



Elementary prediction of gas permeability in glassy polymers



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ABSTRACT

The transport model proposed by Minelli and Sarti for the representation of gas and vapor permeability in glassy polymers has been extensively applied to various systems, and the model results are thoroughly analyzed. The approach is based on fundamental theory for the diffusion of low penetrant species in polymers, in which the diffusivity is considered as the product of the molecular mobility, and a thermodynamic coefficient, accounting for the concentration dependence of the chemical potential. The model relies on the thermodynamic description of the penetrant/polymer systems provided by the NonEquilibrium Thermodynamics for Glassy Polymers (NET-GP) approach. The penetrant mobility is assumed to depend exponentially on penetrant concentration, and the model contains two parameters only: mobility coefficient at infinite dilution and plasticization factor.

The model parameters obtained from the analysis of the permeability behaviors of various systems have been examined and general correlations are derived. The mobility coefficient is indeed correlated to the properties of the pure penetrants (penetrant molecular size) and pure polymer (fractional free volume and characteristic energy). This allows the derivation of a simple and general expression for the prediction of the permeability of any penetrant species in glassy polymers in the range of low penetrant pressures, as well as the selectivity of any gas pair. Remarkably, the model predictions are able to represent quite accurately the experimental data available in the literature. Furthermore, the plasticization factor is correlated to the swelling produced by the penetrant into the glassy polymer matrix, obtaining thus a reliable tool for the estimation of the pressure dependence of gas permeability on upstream pressure.

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1. Introduction

The transport of gases and vapors in polymeric phases is of great relevance in several different technologies, such as packaging, painting or sensor development, and particularly membrane separation [1–6]. The use of polymeric membranes for the removal of one or more components from a gaseous stream has received great attention for CO₂ capture or for natural gas sweetening applications [7–10], as it offers clear advantages with respect to conventional separation techniques [11].

Therefore, the gas permeability in both rubbery and glassy polymers is often investigated experimentally, to develop materials with best separation and process performance. In parallel, modeling efforts are aimed at the description of the experimental permeability data and their correlation with process parameters, such as temperature, pressure and gas composition. Different approaches have been considered in the last decades to describe the

solution-diffusion mechanism [12] of low molecular weight species in polymer phases [13–18]. In the case of glassy polymers, a particular care is required due to their specific nonequilibrium nature and, for this reason, most of the models commonly employed are empirical in character. The Dual Mode Sorption model (DMS), developed several decades ago [19,20], is still the most frequently used approach to represent sorption and transport behaviors in glassy polymers [21–23], mainly due to its simplicity, although some behaviors experimentally encountered cannot be interpreted by its use. In particular, as far as solubility is concerned, DMS model is qualitatively in contrast with the S-shape solubility isotherm observed e.g. for alkyl alcohols in high free volume glassy polymers as poly(trimethyl silyl propyne) PTMSP [24,25], or addition type poly(trimethyl silyl norbornene) PTMSN [26]. On the other hand, as far as the transport behavior is concerned DMS model is unable to describe the increase in gas permeability observed e.g. for CO₂ permeation in poly(ethyl methacrylate) PEMA [27] or in poly(methyl methacrylate) PMMA [28], unless further ad hoc model parameters are introduced. The application of DMS model may be very useful in different cases, but the consequences derived from a strict interpretation of the basic

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assumptions may be in contrast with actual observations.

The possibility of obtaining correlations between the permeability of some relevant gases and the polymer properties has attracted the efforts of several scientists [29], aiming at the development of possibly simple relationships suitable for predictive purposes [30–33]. Most of such approaches consider the chemical structure of the polymer macromolecule, and use group contribution methods for the evaluation of the permeability of relevant gases, mainly CO₂, CH₄ and N₂, and only in few cases the analysis has been extended to H₂, He, O₂ or even to heavier compounds [34–37]. The required model parameters, relative to each functional group of the polymer structure, are thus retrieved from the extensive literature of permeability data at a reference temperature and upstream pressure. Other methods have been also proposed, such as the graph theoretical approach [38,39], and the artificial neural network [40], although they are only rarely employed.

Furthermore, computer molecular simulations can be conveniently employed to predict gas permeability in polymer membranes, evaluating separately solubility and diffusion coefficients, e.g. by molecular dynamics [41,42], which, however, requires large computational power and long simulation times, in particular for the case of glassy polymers.

