

Prediction of the Gas Permeability of Heterogeneous Polymer Blends

JAN KOLARÍK*

*Institute of Macromolecular Chemistry
Academy of Sciences of the Czech Republic
16206 Prague 6, Czech Republic*

LUCA FAMBRI, ALESSANDRO PEGORETTI, and AMABILE PENATI

*Department of Materials Engineering
University of Trento
38050 Trento, Italy*

A recently introduced predictive scheme is used to calculate the permeability of various types of heterogeneous polymer blends, which are characterized by the ratio of the permeability of constituents in the range 10–10,000. The scheme combines a two-parameter equivalent box model and the data on the continuity of constituting phases acquired by modifying equations proposed by the percolation theory; it takes into account the permeability of components and the interval of phase duality (co-continuity) delimited by the critical volume fractions of components v_{1cr} and v_{2cr} . The scheme can be used in two ways: (i) permeability of blends predicted by using the “theoretical” value of parameters $v_{1cr} = v_{2cr} = 0.16$ should be regarded as a first approximation which may not well approximate experimental data due to the fact that real v_{1cr} and v_{2cr} are affected by relative viscosities of the components, interfacial energy, conditions of blend mixing, phase structure coarsening, etc.; (ii) conversely, by fitting experimental data, it is possible to determine v_{1cr} and v_{2cr} for the studied system; thus the scheme can be alternatively viewed as an efficient tool for phase structure analysis of polymer blends.

INTRODUCTION

Tailoring physical properties of heterogeneous polymer blends for specific applications is a frequent task of materials engineering. As generally known, preparation of polymer blends ranks among the effective ways of upgrading existing polymers (1). To reduce experimental time and costs, it is desirable to have reliable models for the prediction of considered physical properties, such as modulus E_b , yield strength S_{yb} , tensile strength S_{tb} and permeability P_b to various gases. Blends of immiscible or partially miscible polymers are isotropic heterogeneous materials (if no orientation is produced in the course of specimen preparation); their phase structure, which affects all physical properties, depends on volume fractions and melt viscosities of components (2–4),

interfacial energy (5–7), processing conditions (8–11), annealing in the process of test specimen preparation (12, 13), etc. Thus the prediction of blend properties and/or the quantitative analysis of phase structure (based on comparison between theory and experiment) are rather complex problems.

Permeability of polymer blends to gases and vapors frequently codetermines the possibilities of their mass-scale usage. The permeability of homogeneous blends consisting of miscible polymers approximately obeys the logarithmic rule of mixing which was derived (14, 15) under the assumption of additivity of the free volumes of components. On the other hand, heterogeneous blends are known to show an S-shape dependence of the logarithm of permeability on blend composition. This contrasting behavior allows one to distinguish between homogeneous and heterogeneous blends. In our previous publication (16), we have presented several examples showing that models originally

*Corresponding author.

derived for the permeability of composite systems (consisting of a permeable continuous matrix and impermeable discontinuous fillers, ribbons or fibers) are not suitable for heterogeneous blends. Numerous papers (17–24) document that the prediction is not satisfactory even if a real permeability of dispersed component(s) is considered. Anyway, such modified models could be suitable for blends only in marginal composition intervals in which the minority component is discontinuous (dispersed). Models proposed for particulate composites are not suitable for isotropic heterogeneous blends mainly for two reasons: (i) they frequently consider discontinuous elements of a regular shape dispersed in a continuous matrix (e.g., models due to Maxwell, Rayleigh or Runge) so that variable morphology of blends can hardly be approximated (25); (ii) they cannot account for a wide interval of co-continuity of constituting phases. In this context it is worth noting that the minority component in two-component polymer blends may become partially continuous at volume fractions as low as $0.1 < v < 0.2$.

Recently we have proposed (16, 26–28) a versatile predictive scheme for the modulus, yield (or tensile) strength or permeability of heterogeneous polymer blends which takes into account (i) the properties of components, (ii) the interval of phase duality, (iii) interfacial adhesion and (iv) partial miscibility of components (29). The scheme is based on the combination of (i) a two-parameter equivalent box model (EBM) (Fig. 1) and (ii) the concept of phase continuity. This concept is rationalized by extensive experimental evidence (1, 30–34) that physical properties of blends are profoundly affected—though in differing ways—by the degree of the connectivity of individual constituents. We have demonstrated (26–28) that v_{ij} can be approximately calculated *a priori* by using modified equations proposed by the percolation theory; thus we can predict selected physical properties for which we can derive equations in terms of the EBM. The objective of this paper is to show that the scheme can be used in two ways: (i) permeability of blends can be predicted by using the “theoretical” values of the critical volume fractions of components $v_{1cr} = v_{2cr} = 0.16$; however, this should be regarded as a first approximation which may not well approximate experimental data due to the fact that real v_{1cr} and v_{2cr} are affected by the relative viscosities of components, conditions of blend mixing, phase structure coarsening, etc.; (ii) conversely, by fitting experimental data it is possible to determine *a posteriori* v_{1cr} and v_{2cr} characterizing better the studied system; thus the scheme can be alternatively viewed as an efficient tool for analysis of the phase structure of blends.

