

Transport Properties of Filled Elastomeric Networks

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Synopsis

The transport properties of networks filled with carbon black have been studied in order to obtain information on the rubber-filler interactions. The obtained results show that the filling particles can be completely or partially excluded from the transport phenomena which occur mainly in the rubberlike matrix. The transport properties of the pure components, compared with the filled system, allow to obtain a possible evaluation of the interphase phenomena.

INTRODUCTION

The use of carbon black as filling component in elastomeric networks is a mature technology to improve durability and mechanical properties. However, the filling mechanism is not completely clear and the current literature on this topic is still now very rich. Filling mechanism and interphase phenomena have been studied using many different analytical approaches and the argument has been reported in several reviews.¹⁻⁵ In this study we report some preliminary results obtained analyzing the transport properties of filled networks; the aim is to verify the possibility that transport parameters can be used to investigate topology and interactions between matrix and filler. The analysis of transport properties has indeed been used to investigate the structural organization and the molecular mobility in semicrystalline polymers^{6,7}; in these systems the crystalline component is impermeable and the transport phenomena occur in the amorphous component only. Such a selectivity is a very useful base that permits one to analyze the transport parameters as directly related to the morphological organization of the crystalline impermeable phase, and to the thermodynamic state of the amorphous phase, mainly in terms of molecular motions and relaxations.^{8,9} In some aspects, a semicrystalline polymer, over its glass transition, can be considered as a filled system in which rigid filling particles, the crystalline domains, are dispersed in a mobile amorphous matrix. Of course this model is roughly acceptable only when the crystallinity is not so high as to drastically reduce the molecular mobility and to interrupt the continuity of the amorphous phase which behaves as the matrix of the biphasic system. This is a possible base to adopt the analysis of the transport properties as an experimental approach to study the structural organization of rubbers filled with carbon black. However it is not known *a priori* if the carbon black behaves as an impermeable component; it is not known to what extent the surface of the filling particles can contribute to the transport phenomenon, and, at last, one

cannot predict if eventual interphase layers can behave differently from the rubberlike matrix. In this article we try to give an answer to these preliminary questions and conclude that a systematic analysis of the transport properties can indeed be useful to clarify some aspects of the complex mechanism of the filling phenomenon.

TRANSPORT PROPERTIES

The analysis of the transport properties adopted here allows us to obtain the diffusion coefficient \bar{D} , and the equilibrium concentration of the permeant in the bulk polymer C_{eq} , and, from these parameters, the permeability and the sorption can be derived. In particular the experimental method we used is the microgravimetric method previously described¹⁰; the sample is suspended to a calibrated quartz spring (20 mm/mg) and immersed in the permeant vapors atmosphere at the chosen activity (P/P_0), where P is the actual pressure and P_0 is the saturation pressure at the experiment temperature. The sample weight is detected as a function of time and, if the observed behavior is fickian, the initial stage of the permeation phenomenon, in a wide time range, can be described by the following equation⁷

$$C_t/C_{\text{eq}} = 4/d\sqrt{\bar{D}t/\pi} \quad (1)$$

where C_t is the concentration at time t and d the sample thickness. At each vapor activity, \bar{D} can be obtained from the slope of the straight line C_t/C_{eq} vs. \sqrt{t} . In a biphasic system in which one component only is permeable, \bar{D} and C_{eq} are related to structural and thermodynamic parameters according to the following relationships. The first relates \bar{D} to a structural parameter ψ

$$\bar{D} = D_p \cdot \psi \quad (2)$$

where D_p is the specific diffusion coefficient of the permeable phase and ψ is a parameter, always less than or equal to 1, that takes into account the tortuosity of the diffusion path, and the presence of blocking factors, both depending on the amount and morphology of the impermeable phase. Moreover \bar{D} is related to the permeant concentration according to

$$\bar{D} = D_0 \exp(\gamma c) \quad (3)$$

where D_0 is the thermodynamic diffusion coefficient of the dry polymer ($c = 0$). The concentration coefficient γ is related to the fractional free volume F by the simple relationship

$$\gamma = B/F^2 \quad (4)$$

where B is a constant related to the system polymer-permeant.⁸ It is well known that, according to the Doolittle theory,¹¹ the fractional free volume is directly correlated to the molecular mobility, and it is increasing when the latter increases. D_0 is also depending on F according to

