Gas permeability in glassy polymers: A thermodynamic approach

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ABSTRACT

The permeability of various low molecular weight species (both gases and vapors) in a series of glassy polymers has been extensively analyzed by means of a thermodynamic based approach for solubility and diffusivity, recently proposed and already applied to a few penetrant/polymer systems. The model relies on the thermodynamic description of the solubility behaviors of the solutes provided by the nonequilibrium thermodynamic model for glassy polymers (NET-GP), while the diffusivity is the product of the mobility coefficient, a purely kinetic quantity, and the thermodynamic factor, accounting for the dependence of the penetrant chemical potential on its concentration in the glassy polymer matrix.

The model is applied to permeability data of many penetrant species from very light gases, such as hydrogen or helium, to hydrocarbons and fluorocarbons, in several different glasses, including very high free volume materials, polyimides and fluoropolymers. The model proved to be effective in the representation of all types of permeability behaviors with respect to penetrant upstream pressure, which may be either decreasing, increasing, or with a nonmonotonous trend showing a minimum value at the so-called plasticization pressure.

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1. Introduction

The transport of various low molecular weight species in polymeric systems has a great relevance for many different applications [1–6], such as, among the others, membrane processes for the separation of the different components of gaseous streams [7–9]. To this aim, several experimental works have been devoted to the characterization of conventional as well as novel materials, seeking for the best performances in terms of gas permeability and selectivity versus the compounds of interest [10,11]. Glassy polymers are often envisioned as potential candidates for the development of membrane materials, able to meet the requirements for industrial processes. Therefore, the understanding of the mechanism of dissolution and transport of the different penetrants in the glassy polymeric systems is of crucial relevance for the proper design of the membrane modules and for the description, or even prediction, of their properties in different conditions of application (e.g. different temperature, pressure or composition). An appropriate modeling tool based on actual physical properties rather than on empirical parameters is also able to provide interesting suggestions

for the development of novel materials, as well for the improvement of the conventional systems.

The permeability P_1 measuring the rate of transport of the permeating species 1 at steady state is defined as follows:

$$P_1 = \frac{\dot{N}_1 \, l}{p_1^u - p_1^d} \tag{1}$$

in which $\dot{N}_1$ is the molar flux of species 1 in a polymer film of thickness l, and the difference in partial pressures $(p_1^u - p_1^d)$ between the upstream and downstream phases is the driving force of the process.

Very few modeling approaches are able to describe successfully the peculiarity of the transport of gases and vapors in glassy polymers, as qualitatively very different behaviors are experimentally observed. Indeed, it has been reported that gas permeability can show either constant, decreasing or increasing trends with upstream penetrant pressure, or even nonmonotonous behavior undergoing through a minimum value at the so-called plasticization pressure [12]. The dual mode sorption model (DMS) [13], empirical in character and with no predictive capability, is the most popular framework considered to represent the transport of gases and vapors in polymer glasses, mainly due to its remarkable simplicity, even though it encounters severe limitations, as it is

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intrinsically unable to describe permeabilities that either increase or are nonmonotonous with pressure.

Recently Minelli and Sarti proposed a simple but effective model able to describe with a remarkable accuracy all the different behaviors observed experimentally [14], including the nonmonotonous trends. The model is based on fundamental expressions for the transport of penetrant species, considering the gradient in chemical potential across the polymer film as the driving force of the diffusive flux, and it relies on the well established nonequilibrium thermodynamic approach for glassy polymers (NET-GP) [15,16] to evaluate the thermodynamic properties of the penetrant/polymer glassy phases. This leads to represent the diffusion coefficient as the product of a purely kinetic factor, the mobility coefficient L, and a thermodynamic factor α, accounting for the dependence of the penetrant chemical potential on its concentration in the membrane. Interestingly, this model has been successfully applied to describe the CO_2 permeability in a series of different conventional glasses [14], as well as on glassy blends, copolymers [17] and semicrystalline polymers [18]; more recently, the transport properties of light gases or vapors have also been analyzed [19,20].

In this work, the thermodynamic transport model is applied to describe the permeability of CO_2, light gases, hydrocarbons and fluorocarbons in a broad series of unconventional or novel glassy polymers with relevant potential for application as gas separation membranes, such as those endowed with a very high free volume, selected polyimides and fluorinated amorphous Teflons. Indeed, all such polymers are of great relevance in membrane science, both from the academic and industrial point of view, and significant research studies have been devoted to their characterization as well as to the modeling analysis of their performance. However, the description of the permeation behavior in such polymers still relies on mere empirical correlations and sometimes seems to require the pretended porous structure of the matrix.

