ELSEVIER

Estimating models for predicting effective permeability of mixed matrix membranes

Elio E. Gonzo, Mónica L. Parentis, Juan C. Gottifredi *

*Instituto de Investigaciones para la Industria Química (INIQUI), UNSa, CONICET, Facultad de Ingeniería,
Buenos Aires 177, A4402DFC SALTA, Argentina*

Abstract

Mixed matrix membranes have become a highly potential unique materials in many engineering application to overcome limitations presented by other products. In this contribution, an improved form of Maxwell's equation (the extended Maxwell equation) based on the hard-sphere model fluid proposed by Chiew and Glandt [Y.C. Chiew, E.D. Glandt, The effect of structure on the conductivity of a dispersion, J. Colloid Interface Sci. 94 (1983) 90–104] is evolved. The resulting equation allows the estimation of the effective permeability of composite membranes as a function of the reduced permeation polarizability and the volume fraction of the filler. This method can be applied to estimate effective permeability of gases and liquids through mixed matrix membranes prepared with different polymer matrix, as continuous phase, and organic (polymer or liquid crystal mixture) or inorganic (zeolites, activated carbons) compounds as filler even at relatively high volume fractions of this compound.

A comparison among estimated values of the effective permeability and experimental data reported in the literature generally shows good agreement although there are a number of observations that are not easily explained with any of these models.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Mixed matrix; Membrane; Permeation; Selectivity; Maxwell model

1. Introduction

Composite materials, formed by the inclusion of a solid dispersed phase into a continuous media, are of great interest in many engineering fields due to the unique properties of these solids [1,2]. Mahajan and Koros [3] reviewed the state of the art, the main achievements and also the limitations of artificial membranes in separation processes especially those related with permeation of gases. They suggested the need to develop new composite materials to increase permselectivity without affecting productivity levels already reached by pure polymer membranes. Robeson [4], on pure theoretical basis of molecular diffusion, constructed an upper bond trade off line between O_2/N_2 ideal permselectivity and O_2 permeability. This relationship establishes an upper limitation for conventional polymers. On the other hand, ceramic sieves media have the ability to work as molecular sieves without the limitation of polymer membranes. The combination of these ceramic materials with a polymer matrix could be an excellent proposal to overcome the

limitations established by Robeson [4], while maintaining the mechanical flexible properties of the polymeric matrix.

The so-called mixed matrix membranes have received much attention in recent years. As will be discussed below a number of composite materials have been used to perform permeation experiments. Lately, a great number of efforts have been devoted to develop materials comprising molecular sieve entities embedded in a polymeric network with the scope to increase selectivity without altering permeability properties of the polymer. An interesting discussion is delivered by Mahajan and Koros [5] showing that from a pure theoretical point of view it should be possible to overcome Robeson [4] limitations. Problems that could arise during mixed matrix membranes formation are pointed out and solutions are given to prepare defect free films that can be safely tested in permeation experiments. In a further contribution [6] the effect of the resulting interfacial region, formed around particle in the polymer network, is discussed setting forward a theoretical model to predict permeabilities in these systems.

A proper selection of materials used to prepare mixed matrix membranes is necessary to succeed in challenging the traditional separation processes. Theoretical predictions of pure species

---

* Corresponding author.

permeability in these types of membranes, with minimum experimental information, are also needed to select adequate compounds combinations to prepare these kinds of membranes.

Petropoulus [7] revised the existing models to predict the permeability of composite membrane. He pointed out that all considered models assume that both solid phases form well defined closed microscopic domains and do not interact with each other or with the penetrant. Moreover, the only parameter used to describe the composite system was the volume fraction. Nevertheless, Petropoulus [7] was able to establish significance of each model based on formulas which were applied in a large empirical way.

In this contribution a theoretical approach developed by Chiew and Glandt [8] is applied to predict permeabilities of pure penetrant in a mixed membrane with the knowledge of the permeabilities of penetrant in both pure compounds and the volume fraction of the dispersed phase. This model takes into account second order interactions between embedded ensemble of particles which are not considered in Maxwell model [9]. Following Chiew and Glandt [8] procedure the permeability of a given penetrant in the composite media results to be an explicit function of volume fraction of the dispersed phase and permeability ratio of penetrant in each compound forming the composite. So there is no need to further experimental knowledge to use this theoretical approach. Theoretical results are used to establish a comparison among predictions obtained with other analytical or semi-analytical expressions commonly used in the literature. At the same time recent experimental reported measurements of permeabilities in composite materials will be compared with theoretical predictions obtained with this new approach and with the model used by the authors of each experiment to correlate their results.

2. Theory

Selective transport of fluids through amorphous porous solids or polymeric membranes occurs through a dissolution–diffusion mechanism. Most experiments are performed with the scope to measure the permeability coefficient (P_A) of a given penetrant (A) through the amorphous structure. As shown in many contributions P_A can be also estimated as the product of diffusivity coefficient (D_A) and solubility coefficient (S_A):

$$P_A = D_A S_A \tag{1}$$

Since D_A and S_A are usually function of solubility, a hence on pressure, D_A and S_A are actually mean values within the membrane and can vary with the applied pressure. The permselectivity, $\alpha_{A/B}$, describes the ideal ability of a membrane to separate fluids A and B and is defined as the ratio of permeability of component A and B.

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A S_A}{D_B S_B} \tag{2}$$

Usually three parameters are used to describe these systems. The permeability and the permselectivity, just defined, and the fractional volume of the respective phases, ϕ.