PREDICTIVE SCHEME

Phase continuity is usually visualized by means of the well-known parallel and series models (26–28, 33, 34). The parallel coupling of components implies that all constituents (phases) are continuous in the direction of the permeant flux (16, 24) (or acting force in

the case of mechanical properties). In the series coupling, all components are discontinuous in the direction of the transport (or acting force). In principle, isotropic heterogeneous materials cannot be adequately represented by a simple parallel or series model (16, 24, 35), but more complex models are required which combine both couplings of components in such a way that the response of the model is equivalent to that of the modeled material. In such models it is assumed (16, 26–28) that (i) the structure and properties of blend constituents are identical with those of parent polymers and (ii) the interphase (created along the interface due to interdiffusion of components) does not perceptibly affect blend properties. Obviously, any predictive model is likely to fail if the mixing process produces a significant change in the structure (e.g., crystallinity) and/or in the considered property of a constituent.

The EBM in Fig. 1 is a two-parameter model as of four its volume fractions v_{ij} only two are independent. The fractions of either component coupled in parallel (subscript p) or in series (subscript s) are related as follows:

$$\begin{aligned} v_p &= v_{1p} + v_{2p}; v_s = v_{1s} + v_{2s}; v_1 = v_{1p} + v_{1s}; v_2 = \\ &v_{2p} + v_{2s} \quad v_1 + v_2 = v_p + v_s = 1 \end{aligned} \quad (1)$$

The contributions of the parallel and series branches to the permeability of the EBM are expressed by following equations (16, 26–28):

$$P_p = (P_1 v_{1p} + P_2 v_{2p}) / v_p \quad (2a)$$

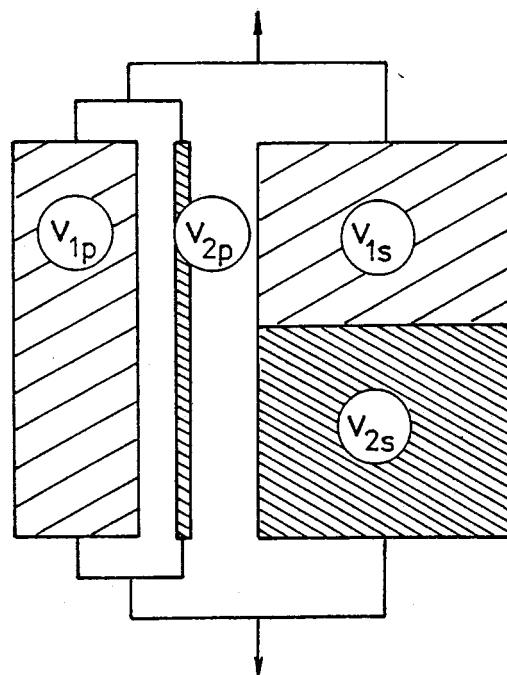


Fig. 1. Equivalent box model for a binary blend 60/40.

$$P_s = v_s / [(v_{1s}/P_1) + (v_{2s}/P_2)] \quad (2b)$$

The permeability of two-component blends is then given as the sum ($P_p v_p + P_s v_s$):

$$P_b = (P_1 v_{1p} + P_2 v_{2p}) + v_s^2 / [(v_{1s}/P_1) + (v_{2s}/P_2)] \quad (3)$$

The second step to implement in the predictive scheme is the derivation of the equations for v_{ij} defined in Fig. 1. Percolation approach leads to analogous formulae for the permeability (36), elastic modulus (37, 38), and diffusion coefficients (for small permeant molecules) (25) of binary blends with negligible contribution of one component to the considered property. If $P_1 \gg P_2$, then

