thermodynamic characteristic of the polymer-diluent pair, although the fact that one of the components, the polymer, is a nonequilibrium glass cannot be ignored. In this regard we point out an observation that may be important or simply fortuitous. In the cases reported here, the smaller the free volume of the diluent, the smaller the volume contraction on mixing. There seems to be some compensating effect between these two issues in their combined effect on total free volume. That is, for a diluent with a high free volume such as DOS, the excess volume of mixing with PPO is strongly negative. Whereas a diluent with a very low free volume such as PNA has a very small negative excess volume of mixing with PSF. TCP, which has a larger free volume than does PSF, causes a reduction in free volume because of its relatively large negative excess volume of mixing with PSF. However, TCP has a lower free volume than PPO, and its volume contraction on mixing with PPO, although large, is not as great as that for DOS, which has a larger free volume. A more extensive investigation of these issues seems warranted.

The mechanical stiffening associated with the classical use of the term antiplasticization seems to be rationalized to an extent by this free volume approach. Further development of this relationship and its limitations would be useful.

As a final point, we wish to emphasize that a free volume analysis of this type cannot fully account for all transport behavior (or mechanical behavior) except in a rather limited context. For example, the free volume of TCP as computed here is less than that of PPO, although the latter is a glass and the former a liquid. Of course, the two have very different molecular weights. As noted earlier,² it is quite reasonable to believe that the "permeability" of gases through TCP is orders of magnitude greater than that through PPO. Thus, permeability or even mobility cannot map one-to-one with free volume across the entire spectrum of PPO-TCP mixtures as eq. (3) suggests. We believe that correlations of the type shown here must be limited in scope. In the present case we believe that these correlations ought to be limited to comparison of systems that are all in the glassy state, and systems close to their T_g or above it should not be compared. Even within this constraint, one should not be surprised to find glassy systems that do not fit the correlations shown because of special solubility considerations or polymer local segmental motions that are not especially sensitive to free volume.

These studies show that incorporation of low molecular weight diluents in glassy polymers can result in improvement in gas barrier characteristics that may be useful in cases where the concomitant decrease in glass transition temperature can be tolerated. As described in another paper,³⁹ the alteration in selectivity of gas transport that sometimes accompanies antiplasticization may be of interest for membrane separation processes.

This research was carried out with the financial assistance of the National Science Foundation, grants DMR-80-01665 and CPE-83-06952.

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Received April 8, 1986

Accepted September 16, 1986