The minimum and maximum values of the effective permeability of a given penetrant, P_{eff}, in a mixed matrix membrane are given by the series and parallel two-layer models, respectively. The minimum value of P_{eff} occurs when a series mechanism of transport through the two phases is postulated:

$$P_{eff} = \frac{P_c P_d}{\phi_c P_d + \phi_d P_c} \tag{3}$$

The maximum value of P_{eff}, occurs when both phases are assumed to work in parallel to the flow direction.

$$P_{eff} = P_c \phi_c + P_d \phi_d \tag{4}$$

The geometric mean model assumes random distribution of phases and the effective permeability is given by the weighted geometric mean of the permeabilities of the two matrixes.

$$P_{eff} = P_c^{\phi_c} + P_d^{\phi_d} \tag{5}$$

where P_c and P_d are the permeability of a given penetrant in the continuous and disperse phases, respectively.

Maxwell [9], using the potential theory for electrical conduction through a heterogeneous media, obtained the exact solution for the conductivity of random distributed and non-interacting homogeneous solid spheres in a continuous matrix. Maxwell equation applied to the effective permeability of a dispersion of spheres in a continuous phase of permeabilities P_d and P_c, respectively, is [9]:

$$P_{eff} = P_c \frac{P_d + 2P_c - 2\phi(P_c - P_d)}{P_d + 2P_c + \phi(P_c - P_d)}$$
$$= P_c \frac{2(1 - \phi) + \alpha(1 + 2\phi)}{(2 + \phi) + \alpha(1 - \phi)}, \quad \text{where} \quad \alpha = \frac{P_d}{P_c} \tag{6}$$

It is useful to define the "reduced permeation polarizability", β, as:

$$\beta = \frac{\alpha - 1}{\alpha + 2} = \frac{P_d - P_c}{P_d + 2P_c} \tag{7}$$

β is a convenient measure of penetrant permeability difference between the two phases; it is bounded by $-0.5 \le \beta \le 1$, where the lower and upper limits correspond to totally non-permeable and to perfectly permeable filler particle (disperse phase), while, $\beta = 0$, implies $\alpha = 1$ (equal permeability in both phases). Eq. (6), as a function of β is reduced to:

$$P_{eff} = P_c \frac{1 + 2\beta\phi}{1 - \beta\phi} \tag{8}$$

Maxwell model (Eq. (6) or (8)) is strictly applicable to a dilute suspension of spheres. However, the range of validity, in terms of ϕ values, also depends on β as will be shown later.

Other expressions have been proposed to predict composite membrane permeability. The analogue dielectric model has been extensively studied [1,10,11]. The more important models developed for two-phase mixed matrix membranes are those of Bruggeman [12], Böttcher, Higuchi (see Ref. [7]), Maxwell–Wagner–Sillar [13] and the simple power law (percolation theory model) [10]. Recently, one of the author [14],

have presented a model to predict effective thermal conductivity of composite granular materials of different characteristics, which was shown to work quite well.

Bruggeman [12] used the effective medium theory approach, which is particularly appropriate when there is small difference in the permeability of the two phases ($\alpha \approx 1$). Since the effective medium theory treats the local permeability as fluctuations about the effective permeability of a uniform medium, no distinction between continuous and dispersed phases is made. He derived an equation valid for dispersions with high filler volume fraction by introducing an asymmetrical integration technique. He used an equation valid at low filler volume fraction and assumed that this equation can be used for calculating the infinitesimal increment of the dispersion dielectric constant after adding an infinitesimal amount of the filler. The infinitesimal increment of the filler volume fraction is integrated to obtain an equation for the dielectric constant at relatively high filler volume fractions. The equivalent equation for the permeation through a dispersion of spheres is:

$$\left(\frac{P_{\text{eff}}}{P_{\text{c}}} - \alpha \right) \left(\frac{P_{\text{eff}}}{P_{\text{c}}} \right)^{-1/3} = (1 - \phi)(1 - \alpha) \tag{9}$$

The formulas of Böttcher and Higuchi [7], considered to be applicable to random dispersions of spherical particles, are, respectively:

$$\left(1 - \frac{P_{\text{c}}}{P_{\text{eff}}} \right) \left(\alpha + 2 \frac{P_{\text{eff}}}{P_{\text{c}}} \right) = 3\phi(\alpha - 1) \tag{10}$$

$$\frac{P_{\text{eff}}}{P_{\text{c}}} = 1 + \frac{3\phi\beta}{[1 - \phi\beta - K_{\text{H}}(1 - \phi)\beta^2]} \tag{11}$$

Parameter K_{H} in Eq. (11) is treated as an empirical constant assigned a value of 0.78 on the basis of experimental data.

It must be noticed that Eqs. (9) and (10) are in fact third order and second order algebraic expressions in P_{eff}. So they are not explicit for P_{eff}. A trial and error procedure is needed to estimate P_{eff} as function of α and ϕ.

The Maxwell–Wagner–Sillar [13] equation for the case of a dilute dispersion of ellipsoids, oriented along the axis of the flux direction is:

$$P_{\text{eff}} = P_{\text{c}} \frac{n P_{\text{d}} + (1 - n)P_{\text{c}} + (1 - n)(P_{\text{d}} - P_{\text{c}})\phi}{n P_{\text{d}} + (1 - n)P_{\text{c}} - n(P_{\text{d}} - P_{\text{c}})\phi} \tag{12}$$

where n denotes the shape factor of the filler. This equation is an analytical solution that can be found by embedding the matrix phase into a phase with the permeability of the composite and undisturbed pressure distribution. For prolate ellipsoids $0 \leq n \leq 1/3$. For spherical filler particles, $n = 1/3$, and reduces to Maxwell equation. For oblate ellipsoids $1/3 \leq n \leq 1$; $n = 0$ corresponds to permeation through a membrane with parallel transport, while $n = 1$ represents permeation perpendicular to the phases.