The broad collection of permeability data available in the literature has been also statistically analyzed, and useful relationships were derived between the separation factor (simply calculated at negligible permeate pressure as: $\alpha_{ij} = P_i/P_j$) and the permeability of the more permeable penetrant P_i , using the well-known Robeson plot [43,44]. The latter trade-off correlation has been derived on the basis of experimental observations, and it represents an important reference widely used to evaluate and compare the performances of new membrane materials. Examination of general correlations between solubility and diffusion coefficients on one side, with gas condensability and molecular size on the other, provided some explanation for such trade-off behavior [45–48]. Later developments provided also indications on the temperature dependence of the permeability/selectivity correlations [49,50], and extension to real gas mixtures [51]. A more fundamental treatment of the trade-off correlation has been provided by Lou et al., following a thermodynamic based approach, although limited to the analysis of solubility coefficient and solubility-selectivity [52].

An alternative method for the description of gas and vapor permeability in glassy (or rubbery) polymers has been recently proposed [53], based on a fundamental treatment of the transport equation for low molecular weight species in dilute binary mixtures. That approach considers the diffusion coefficient as the product of a purely kinetic factor, the mobility coefficient, and of a thermodynamic factor, associated to the concentration dependence of the penetrant chemical potential in the polymer phase [54]. The thermodynamic description of the penetrant/polymer system (both thermodynamic factor and solubility coefficient) is provided by the well-established NELF model [55,56], while the mobility coefficient is endowed with an exponential dependence on penetrant mass fraction, as typically encountered experimentally. The description of the mobility coefficient contains thus only two adjustable parameters of this model, namely the mobility coefficient at infinite dilution and the plasticization factor, accounting for the increase of penetrant mobility with its concentration.

The model proved to be effective in the description of all the different permeability behaviors of CO₂ (with or without “plasticization”), light gases or heavier penetrants as a function of upstream pressure and temperature, in all the cases inspected, including conventional glassy polymers [53,57,58], blends and

copolymers [59], semicrystalline phases [60], as well as high free volume glassy polymers [61]. The two parameters of the physically based model have a precise physical meaning, and thus a clear correlation is expected to hold true between model parameters and the physical properties of both penetrant and polymer species.

In this work, the large collection of mobility parameters retrieved in our previous analyses is used to obtain general correlations between their values and penetrant and polymer properties. To that aim, the molecular size is used as the relevant penetrant property, while fractional free volume and the characteristic energy are the relevant properties considered for the polymer matrix. The correlations obtained are used for the development of a simple and effective procedure for the predictive estimation of gas permeability and selectivity in glassy polymeric membranes, based on the properties of the pure polymer and pure penetrant only. The procedure developed is then applied as an example to obtain in a predictive way the Robeson plots at infinite dilution for CO₂/N₂ and CO₂/CH₄ separations for several interesting membrane materials.

2. Theoretical background

The details of this thermodynamic based model for gas permeability in polymeric membranes have been presented in a previous work [53], and the main features are here only briefly recalled for the sake of clarity.

2.1. Thermodynamic based model for gas permeability

The permeability of a low molecular weight species in polymeric membranes is obtained from the proper averaging of the product between solubility and mobility coefficient, which are both concentration dependent.

The solubility coefficient, $S_1 = \omega_1/p_1$ relating the mass fraction ω_1 in the polymer to the partial pressure in the gas p_1 under phase equilibrium conditions, can be obtained by applying the thermodynamic relationships for solute/polymer mixtures, such as conventional equation of state (EoS) approaches for equilibrium systems (rubbery polymers), or appropriate nonequilibrium thermodynamic models for the glassy state. In this work, use is made of the NonEquilibrium Thermodynamic model for Glassy Polymers (NET-GP) [55,56], which proved to be effective in the description of the solubility of gases and vapors in all the glassy polymers inspected [62–67]. The model describes the nonequilibrium behavior of the polymer glass by using an additional state variable, the actual polymer density, which measures the departure from equilibrium conditions; the approach provides an accurate and effective extension of conventional EoS procedures to the calculation of the thermodynamic properties below T_g [68–70]. The NET-GP approach is applied by using the lattice fluid model by Sanchez and Lacombe [71,72], giving rise to the so-called NonEquilibrium Lattice Fluid (NELF) model, already widely applied and illustrated in previous publications [55].

For the sake of completeness, the details are reported in the Supporting information section, which includes the definition of model parameters and the basic equations of the lattice fluid theory, for both nonequilibrium and equilibrium states (Table S1). The pure polymer and pure penetrant properties are described by means of three characteristic parameters, T^* , p^* and ρ^* , whose values are already available in the literature, as determined from the analysis of pVT (pressure-volume-temperature) data or VLE (vapor-liquid-equilibrium) data. The values of the characteristic parameters are reported in Table S2 and S3 of the Supporting information section.

The penetrant/polymer mixtures are described by using the

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