$$P_{1b} = P_{1o} (v_1 - v_{1cr})^{t_1} \quad (4)$$

where P_{1b} is the permeability of a blend, P_{1o} is a constant, v_{1cr} is the critical volume fraction (the percolation threshold), and t_1 is the critical percolation exponent. The percolation concept means that at $v_1 < v_{1cr}$ the respective component is present only as isolated particles and clusters, while at $v_1 > v_{1cr}$ a fraction of the component becomes continuous. However, either component in a binary heterogeneous blend is characterized by its v_{cr} and t . If $P_1 = P_{1o}(1 - v_{1cr})^{t_1}$ is the permeability of the neat component 1, then Eq 4 can be modified (16, 28, 39, 40) to give the following form:

$$P_{1b} = P_1 [(v_1 - v_{1cr}) / (1 - v_{1cr})]^{t_1} \quad (5)$$

where P_{1b} is the permeability of a blend characterized by $P_1 \gg P_2$. In such a blend, the contribution $P_2 v_{2p}$ of that part of component 2 that is coupled (Fig. 1) in parallel and the contribution of the whole series branch (Eq 3) are negligible in comparison with the contribution $P_1 v_{1p}$ of the component 1. As $P_{1b} = P_1 v_{1p}$ for $P_1 \gg P_2$ (or $P_{2b} = P_2 v_{2p}$ for $P_2 \gg P_1$), v_{1p} and v_{2p} (Fig. 1) can be expressed as functions of blend composition:

$$v_{1p} = [(v_1 - v_{1cr}) / (1 - v_{1cr})]^{t_1} \quad (6a)$$

$$v_{2p} = [(v_2 - v_{2cr}) / (1 - v_{2cr})]^{t_2} \quad (6b)$$

Remaining v_{1s} and v_{2s} are evaluated by using Eq 1. Obviously, the values of v_{ij} introduced into the equations (derived in terms of the EBM) for various physical properties of blends must be identical.

Equations 6 contain four parameters, namely v_{1cr} , v_{2cr} , t_1 , and t_2 . The reported values of t are equal to 1.6–1.7 (25, 41), 1.7 (36) and 2 (42) comply well with the theoretical prediction (37) $t = 1.8$; besides, it is easy to show that the effect of such variations in t on v_{ij} is rather small. Thus $t_1 = t_2 = 1.8$ will be considered in our calculations as a constant in order to have only two parameters in the scheme. Theoretical critical volume fraction $v_{cr} = 0.16$ was calculated (25, 38, 41, 43) for random spatial array of discrete spherical domains, while real values (16, 26–28, 36, 41) marking the onset of the continuity of components in polymer blends may be higher or lower than 0.16. Produced phase structures are affected not only by

volume fractions of components and their relative viscosities, but also by the mixing machine and conditions. These effects are so complex that no attempt has been made so far to quantitatively foresee v_{cr} for components of produced blends. It should be noted that any appreciable change in viscosity of one component will influence both v_{1cr} and v_{2cr} (16, 44). As the factors affecting v_{cr} also control the interval of phase duality, a “basic” symmetric interval $0.16 < v < 0.84$ can be viewed as a first approximation when relative viscosities of the components are close to each other. If they are different then the component with a lower viscosity exhibits a stronger tendency to the formation of a (co-)continuous phase, which leads (45) to a lower v_{cr} (in comparison with that of the other component) and an asymmetric interval of the phase duality. The “phase inversion point,” which might be identified with the center of the phase duality interval, is approximately related (1–4) to melt viscosities η_1 and η_2 by a simple empirical rule $(\eta_1/\eta_2) = (v_1/v_2)_{inv}$.

In general, as real v_{1cr} and v_{2cr} characterizing a series of binary blends are not known *a priori*, the primary prediction of considered physical properties can be based on universal (theoretical) values $v_{1cr} = v_{2cr} = 0.16$; however such prediction should be regarded as a first approximation which may not well approximate experimental data. On the other hand, we can *a posteriori* adjust real v_{1cr} and v_{2cr} by fitting experimental data; thus the outlined scheme can be alternatively viewed as an efficient tool for the analysis of the phase structure of blends. In the marginal zone $0 < v_1 < v_{1cr}$ (or $0 < v_2 < v_{2cr}$), where only component 2 (or 1) is continuous, simplified relations $v_{1p} = 0$, $v_{1s} = v_1$ (or $v_{2p} = 0$, $v_{2s} = v_2$) can be used for the minority component. It is worth noting that the minority phase—though it does not show any continuity in the region $0 < v < v_{cr}$ —markedly reduces the continuous fraction v_p of the majority phase (26).