According to the percolation theory, the relation between composite permeability and filler concentration in the vicinity of the percolation threshold can be described by a simple power law:

$$P_{\text{eff}} = P_{\text{d}}(\phi - \phi_{\text{t}})^t \tag{13}$$

where ϕ_{t} is the percolation threshold (critical volume fraction of the filler) and t is the critical exponent.

In this contribution an extension of Maxwell model, as proposed by Chiew and Glandt [8], is evolved for the specific case of permeation through mixed matrix membranes. In actual facts, an expansion of Eq. (8) in terms of ϕ yields:

$$\frac{P_{\text{eff}}}{P_{\text{c}}} \approx 1 + 3\beta\phi + 3(\beta\phi)^2 + O(\phi^3) \tag{14}$$

The second term represents the interaction between particles and continuous media and the third the interaction between particles. Strictly speaking P_{eff} of a homogeneous dispersion is a statistical property that depends on the nature and permeating properties of the continuous and disperse phases and, of course, on the spatial distribution of the particles in the mixed matrix. Nevertheless, from and engineering point of view, it is convenient to describe the permeation system behavior with only two parameters β and ϕ. To improve this macroscopic description a great number of experimental efforts would be needed to characterize mixed matrix membranes. Thus, ϕ can be regarded as the only parameter used to describe an ensemble of identical spheres which, depending upon the value of ϕ, interact with the continuous media and also with them.

Maxwell [9] deduced his popular expression neglecting, in principle, particle to particle interactions. He assumed that the particle size was negligible when compared with mean distance within particles. However, as shown by Eq. (14), second order interactions are included in Maxwell resulting expression although they are not exactly described. Chiew and Glandt [8] pointed out that Eq. (14) is exact up to term of order ϕ. By taking the original Maxwell equation they proposed:

$$\frac{P_{\text{eff}}}{P_{\text{c}}} = \frac{1 + 2\beta\phi + (K - 3\beta^2)\phi^2}{1 - \beta\phi} + O(\phi^3) \tag{15}$$

An expansion of this expression in terms of (ϕ) gives:

$$\frac{P_{\text{eff}}}{P_{\text{c}}} = 1 + 3\beta\phi + K\phi^2 + O(\phi^3) \tag{16}$$

Thus, a proper estimation of K would give the needed correction of Maxwell expression. K values were calculated using appropriated statistical functions to describe the interaction of the "ith" particle with the surrounding ensemble and then a second integration to sum up all the resulting interaction contributions. As expected K is not only function of β but also of ϕ. The values of K cannot be easily calculated but Chiew and Glandt [8] presented the resulting values as function of β and ϕ in their Table 2. In this contribution their tabulated results were fitted by the following expressions:

$$K = a + b\phi^{3/2} \tag{17}$$

where the parameters a and b are functions of β:

$$a = -0.002254 - 0.123112\beta + 2.93656\beta^2 + 1.6904\beta^3$$
$$b = 0.0039298 - 0.803494\beta - 2.16207\beta^2 + 6.48296\beta^3 + 5.27196\beta^4 \tag{18}$$

Clearly when $\phi \ll 1$ Eq. (16) must give exactly the same results as Maxwell predictions since, as shown terms of order ϕ^2 will be negligible in comparison with terms of order ϕ. By the way, it should be noticed that Brudgeman and Böttcher expressions also reduces to Eq. (14) up to terms of order ϕ. However, Higuchi [7] expression reduces to:

$$\frac{P_{\text{eff}}}{P_{\text{c}}} \approx 1 + \frac{3\beta\phi}{1 - K_{\text{H}}\beta^2} + O(\phi^2) \tag{19}$$

which can produce inexact results even when $\phi \ll 1$.

Table 1 presents a comparison among results produced by the different expressions analyzed in this contribution. P is used as the ratio ($P_{\text{eff}}/P_{\text{c}}$) and subindexes are given below the table to a better understanding of the results. The first thing to be noticed is that the differences between models not only depend on ϕ but also on β. Within the range of values analyzed it can be concluded that Maxwell equation produce acceptable prediction up to $\phi = 0.2$. Nevertheless, for values of α bounded by $(0.1 \leq \alpha \leq 10)$ it can even be safely used up to $\phi \approx 0.3$. Brudgeman Eq. (9) produces estimates in close agreements with those obtained using the Chiew and Glandts model. Böttcher and Higuchi [7] models do not follow the same trend.

An interesting conclusion is that the first order approximation can be used in all cases when $\phi \leq 0.1$. This finding could be very important to better deal with a more complex model recently presented by Moore et al. [15] to take into account interactions between particle and continuous media in the nearby particle region. However, it must be reminded that the maximum attainable system density is the random packing limit $\phi \approx 0.637$ (Churchill [16]).