TABLE I
Chain Microstructure and Molecular Weight

	HCBR	HVBR	SBR
1,4 cis %	97.0	11.5	10.4
1,4 trans %	2.0	16.5	51.8
1,2 vinyl %	1.0	72.0	11.8
Styrene %	—	—	26.0
$M_w \times 10^{-3}$	457	310	306
$M_n \times 10^{-3}$	102	136	90
M_w/M_n	4.5	2.3	3.4

$$D_0 = A \exp(-k/F) \quad (5)$$

where k and A are constants, and finally C_{eq} can be described as a linear function of F . Therefore, D_0 and γ exponentially, C_{eq} linearly, the transport parameters can be correlated to the molecular mobility in the permeable phase. Eqs. (2), (3), (4), and (5) show quantitatively how the transport parameters are related to thermodynamic and structural features.

MATERIALS AND EXPERIMENTAL

Three different polymeric systems were analyzed, a high cis-1,4 polybutadiene (HCBR), a high vinyl-1,2 polybutadiene (HVBR), and a styrene-butadiene random copolymer (SBR). The chain microstructure and molecular weights are reported in Table I. The filler was a carbon black produced by Phillips Carbon Black Italiana S.p.A.; commercial code HAF N375.

Filled samples (herein indicated as black) and unfilled samples (indicated as gum) were vulcanized using a peroxide as initiator, and curing at 160°C for 40 min. The composition of the curing mixtures is reported in Table II, and is given as parts in weight.

The transport properties were analyzed at 25°C according to the procedure previously reported.¹⁰ Methylene chloride and n-pentane were used as permeant

TABLE II
Crosslinked Samples

	HCBR	HVBR	SBR
<i>Gum samples</i>			
Polymer	100	100	100
Peroxide	0.80	0.31	1.75
<i>Black samples</i>			
Polymer	100	100	100
Carbon black	50	50	50
Peroxide	0.80	0.31	1.75

TABLE III
Mechanical Parameters

Sample	$\sigma_{\lambda=1.5}$	$\sigma_{\lambda=4}$	σ_f	λ_f
HCBR gum	0.89	—	1.2	1.85
HCBR black	1.12	10.0	17.6	5.30
HVBR gum	1.24	—	1.3	1.55
HVBR black	1.05	6.4	12.8	6.0
SBR gum	0.58	—	2.3	3.60
SBR black	1.1	10.7	19.5	5.70

σ is given in MPa.

vapors. Some significant mechanical parameters were obtained using an Instron dynamometer.

RESULTS

Mechanical Properties

In Table III we report some mechanical parameters of gum and black samples. In particular the stress σ_λ is reported at different strain values λ , and the ultimate properties are reported as stress σ_f and strain λ_f at fracture.