The main aim of this work is, on one hand, to prove the applicability and the effectiveness of this approach to any kind of penetrant/polymer pairs, and, on the other hand, to retrieve a series of model parameters for the various systems investigated. The correlations for the model parameters with the physical properties of both penetrant and polymer are of great interest for predictive purposes.

2. Theoretical background

The model for the description of gas permeability in glassy polymers has been already presented in detail in a previous publication [14]; however, the main features are here recalled for clarity sake. The model takes advantage of the fundamental expression derived for the diffusion of low molecular weight species 1 in binary (or pseudo-binary) mixtures, as the product of a kinetic coefficient, the mobility L_1, and the thermodynamic factor α [21]:

$$D_1 = \frac{\partial \mu_1 / RT}{\partial \ln \omega_1} \cdot L_1 \equiv \alpha \cdot L_1 \tag{2}$$

The factor α can be readily calculated from the analysis of the experimental solubility isotherm of component (1) in the polymer (2) of interest, or can be provided by the NET-GP model with no need of additional parameters. Conversely, the mobility coefficient is a purely kinetic quantity, which depends on the nature of the polymer and of the penetrant, as it depends on the polymer free volume and on the size of the probe molecules, as it has been already mentioned in previous works [19,20]. Several expressions are suitable to account for such dependences, and in particular the

behavior of the penetrant mobility at increasing concentration in the membrane. Among the others, the free volume theory developed by Vrentas and Duda [22,23] is noteworthy, together with the subsequent modifications to account for the out-of-the-equilibrium state of glassy polymers [24]. However, an exponential behavior with respect to penetrant concentration has been found sufficient to that aim so far, as typically encountered experimentally in the concentration range here of interest. One thus has:

$$L_1(\omega_1) = L_{10} \cdot e^{\beta \omega_1} \tag{3}$$

in which the infinite dilution mobility coefficient L_{10} and the plasticization factor β are the only two adjustable parameters of this model; their value can be retrieved from either diffusion data from transient sorption or obtained in steady state permeation data.

The permeability of species 1 at steady state can be obtained conveniently by integrating the expression for penetrant diffusivity as the product of mobility and thermodynamic factor (Eq. (2)). In the common case in which the upstream side of the membrane is at partial pressure p_1^u, while at the downstream side is at $p_1^d \simeq 0$, the following expression is derived [14]:

$$P_1 = \frac{1}{M_1 p_1^u} \int_0^{p_1^u} \rho_2 L_{10} \exp(\beta \omega_1) \frac{\omega_1}{p_1} z_1 \, dp_1 \tag{4}$$

in which M_1 is the penetrant molecular weight and z_1 is the compressibility factor of the gas phase (evaluated e.g. by the Peng–Robinson equation of state), while ρ_2 is the polymer density and $\frac{\omega_1}{p_1}$ represents the solubility coefficient of species 1 in the polymer 2. The model requires the thermodynamic description of the penetrant/polymer system in the conditions of interest, which is provided by the nonequilibrium lattice fluid model approach (NELF) [15]. The evaluation of the solubility coefficient $\frac{\omega_1}{p_1}$ allows then to retrieve the model parameters L_{10} and β from the analysis of the permeability data at various upstream pressures.

2.1. NELF model description for gas/vapor solubility

The description of the thermodynamic behavior of the solute/polymer mixtures below T_g at the various penetrant pressures is provided by the nonequilibrium lattice fluid model (NELF) [15], which makes use of the lattice fluid theory after Sanchez and Lacombe [25,26] in the framework of the NET-GP approach. Several publications reported the very effective ability of NELF to evaluate the solubility isotherms of gases, vapors or liquids, as well as of their mixtures, in glassy polymers [16,27–30]. Recently, the latest development of this model proved its ability also in the prediction of polymer dilation during sorption, allowing the determination a priori of penetrant solubility [31,32] even in the presence of a significant swelling.

The basic feature of the NET-GP approach is to account for an additional state variable, the actual polymer density ρ_2^{NE}, in order to describe the nonequilibrium behavior of a system in the glassy state: ρ_2^{NE} practically measures the departure from the equilibrium conditions. In this framework, the thermodynamic state of the nonequilibrium penetrant/polymer mixture is described by the usual set of state variables, namely T, p and ω_1, together with the actual polymer density ρ_2^{NE}. Finally, the determination of the gas or vapor solubility is provided from phase equilibrium calculations, i.e. when the penetrant chemical potential in the polymer phase is equal to that in the external fluid phase.

This approach relies on an equation of state model for the evaluation of both equilibrium and nonequilibrium properties, following the appropriate EoS (lattice fluid model in this case). The