Table 1
Comparison between models

ϕ	P_{M}	P_{M1}	P_{M2}	P_{CG}	P_{Br}	P_{Bt}	P_{H}
$\alpha = 10$, $\beta = 0.75$							
0.05	1.117	1.113	1.117	1.118	1.120	1.124	1.206
0.1	1.243	1.225	1.242	1.250	1.257	1.257	1.424
0.2	1.530	1.450	1.518	1.568	1.592	1.678	1.902
0.3	1.871	1.675	1.827	1.990	2.020	2.260	2.443
0.4	2.28	1.90	2.17	2.57	2.59	3.04	3.06
0.5	2.80	2.12	2.5	3.40	3.30	4.00	3.77
$\alpha = 0.1$, $\beta = -0.429$							
0.05	0.937	0.935	0.935	0.937	0.937	0.936	0.927
0.1	0.877	0.871	0.877	0.876	0.875	0.872	0.859
0.2	0.763	0.743	0.765	0.758	0.756	0.747	0.735
0.3	0.658	0.614	0.664	0.645	0.644	0.625	0.625
0.4	0.561	0.486	0.574	0.535	0.540	0.508	0.526
0.5	0.471	0.357	0.495	0.423	0.440	0.400	0.437
$\alpha = 0.01$, $\beta = -0.4925$							
0.05	0.928	0.926	0.928	0.928	0.927	0.926	0.913
0.1	0.859	0.852	0.859	0.857	0.856	0.852	0.832
0.2	0.731	0.704	0.734	0.723	0.719	0.705	0.688
0.3	0.614	0.557	0.622	0.594	0.592	0.558	0.564
0.4	0.506	0.409	0.526	0.465	0.473	0.413	0.454
0.5	0.407	0.261	0.443	0.334	0.363	0.271	0.358

Subindexes: M, Maxwell Eq. (8); M1, $P_{\text{M1}} = 1 + 3\beta\phi$; M2, Eq. (14); CG, Eq. (15); Br, Eq. (9); Bt, Eq. (10); H, Eq. (11).

3. Comparison with experimental reported data

Eqs. (9)–(11) have been used to estimate electrical conductivities of mixed matrix materials and have been shown to produce good results [7]. However, electrical proprieties strongly depends on the so-called percolation threshold. When its critical value is reached a dramatic increase on conductivity is noticed. However, mass and electrical charge transport in mixed matrix membranes are not completely analogous phenomena.

Reproducibility is serious challenge in preparing and testing permeability properties of mixed matrix membranes as recently discussed by Mahajan and Koros [5,6]. The presence of a filler in the polymeric network, specially inorganic particles, can create voids at the polymer–filler interface that will reduce the resulting membrane separation performance.

Eq. (15) will be tested against a number of well recognized experimental studies in which permeability results of pure species in mixed matrix membranes are presented with basic data (α and ϕ) of each experiment. In same cases theoretical predictions presented in each contribution will be also reported to compare already published results with new predictions derived from Eq. (15).

Robeson et al. [17], using the Maxwell equation analyzed a series of polysulfone (PS)/poly(dimethylsiloxane) (PDMS) block copolymer to interpret O_2 permeability data. The O_2 permeability of the unfilled poly(dimethylsiloxane) determined by extrapolation, was found to be 7.2×10^{-8} ($cm^3/cm\ s\ 10\ Torr$), while, the O_2 permeability in (PS) was 1.3×10^{-10} ($cm^3/cm\ s\ 10\ Torr$). Fig. 1 presents comparison among ($P_{\text{eff}}/P_{\text{d}}$) experimental values and those predicted by Eq. (15) and by Maxwell Eq. (8). It is clearly seen that Eq. (15) shows a better fitting behavior ($1/\alpha = 554$; $\beta = -0.4986$).

The study of the diffusion/sorption property of zeolite 13X incorporated in Udel P-1700 polysulfone glassy polymer membrane, and its effect on gas permeation, was carried out by Gür [18]. The 13X particles, 2–8 μm in size, were
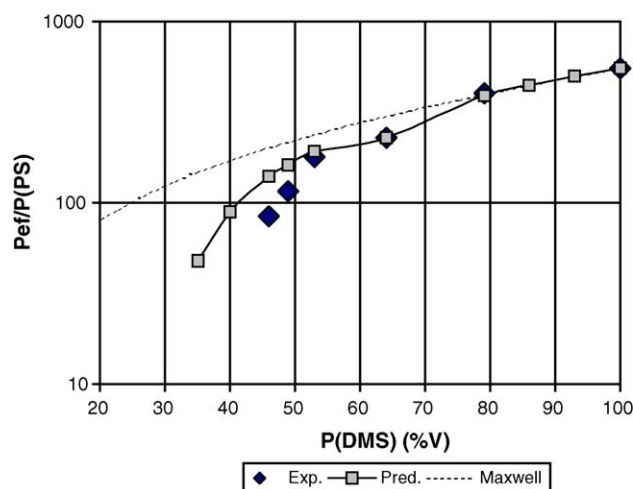
Fig. 1. Relative permeability of O_2 vs. composition for PS in PDMS matrix membranes (Robeson et al. [17]).

Table 2
Permeability values (experimental and predicted) for different gases in molecular sieve 13X filled polysulfone

2 M membrane	Permeability (Barrer)					
	CO_2 exp.	CO_2 est.	He exp.	He est.	H_2 exp.	H_2 est.
ϕ (vol.%)/β	−0.2	−0.2	0.05	0.05	0.22	0.22
0	6.5	6.5	12.4	12.4	13.2	13.2
10	6.1	6.1	12.8	12.6	14.4	14.1
20	6.1	5.8	12.5	12.8	14.7	15.0

Gür [18].

distributed uniformly through the polymer matrix. Table 2 summarizes the experimental and predicted permeability values of CO_2, He and H_2 in 0, 10 and 20 vol.% molecular sieve 13X filled membranes. The estimated values agree very well with experimental data with maximum deviation below 5%.