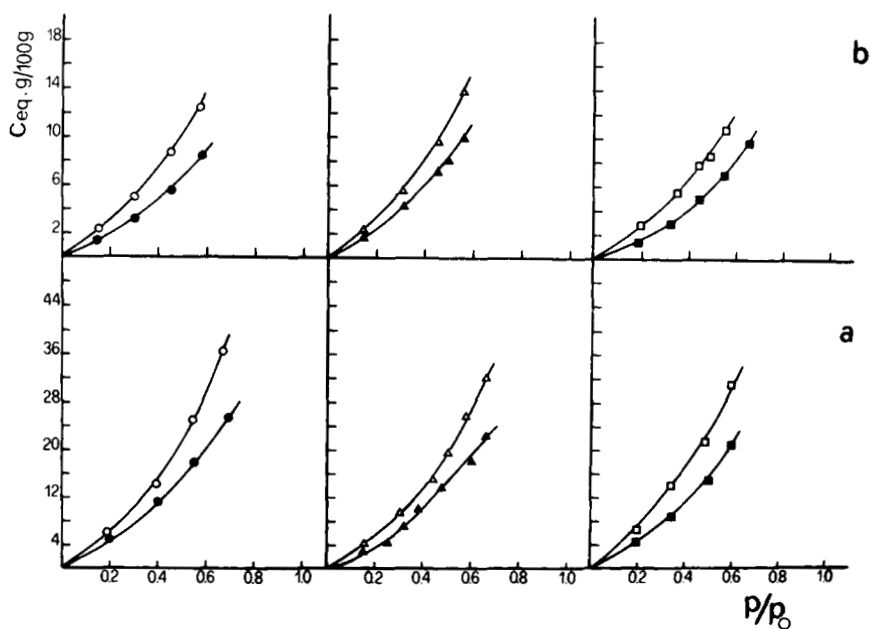


Fig. 1. The equilibrium concentration C_{eq} (grams of permeant in 100 g of dry network) vs. the vapor activity. (a) methylene chloride; (b) n-pentane. HCBR: (○) gum, (●) black; HVBR: (△) gum, (▲) black; SBR: (□) gum, (■) black.

Transport Properties

In Figure 1 we report C_{eq} as a function of the vapor activity for the three systems as gum and black samples. Figures 1a and 1b refer to data obtained with methylene-chloride and *n*-pentane respectively. At any activity C_{eq} is higher in the gum samples. In Figure 2 the concentration in the pure carbon black powder is reported as a function of the vapor activity. Data of Figures 1 and 2 allow us to evaluate the specific concentration in each component at any given vapor activity. On this basis the expected concentration in the filled system, assuming additive effect, can be obtained and this value can be compared with the concentration actually detected. In Table IV the observed and calculated values are reported for two different vapor activities. C_{eq}^0 is the equilibrium concentration in the pure components; i.e., gum samples and carbon black powder; C' is the calculated specific concentration in each component given by $C_{eq}^0 \cdot \alpha_m$, where α_m is the mass fraction in the filled system; C_{add} is the concentration given by additive effect and C_{eq} is the actually detected concentration. In Tables IVa and IVb data refer to methylene chloride and *n*-pentane respectively. It is clearly shown that the additive model cannot be assumed and that C_{eq} is always lower than C_{add} . A deeper analysis shows further interesting elements; C_{eq} in HCBR and SBR is also lower when compared to C' (relative to the rubberlike component) both with methylene chloride and *n*-pentane. The only exception is in HCBR with methylene chloride at $P/P_0 = 0.5$. On the

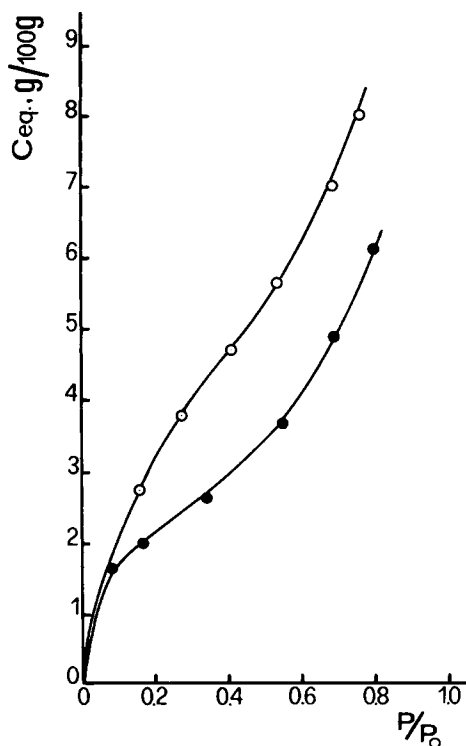


Fig. 2. Equilibrium concentration (grams of permeant in 100 g of dry sample) in the carbon black powder: (○) methylene chloride; (●) *n*-pentane.