RESULTS AND DISCUSSION

The data on permeability of various binary blends (23, 35, 44, 46) are confronted with the theoretical prediction rendered by the outlined scheme in Figs. 2–5. In all Figures, the “basic” dependence (dashed line) of the relative blend permeability P_{br} is calculated by using the universal (theoretical) constants $v_{1cr} = v_{2cr} = 0.16$ and $t_1 = t_2 = 1.8$. In Fig. 2, the data (23) are given on blends where relative permeabilities of components, i.e., $P_{1r} = 1$ and $P_{2r} = 7.5$, are of the same order of magnitude. As can be seen, the “basic” curve plausibly approximates the experimental data. However, Eq 3 fits experimental data very well if adjusted values $v_{1cr} = 0.16$ and $v_{2cr} = 0.30$ are used. This result implies that phase duality occurs in the interval $0.16 < v_1 < 0.70$; its asymmetry is probably caused by $\eta_1 < \eta_2$.

In Figs. 3–5 the semilogarithmic plot is used because it is more instructive than the linear one for the blends of polymers with very different permeability. Similarly enough to Fig. 2, also in Fig. 3, the universal

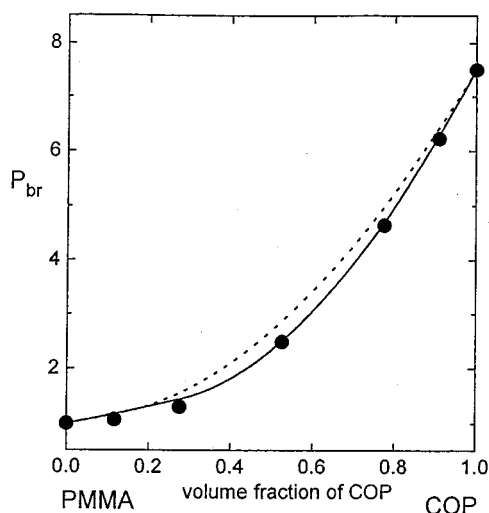


Fig. 2. Relative permeability to oxygen as a function of the composition of poly(methyl methacrylate)/siloxane copolymer blends (experimental data from ref. 23). Full line: $v_{1cr} = 0.16$; $v_{2cr} = 0.30$; $t_1 = t_2 = 1.8$; dashed line: $v_{1cr} = v_{2cr} = 0.16$; $t_1 = t_2 = 1.8$.

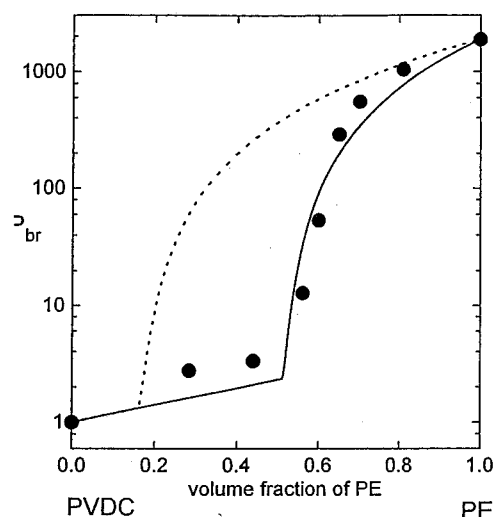


Fig. 4. Relative permeability to oxygen as a function of the composition of polyethylene/poly(vinylidene chloride) blends (experimental data from ref. 11). Full line: $v_{1cr} = 0.16$; $v_{2cr} = 0.51$; $t_1 = t_2 = 1.8$; dashed line: $v_{1cr} = v_{2cr} = 0.16$; $t_1 = t_2 = 1.8$.

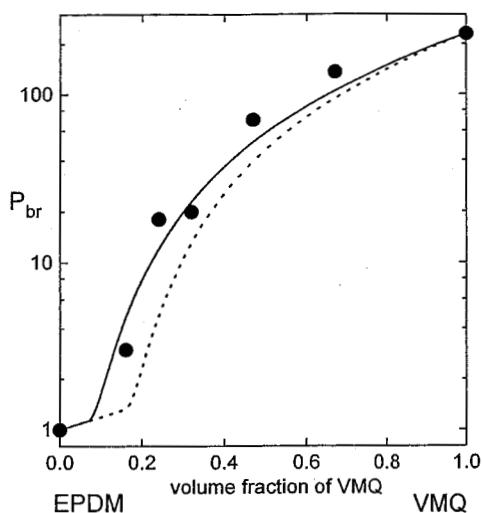


Fig. 3. Relative permeability to methanol vapor as a function of the composition of crosslinked blends of a terpolymer of ethylene, propylene and ethylenenorbornene (EPDM) with poly(dimethylvinyl-methyl)siloxane (VMQ) (experimental data from ref. 35). Full line: $v_{1cr} = 0.16$; $v_{2cr} = 0.07$; $t_1 = t_2 = 1.8$; dashed line: $v_{1cr} = v_{2cr} = 0.16$; $t_1 = t_2 = 1.8$.