The permeability of 1,1,1-trichloroethane in filled membranes of activated carbon in polyether-block-polyamide matrix, was investigated by Ji et al. [19]. Pervaporation experiments from dilute aqueous solution using 2 M membranes prepared introducing activated carbon particles of 900 m^2/g of surface area, 0.8 g/cm^3 density and pore volume of 0.23 cm^3/g (pores < 2 nm), 0.23 cm^3/g (2 nm < pores < 300 nm) in the polymer phase, were performed. The reduced experimental permeabilities (P_{eff}/P_c) in 0, 8 and 15 vol.% of activated carbon membranes are presented together with predicted values in Table 3. As can be seen, the permeability predicted values of this pervaporation process follow the trend and show a reasonable agreement with the experimental data (relative percent error smaller than 20%).

Netke et al. [20] carried out the pervaporation of acetic acid from concentrated aqueous solution through silicalite (Si/Al ratio of 140, pore diameter 0.6 nm, pore volume 1.5 cm^3/g) filled PDMS membranes, with 0, 20 and 40 wt.% (0, 17 and 33 vol.%) loading. Experimental results of the reduced permeability as a function of ϕ, are compared in Fig. 2, with predicted values. Experimental data correspond to pervaporation of acetic acid from 50 wt.% water solution. The filler is practically impermeable to the acetic acid ($\alpha \approx 0$ and $\beta = -0.5$). The agreement between experimental and estimated values is really very good.

A very interesting work was done by the Drioli's research group [13]. Composite membranes have been prepared using as polymer matrix, vinylidene fluoride-hexafluoropropene. Instead of a commonly used solid filler, a liquid crystalline mixture E7

Table 3
Relative permeability of trichloroethane from water solution in activated carbon filled polyamide

ϕ (vol.%)	(P_{eff}/P_c) exp.	(P_{eff}/P_c) pred.
0	1.00	1.00
8	1.358	1.27
15	1.925	1.57

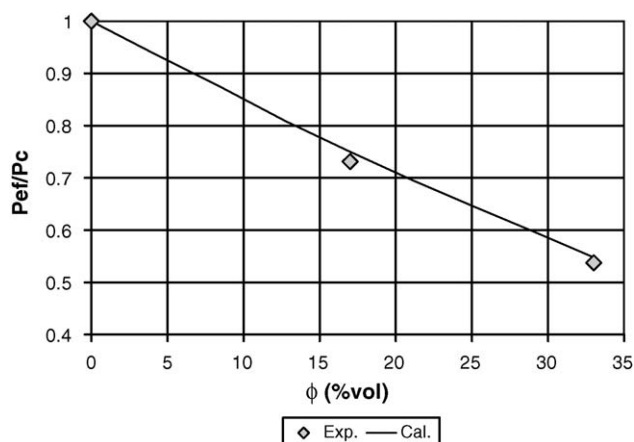$\alpha = 148$; $\beta = 0.98$, Ji et al. [19].

Fig. 2. Relative pervaporation rate of acetic acid from 50% water solution in membranes of silicalite in PDMS polymer matrix (Netke et al. [20]).

was used. Microscopic droplets of the liquid crystal at a concentration of 3.5–37.3 vol.% in the polymeric membrane were prepared. The diameter of the droplets changes with the concentration of E7, varying from 300 nm (at low concentration) to 2 μm at the highest concentration. The oxygen permeability in the polymer matrix equals 1.9 Barrer at 40 °C. The filler permeability was not possible to be measured. However, Bouma et al. [13] used Bruggeman equation to predict O_2 permeability on E7 relative to the permeability of the continuous matrix ($\alpha = 10$). With this value of α, which corresponds to a β value of 0.75, predictions of the oxygen permeability of the mixed matrix membranes by Eq. (15), are presented in Fig. 3, together with the experimental findings. In this case, as expected (see Table 1), the estimated values of P_{eff}/P_c from Bruggeman [12] equation are almost identical to the values obtained with our Eq. (15). The estimations are quite good and follow the same trend as the experimental values. Fig. 3 also shows the Maxwell equation estimations.

Mahajan et al. [21] investigated the zeolite 4A–Matrimid (Polyimide) system and discovered that the permeabilities of oxygen and nitrogen at 35 °C, were higher than that for pure
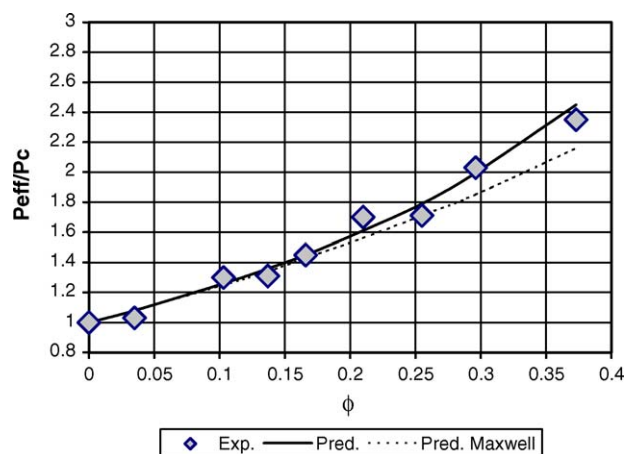

Fig. 3. The oxygen permeability of a co-PVDF membrane with dispersed E7 liquid crystalline droplets (Drioli and co-workers [13]).

Table 4
Permeability of O_2 and N_2 in PVAc membranes filled with zeolite 4A

ϕ (vol.%)	P_{O_2} exp.	P_{O_2} pred.	P_{N_2} pred.	(P_{O_2}/P_{N_2}) pred.	(P_{O_2}/P_{N_2}) exp.
0	0.5	0.5	0.0847	5.9	5.9
15	0.45	0.535	0.0724	7.4	7.45
25	0.4	0.558	0.0648	8.6	8.45
40	0.315	0.593	0.0538	11.0	10.1

Experimental and predicted ideal (O_2/N_2) selectivity. Permeability in Barrer. $\alpha_{O_2} = 1.54$, $\beta_{O_2} = 0.1525$; $\alpha_{N_2} = 0.246$, $\beta_{N_2} = -0.336$, Mahajan et al. [21].