TABLE IV
Experimental and Calculated Equilibrium Concentration Data

(a) <i>Methylene chloride</i>				
	C_{eq}^0	C'	C_{add}	C_{eq}
Carb. black	4.0	1.3	—	—
HCBR	9.8	6.6	7.9	6.4
HVBR	9.8	6.6	7.9	7.0
SBR	11.2	7.5	8.8	7.0

$P/P_0 = 0.3$.

	C_{eq}^0	C'	C_{add}	C_{eq}
Carb. black	5.8	1.9	—	—
HCBR	20.0	13.4	15.3	14.0
HVBR	20.4	13.7	15.6	14.6
SBR	23.8	15.9	17.8	15.8

$P/P_0 = 0.5$.

(b) <i>n-Pentane</i>				
	C_{eq}^0	C'	C_{add}	C_{eq}
Carb. black	2.6	0.9	—	—
HCBR	4.9	3.3	4.2	2.9
HVBR	5.5	3.7	4.6	4.0
SBR	4.5	3.0	3.9	2.8

$P/P_0 = 0.3$.

	C_{eq}^0	C'	C_{add}	C_{eq}
Carb. black	3.5	1.1	—	—
HCBR	9.6	6.4	7.5	6.0
HVBR	11.4	7.6	8.7	8.4
SBR	9.4	6.3	7.4	6.2

$P/P_0 = 0.5$.

The concentration values are given in g permeant/100 g dry sample.

other hand in HVBR, C_{eq} is always higher than C' , and the difference increases as the vapor activity increases.

In a completely different model, one can assume that, in the black samples, the sorption occurs in the rubber matrix only, and the specific concentration C_{sp} can be derived as C_{eq}/α_r , where α_r is the mass fraction of the rubbery component. Of course in the gum samples $C_{eq} = C_{sp}$. Calculating α_r from the data in Table II, C_{sp} was obtained and reported in Figure 3. Figures 3a and 3b again refer to methylene-chloride and *n*-pentane respectively. Figure 3 reflects the trend in Table IV; as a matter of fact, in HVBR C_{sp} is always higher in black samples, while in HCBR and SBR the opposite trend is observable. In the last two samples, at high vapor activity C_{sp} vs. P/P_0 seems to be substantially an unique function for gum and black samples. The diffusion parameters have