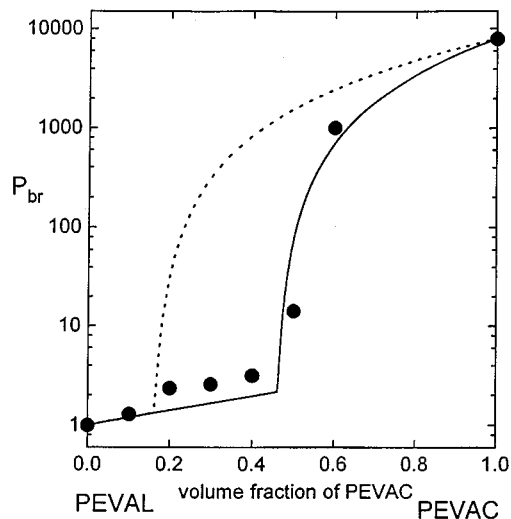


Fig. 5. Relative permeability to oxygen as a function of the composition of poly(ethylene-co-vinyl alcohol) (PEVAL) / poly(ethylene-co-vinyl acetate) (PEVAC) blends (experimental data from ref. 46). Full line: $v_{1cr} = 0.16$; $v_{2cr} = 0.46$; $t_1 = t_2 = 1.8$ Dashed line: $v_{1cr} = v_{2cr} = 0.16$, $t_1 = t_2 = 1.8$.

dependence predicted by Eq 3 with the “basic” constants is rather close to experimental results (35). However, in contrast to Fig. 2, a better coincidence is attained when $v_{2cr} = 0.10$ is selected, which is lower than the theoretical value. On the other hand, $v_{1cr} = 0.16$ is only approximate because the dependence P_{br} vs. composition is generally insensitive to this parameter as long as $P_1 \ll P_2$. Nonetheless, the relation $v_{1cr} > v_{2cr}$ is in accord with rheological data (35) showing that the relative viscosity of EPDM is more than

four times higher than that of poly(dimethylvinyl-methyl)siloxane (VMQ1). It is interesting to note that VMQ1 contained about 12 vol% of silica which means that Eq 3 suits well even for a ternary system. In this case it is probably so because VMQ1-silica composite behaves as a component with constant structure and properties.

Figures 4 and 5 bring examples of blends consisting of components that differ by 3–4 orders of magnitude in their permeability ($P_2/P_1 = 1878$ and 7950). The

“basic” curves calculated for $v_{1cr} = v_{2cr} = 0.16$ deviate a lot from experimental data. Obviously, the components with a higher relative permeability, which controls P_{br} , are characterized by v_{2cr} higher than 0.16. The melt viscosity ratio PE/PVDC was about 0.1 (44); unfortunately, no viscosity data are given in (46). These examples illustrate how the dependence P_{br} vs. blend composition can be shifted along the composition scale by the ratio of relative viscosities (cf. also refs. 16, 35). The value of v_{2cr} , which is manifested as a break (discontinuity) in the slope of the P_{br} vs. composition curve, could be adjusted in these cases with accuracy of about 0.01 due to very high P_{2r} s. Moreover, it can be seen in Figs. 3–5 that the calculated curves do not show any inflexion point at $v_2 > v_{2cr}$ which may be sometimes observed on empirical curves drawn through experimental data.

CONCLUSIONS

The permeability of heterogeneous polymer blends to gases or vapors can be approximately predicted with the aid of the proposed scheme. The procedure is based on (i) the equation derived for a two-parameter equivalent box model and (ii) the data on the phase continuity of constituents calculated from modified equations proposed by the percolation theory. The scheme takes into account the permeability of either component and the interval of phase duality (co-continuity) delimited by the critical volume fractions v_{1cr} and v_{2cr} which are the only parameters because the critical percolation exponent is considered to be a constant ($t_1 = t_2 = 1.8$). Permeability predicted by using a universal value $v_{1cr} = v_{2cr} = 0.16$ may not accurately approximate experimental data because v_{1cr} and v_{2cr} in real blends are frequently different being affected by relative viscosities of components, conditions of blend mixing, phase structure coarsening in the process of test specimen preparation, etc. *Vice versa*, it is possible to select such values of v_{1cr} and v_{2cr} for individual series of blends that the calculated dependence P_{br} vs. blend composition fits well experimental data; in this way the scheme becomes an efficient tool for the analysis of the phase structure of polymer blends.

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