Matrimid although no improvement in selectivity was found. These results were consistent with those found in SEM photograph of the filled membranes, since voids, between the two materials, were detected. These voids allows the gas to simply bypass the sieve, resulting in higher permeability with no selectivity improvement. The same research group, Mahajan and Koros [3], prepared mixed matrix membranes with poly(vinylacetate) (PVAc) and zeolite 4A. The PVAc is more compatible with zeolite than polyimide polymer. They also found that, priming the zeolite by adsorbing a layer of polymer before dispersal, a good contact between PVAc and the aluminosilicate type 4A zeolite, was observed. The experimental results of ideal selectivity along with theoretical predictions are shown in Table 4, together with O_2 experimental permeability. O_2 and N_2 permeabilities in pure PVAc were experimentally determined as 0.5 and 0.0847 Barrer, respectively. Zeolite 4A crystals are estimated to have an O_2 permeability of approximately 0.77 Barrer and an O_2/N_2 selectivity of 37. From membrane performance predictions shown in Table 4, increased addition of zeolite 4A simultaneously leads to large increases in O_2/N_2 selectivity with small reductions in the predicted composite membrane O_2 permeability. There is reasonable agreement between the experimental and predicted permselectivity values. However, as the loading increases, the deviation becomes more pronounced. On the other hand while predictions indicate an increase in O_2 permeability experimental results show an opposite effect. An explanation of this anomalous behavior was recently offered by Moore et al. [15]. A new model was introduced in which three phases are involved to predict permeability coefficients. In fact it is reduced as two component systems in which one is the result of a special polymer solid interaction. However, two new parameters are introduced that must be fitted with experimental results.

Tantekin-Ersolmaz et al. [22] investigated vapor permeability trough a polydimethylsiloxane (PDMS) membrane embedded by zeolite 5A particles. SEM analysis revealed zeolite particles completely covered by polymer and the absence of voids nearby zeolite polymer interface. They used a volumetric method to measure n-pentane vapor permeabilities at 65 °C. Their results are presented as points in Fig. 4 together with the curve produced by Eq. (15) ($\alpha = 0.22$; $\beta = -0.35$). The agreement is fairly good except for the point located at $\phi = 0.57$ nearby the region where particles almost touch one to the other.

Pechar et al. [23] studied the permeation of He, O_2, N_2, CH_4 and CO_2 through a glassy polyimide intruded by modified zeolite (ZSM-2) particles. They presented data obtained
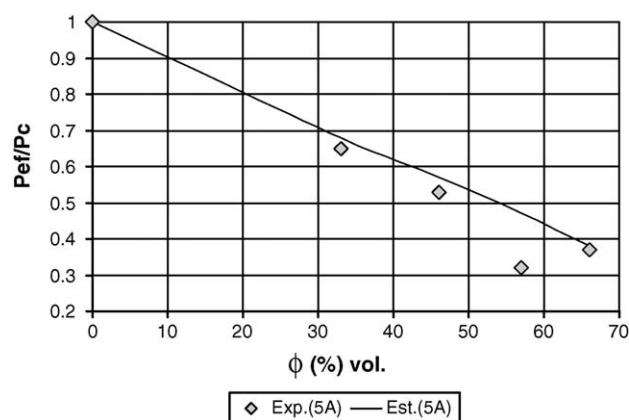

Fig. 4. Relative permeability of n-pentane in zeolite 5A filled PDMS membranes (Tantekin-Ersolmaz et al. [22]).

with 20 wt.% (16 vol.%) membrane determined in constant volume, variable pressure, facility using time-lag procedure. They results are reproduced in Table 5 with Eq. (15) predictions. A fair agreement is shown. Permeability coefficients in pure polyimide and estimated values in ZSM-2 are given in Table 6. The ideal permselectivities, experimental and predicted by Eq. (15), for certain gas pair are presented in Table 7. The agreement here is very good.

Table 5
Experimental and estimated relative permeabilities of different gases in 16 vol.% ZSM-2 zeolite/polyimide membranes

Gases	(P_{eff}/P_c) exp.	(P_{eff}/P_c) pred.	α	β
He	0.871	0.876	0.36	−0.27
CO_2	0.726	0.77	0.013	−0.49
O_2	1.259	1.26	4	0.5
N_2	1.237	1.235	3.45	0.45
CH_4	0.904	0.898	0.46	−0.22

Pechar et al. [23].

Table 6
Permeability values (Barrer) in pure polyimide and ZSM-2

Gases	Polyimide	ZSM-2
He	35.58	12.8
CO_2	21.97	0.29
O_2	4.55	18.2
N_2	0.97	3.3
CH_4	0.73	0.34

Pechar et al. [23].

Table 7
Ideal permselectivities for the 16 vol.% membranes

Pair gases	Exper.	Predict.
O_2/N_2	4.78	4.78
CO_2/CH_4	24.18	25.8
N_2/CH_4	1.82	1.83
He/CO_2	1.94	1.84
O_2/CH_4	8.68	8.7

Pechar et al. [23].