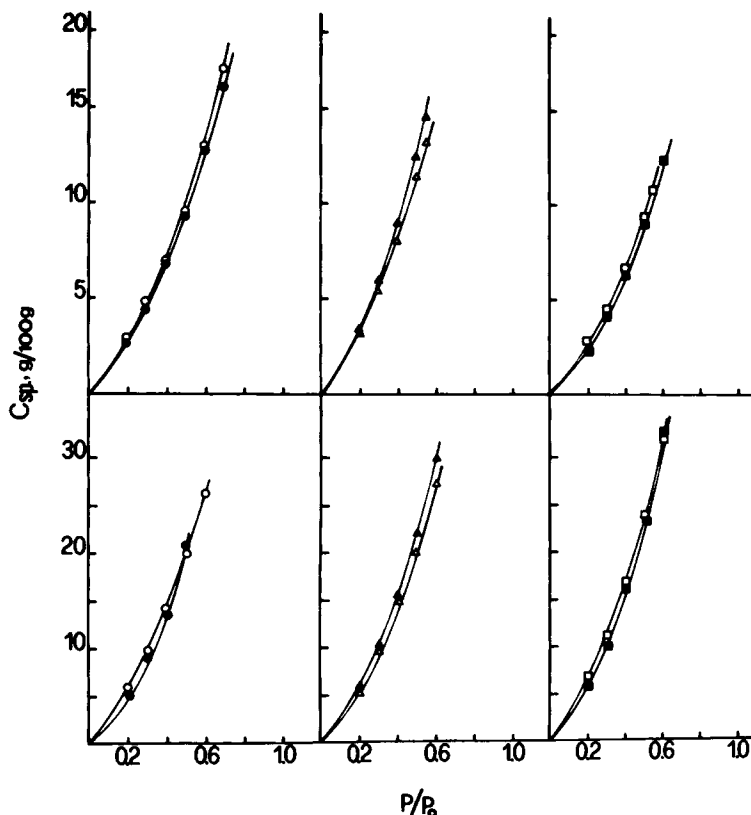


Fig. 3. The specific concentration C_{sp} vs. the vapor activity. (a) methylene chloride; (b) *n*-pentane. HCBR: (○) gum, (●) black; HVBR: (△) gum, (▲) black; SBR: (□) gum, (■) black.

been analyzed using *n*-pentane as permeant; results are reported in Figure 4. Figure 4 shows that the three samples present a dependence of \bar{D} on C_{sp} ($\gamma \neq 0$). Sample HCBR does not show effects related to the filler and the observable D_0 is about 10 times larger than in HVBR and SBR samples. On the other hand HVBR and SBR show relevant effects related to the presence of carbon black. As matter of fact D_0 is higher and γ is lower in the filled samples.

DISCUSSION

The transport properties of filled elastomers have been analyzed with the aim to obtain information on the reinforcement phenomenon. In this sense the reported results give some interesting preliminary indications. The analysis of the sorption properties of the pure carbon black powder shows a trend typical of a two stages mechanism. The sigmoidal shape of the C_{eq} vs. P/P_0 curve can be generally ascribed to the superposition of two curves^{7,9,12}; the first characterized by a fast initial increase followed by saturation conditions, and the second characterized by a Flory-Huggins behavior in which the derivative C_{eq} vs. P/P_0 increases on increasing P/P_0 . The first is generally due to transport

phenomena occurring through voids and/or through permeation sites present on the surface, the second is generally related to a bulk phenomenon. Considering the high crystallinity of carbon black,¹³ also this second mechanism could regard mainly superficial layers. On this basis the observed trend; i.e., C_{eq} always lower than C_{add} (see Table IV), could suggest that in the filled system the surface of the carbon black particles is not available, at least not completely available for the transport phenomena. Moreover the comparison between C_{eq} and C' calculated for the rubbery matrix, assuming a behavior perfectly equal to the pure rubbery component, shows that, in HCBR and SBR, C_{eq} is also lower than C' , with the exception of HCBR using methylene chloride at high activity. A different trend is observed for sample HVBR where C_{eq} is intermediate between C' and C_{add} . The possible explanation for these results could be based mainly on the well known and developed concept of interphase interactions between the matrix and the filler particles.¹⁻⁵ The interaction between filler and matrix excludes the surface of the filling particles, and the additive model is not applicable. The comparison between C' , C_{eq} , and C_{add} gives information on the entity of the exclusion phenomenon, and, in this sense, the different samples give a different indication. In HCBR and SBR, C_{eq} lower than C' suggests that not only the surface of the carbon black is excluded, but also the matrix is partially excluded by the transport phenomenon. This means a very strong interaction between matrix and filler, and only at high vapor activity (see Figure 3 on the effect observed in HCBR with methylene chloride) the permeant plays a competitive role on the interphase interaction phenomena. Following this model, the observed behavior of HVBR suggests that in this sample the interaction between matrix and filler is not so strong, in fact a fraction of the carbon black surface could be available and this fraction seems to increase on increasing the vapor activity (see Table IV). The vapor tends to reduce the contact matrix-filler, probably diffusing through the interphase layers. It is interesting to note that the mechanical parameters in Table III indicate that in sample HVBR the filling effect is indeed very poor. As for the