Vu et al. [24,25] incorporated carbon molecular sieves into two different polymers to form mixed matrix membrane films for gas separation. Permeability measurements of the composite membrane films and pure polymer films were performed using a manometric (or constant volume) method. Pure gas permeation data and CO_2/CH_4 permselectivities of Matrimid 5218 and Ultem 1000 composite membranes evaluated at 35 °C are presented in Tables 8 and 9, together with the predicted values according Eq. (15). The carbon molecular sieves used as the dispersed particle phase in the mixed matrix films were generated by pyrolysis of the polyimide (Matrimid 5218). The perme-

ation rate of pure disperse sieve phase (activated carbon) were 44.0 Barrer for CO_2 and 0.22 Barrer for CH_4. For both films the model here presented provides better CO_2 and CH_4 permeability predictions than the Maxwell model. Both models give comparable permselectivity predictions at low activated carbon loading (up to 20 vol.%) that compare reasonably well with experimental results.

Recently, Bhardwaj et al. [26], carried out a study of CO_2 and CH_4 permeation through a carbon black filled polysulfone membrane. A standard coating silicone technique was used to ensure defect free structure. Table 10 shows experimental and predicted permeabilities of CO_2 and CH_4 for three ϕ values reported (1.4, 3.5 and 7.1%). In the last two column ideal permselectivity values are also reported. In this case an unusual unexpected phenomena is noticed at lowest filler loading. In fact at $\phi = 0.035$ CH_4 experimental permeability exhibits a peak while CO_2 shows a depression. These results are difficult to explain, as stated by the authors [26], but again, the peculiar behavior of the CO_2/filler system is shown. Eq. (15) does not explain this special situation at $\phi = 0.035$, but predicts relative permeation rate and selectivity reasonably well in the remaining range of ϕ.

Table 8
Experimental and estimated permeation properties of membranes using Matrimid as continuous matrix at various loading of carbon molecular sieve insert (CMS)

2 M membrane	Permeability (Barrer)				Permselectivity		Error in selectivity (%)
	CO_2 exp.	CO_2 est.	CH_4 exp.	CH_4 est.	C/M exp.	C/M est.	
ϕ (vol.%)/β	0.5	0.5	−0.077	−0.077			
0	10.0	10.0	0.28	0.28	35.3	35.3	0
17	10.3	12.8	0.23	0.27	44.4	47.6	7.2
19	10.6	13.2	0.23	0.27	46.7	49.2	5.4
33	11.5	16.1	0.24	0.26	47.5	61.8	30
36	12.6	16.9	0.24	0.26	51.7	65.6	29

Vu et al. [24,25].

Table 9
Experimental and estimated permeation properties of membranes using Ultem as continuous matrix at various loading of carbon molecular sieve insert (CMS)

2 M membrane	Permeability (Barrer)				Permselectivity		Error in selectivity (%)
	CO_2 exp.	CO_2 est.	CH_4 exp.	CH_4 est.	C/M exp.	C/M est.	
ϕ (vol.%)/β	0.907	0.907	0.622	0.622			
0	1.45	1.45	0.037	0.037	38.8	7.3	0
16	2.51	2.25	0.058	0.050	43	45.3	5
20	2.90	2.52	0.060	0.053	48.1	47.4	1.5
35	4.48	4.10	0.083	0.071	53.7	57.3	7

Vu et al. [24,25].

Table 10
Relative permeability of CO_2 and CH_4 in coated carbon black filled polysulfone membranes

ϕ	P_{eff}/P_c				Permselectivity	
	CO_2 exp.	CO_2 pred.	CH_4 exp.	CH_4 pred.	(CO_2/CH_4) exp.	(CO_2/CH_4) pred.
0	1	1	1	1	41.0	41.0
1.4	0.885	0.98	1.03	1.03	35.3	38.9
3.5	0.798	0.95	2.27	1.08	14.4	36.1
7.1	0.872	0.90	1.162	1.17	30.8	31.5

Bhardwaj et al. [26]. Permselectivity P_{CO_2}/P_{CH_4}.

4. Conclusions

A new model to predict permeability coefficients of pure penetrant through so-called matrix mixed membranes is presented. As Maxwell model it is assumed that permeabilities of penetrant through compounds forming the new membrane and the volume fraction of the filler (ϕ), are known.

It is clearly shown that this new proposal evolves from an early contribution of Chiew and Glandt [8] aimed at finding an exact contribution of particle-to-particle interactions which are not properly estimated by Maxwell model. In performing this achievement the matrix mixed structure is assumed as an ensemble of particles within a continuous phase described spatially through proper statistical functions. A final explicit expression is found (Eq. (15)) to predict the relative permeability as function of ϕ and β which must be considered as an extension of Maxwell expression.

By comparing generated predictions of Eq. (15) with Maxwell and other proposed expressions some interesting findings can be pointed out. Maxwell equation can be safely used, for most applications, when $\phi < 0.2$ but the range can be extended even for larger values depending upon the value of β. It was also shown that Bruggeman (Eq. (9)) expression also produces results in close agreements with Eq. (15) in a relative great range of β and ϕ values as shown in Table 1.

Eq. (15) was also tested against some experimental data reported in the literature. As expected produces predictions in good agreement with experimental findings when a good knowledge of permeability of penetrant in both compounds forming the mixed matrix membrane exists. Some more complex phenomena cannot be explained by any of the models developed on theoretical basis. More experimental information regarding micro media formed in the resulting membrane is needed. As expected Eq. (15) is able to produce good results even when volume fraction of filler reaches high values.

Acknowledgements

Nomenclature

a	dimensionless parameter defined by Eq. (14)
b	dimensionless parameter defined by Eq. (14)
D	effective diffusivity (cm^2/s)
K	dimensionless parameter defined by Eq. (13)
n	dimensionless geometrical parameter
P	permeability coefficient (Barrer)
S	solubility coefficient (cm^3(STP)/cm^3 cmHg)
t	dimensionless critical exponent (see Eq. (11))

Greek letters

α	permselectivity
β	reduced permeation polarizability Eq. (7)
ϕ	fractional volume

Subscripts

A	refer to species A
B	refer to species B
c	refer to permeability of a penetrant in the continuous phase c
d	refer to permeability of a penetrant in the disperse phase d
eff	refer to permeability in the composite membrane

References

[1] Q.Z. Xue, The influence of particle shape and size on electric conductivity of metal–polymer composites, Eur. Polym. J. 40 (2004) 323–327.

[2] C.M. Zimmerman, A. Singh, W. Koros, Tailoring mixed matrix composite membranes for gas separation, J. Membr. Sci. 137 (1997) 145–154.

[3] R. Mahajan, W.J. Koros, Factor controlling successful formation of mixed-matrix gas separation materials, Ind. Eng. Chem. Res. 39 (2000) 2692–2696.

[4] L.M. Robeson, Correlation of separation factor versus permeability for polymeric membranes, J. Membr. Sci. 62 (1991) 165–185.

[5] R. Mahajan, W.J. Koros, Mixed matrix membrane materials with glassy polymer, Polym. Eng. Sci. 42 (2002) 1420–1431 (Part 1).

[6] R. Mahajan, W.J. Koros, Mixed matrix membrane materials with glassy polymer, Polym. Eng. Sci. 42 (2002) 1432–1441 (Part 2).

[7] J.H. Petropoulos, A comparative study of approaches applied to the permeability of binary composite polymeric materials, J. Polym. Sci. Polym. Phys. Ed. 23 (1985) 1309–1324.

[8] Y.C. Chiew, E.D. Glandt, The effect of structure on the conductivity of a dispersion, J. Colloid Interface Sci. 94 (1983) 90–104.

[9] C. Maxwell, Treatise on Electricity and Magnetism, vol. 1, Oxford University Press, London, 1973.

[10] G. Chen, W. Weng, D. Wu, C. Wu, PMMA/graphite nanosheets composite and its conducting properties, Eur. Polym. J. 39 (2003) 2329–2335.

[11] P. Pötschke, A.R. Bhattacharyya, A. Janke, Melt mixing of polycarbonate with mulyiwalled carbon nanotubes: microscopic studies on the state of dispersion, Eur. Polym. J. 40 (2004) 137–148.

[12] G. Banhegyi, Comparison of electrical mixture rules for composites, Colloid Polym. Sci. 264 (1986) 1030–1050.

[13] R.H.B. Bouma, A. Checchetti, G. Chidichimo, E. Drioli, Permeation through a heterogeneous membrane: the effect of the dispersed phase, J. Membr. Sci. 128 (1997) 141–149.

[14] E.E. Gonzo, Estimating correlations for the effective thermal conductivity of granular materials, Chem. Eng. J. 90 (2002) 299–302.

[15] T.T. Moore, R. Mahajan, D.Q. Vu, W.J. Koros, Hybrid membrane materials comprising organic polymers with rigid dispersed phases, AIChE J. 50 (2004) 311–321.

[16] S.W. Churchill, The thermal conductivity of dispersions and packed beds: an illustration of the unexploited potential of limiting solution correlation, in: A. Mujumdar, R. Mashelkar (Eds.), Advances in Transport Processes, vol. IV, Wiley, New Delhi, 1986, pp. 394–418.

[17] L.M. Robeson, A. Noshay, M. Matzner, C.N. Merriam, Physical property characteristics of polysulfone/poly-(dimethylsiloxane) block copolymer, Angew. Makromol. Chem. 29/30 (1973) 47–62.

[18] T.M. Gür, Permselectivity of zeolite filled polysulfone gas separation membranes, J. Membr. Sci. 93 (1994) 283–289.

[19] W. Ji, S.K. Sikdar, S.T. Hwang, Sorption, diffusion and permeation of 1,1,1-trichloroethane through adsorbent-filled polymeric membranes, J. Membr. Sci. 103 (1995) 243–255.

[20] S.A. Netke, S.B. Sawant, J.B. Joshi, V.G. Pangarkar, Sorption and permeation of acetic acid through zeolite filled membrane, J. Membr. Sci. 107 (1995) 23–33.

[21] R. Mahajan, W.J. Koros, M. Thundyl, Mixed matrix membranes: important and challenging, Membr. Technol. 1999 (105) (1999) 6–8.

[22] S.B. Tantekin-Ersolmaz, L. Senorkyan, N. Kalaonra, M. Tather, A. Erdem-Senatalar, *n*-Pentane/*i*-pentane separation by using zeolite-PDMS mixed matrix membranes, J. Membr. Sci. 189 (2001) 59–67.

[23] T.W. Pechar, M. Tsapatsis, E. Marand, R. Davis, Preparation and characterization of a glassy fluorinated polyimide zeolite-mixed matrix membrane, Desalination 146 (2002) 3–9.

[24] D.Q. Vu, W.J. Koros, S.J. Miller, Mixed matrix membranes using carbon molecular sieves. I. Preparation and experimental results, J. Membr. Sci. 211 (2003) 311–334.

[25] D.Q. Vu, W.J. Koros, S.J. Miller, Mixed matrix membranes using carbon molecular sieves. II. Modeling permeation behavior, J. Membr. Sci. 211 (2003) 335–348.

[26] V. Bhardwaj, A. Macintosh, I.D. Sharpe, S.A. Gordeyev, S.J. Shilton, Polysulfone hollow fiber gas separation membranes filled with submicron particles, Ann. N. Y. Acad. Sci. 984 (2003) 318–328.