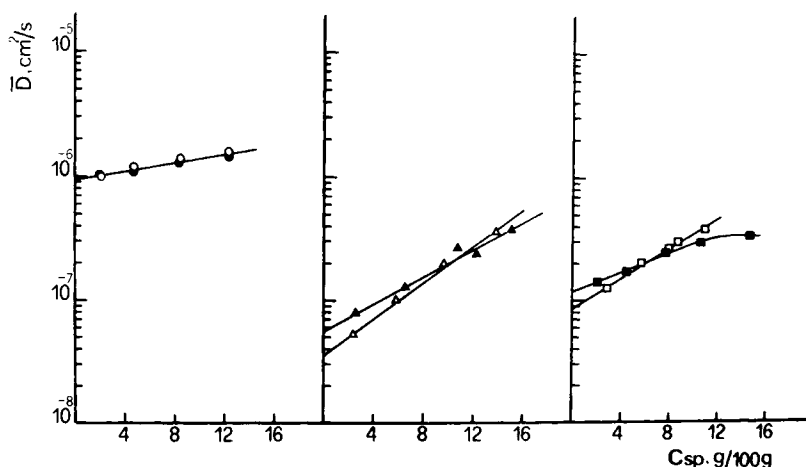


Fig. 4. The diffusion coefficient \bar{D} vs. the specific concentration C_{sp} , obtained using *n*-pentane as permeant. HCBR: (○) gum, (●) black; HVBR: (△) gum, (▲) black; SBR: (□) gum, (■) black.

diffusion data, it is important to point out that D is mainly a kinetic parameter which takes into account not only thermodynamic properties, like the fractional free volume and the molecular mobility, but also topological and structural features. The presence of voids and impermeable obstacles to the diffusion, both can affect D . Therefore D gives more information than C_{sp} , which is mainly a thermodynamic parameter, but the analysis of D can be, as a consequence, more complex and less univocal. On the basis of these remarks one can consider the obtained results shown in Figure 4. Figure 4 shows that in HCBR D_0 is 10 times larger than in HVBR and SBR. It is important to point out that the molecular mobility in the highly flexible cis system is very high at room temperature, that is about 125°C over its glass transition T_g (calorimetrically $T_g = -104^\circ\text{C}$). The permeant molecules moving in the rubbery matrix "see" a system so mobile that any effect related to the influence of carbon black does not appear in evidence. Quite different is the situation in HVBR and SBR (T_g is -38 and -49°C respectively), where the lower D_0 and the higher γ , both indicate a less mobile matrix according to the higher T_g . HVBR and SBR show an appreciable effect related to the presence of carbon black. In particular the carbon black induces an increase of D_0 and a decrease of γ , and such effects could apparently be related to an increased mobility in the matrix when the carbon black is present. This possible explanation contradicts the general knowledge on a filled system where the presence of the rigid filling particles can decrease but never increase the segmental mobility in the amorphous fraction. On the other hand, as pointed out, the diffusion can be affected by topological features as voids which, at least partially, can induce a diffusion mechanism based on a capillary regime. Indeed the presence of rigid particles in the mixing and subsequent crosslinking process can induce a fluctuation of density at microscopic levels and the probable appearance of microvoids.

CONCLUSIONS

The reported results indicate that the analysis of transport properties can be a suitable method to investigate the filler-rubber interactions. The sorption data show that in HVBR the surface of the filling particles is partially involved in the transport phenomenon; this result can be considered as evidence of weak interphase interactions. In HCBR and SBR, on the other hand, the obtained results suggest that, not only the filling particles, but also a small fraction of the rubbery matrix, are excluded from the transport phenomenon. This experimental evidence seems to indicate the presence of strong interphase interactions. However further work is necessary in changing some of the composition parameters—like the content and the surface activity of the filler, and/or the crosslinking density.

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