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An equation of state (EoS) based model for the fluid solubility in semicrystalline polymers

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ABSTRACT

It is well known that semicrystalline polymers absorb lower amounts of fluid than the corresponding wholly amorphous polymers. This behavior is due primarily to the fact that the crystalline domains do not absorb fluid molecules but additionally, in some cases, to a reduced sorption capacity of the amorphous phase with respect to the pure amorphous polymer. To represent such behavior, we hypothesize that the amorphous domains of semicrystalline polymers are mechanically constrained by the crystallites, and that such effect can be represented by a constraint pressure, p_c, applied on the amorphous phase in addition to the pressure p prevailing in the fluid phase. In this way, any equation of state (EoS) model can be used to evaluate the density, chemical potential, solubility and swelling of the amorphous phase. In particular, we used the Sanchez Lacombe Equation of State (SL EoS), as it describes accurately the behavior of amorphous polymer phases. The binary parameter for the fluid–polymer energetic interactions, k_{ij}, and the constraint pressure p_c are adjusted on the experimental solubility data above and below the polymer melting point T_m, respectively. For polyolefines, the values of p_c lie on a single mastercurve that increases exponentially with the polymer crystalline fraction and decreases exponentially with temperature.

The approach describes accurately the experimental solubility behavior of different gases and vapors in conventional semicrystalline polyolefines like polyethylene and polypropylene of different types, as well as in polyethers such as poly(ethylene oxide) (PEO), in wide temperature ranges.

1. Introduction

The solubility of fluids in polymers is of great importance in a variety of applications, from the food packaging to the chemical, process and pharmaceutical industry, as well as in the oil and gas sector [1–5]. On the other hand, the determination of the phase behavior of polymer–solvent systems is crucial for practical application in polymer production and processing [6–8].

Semicrystalline polymers, such as poly(ethylene) (PE), poly(propylene) (PP) or poly(ethylene terephthalate) (PET) are employed widely in a variety of different fields, in view of their good stability, mechanical and barrier properties. Therefore, the sorption of gases and vapors in such polymers has been extensively characterized, both above and below the polymer melting temperature [9–15].

Several models have been developed to represent the gas and vapor transport in semicrystalline polymers: in such approaches two main factors affect the mass transport. The first one is the hindrance to the diffusion of small molecules, which have to wiggle around the impermeable crystalline domains, and the second one is the partial immobilization of the polymer chains within the amorphous region, due to the surrounding rigid crystalline phase [16,17].

On the other hand, the solubility of gases and vapor in semicrystalline polymers is often treated simply by assuming that the crystalline phase does not absorb fluid molecules, and that the solubility in the amorphous phase is equal to the value measured or estimated in the corresponding wholly amorphous polymer [16,17]. This additive model has been used thoroughly, also as the basis for the description of gas and vapor permeability [18–23], and it allowed an accurate description of the light gases solubility in polyethylene, or of CO_2 in polymers in a limited range of pressure [24–27].

However, the sorption of fluids in biphasic solid media can be a rather complex process, especially in those cases in which the swelling of the polymer matrix induced by the sorbed molecules is relevant, because the crystallites are covalently bonded to the macromolecules of the amorphous phases to form a network [28,29]. Therefore, the presence of the crystalline domains can lower the gas and vapor solubility of the amorphous phase with respect to the corresponding unconstrained amorphous phase [30]. The analysis of many solubility isotherms of different solutes, gases

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and vapors, in polyethylene carried out by Maity [31] revealed a clear discontinuity of the solubility in the amorphous phase of the polymer across the melting temperature. The use of the Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) equation of state [32] showed that the solubility depression below T_m was much larger than what predicted based on a simple additive model in which the solubility in the crystalline domains is neglected, and that in the amorphous phase is assumed equal to the values calculated in the pure rubbery polymer. Such findings, indeed, indicate that an amorphous phase surrounded by crystallites has a different behavior than that observed in the corresponding unconstrained liquid-like polymer.

The effect of crystallites on the amorphous phase has been explicitly pointed out by Bonavoglia et al. [33], who investigated the solubility and swelling behavior of different semicrystalline polymers, in the presence of supercritical CO_2. The modeling approach relied on the Sanchez Lacombe equation of state (SL EoS) [34,35] and its modified version to account for polymer crosslinking [36] and for nonequilibrium behaviors [37]. The introduction of an elastic term in the lattice fluid representation of polymer/penetrant mixture was also employed to describe the semicrystalline polymer behavior [38]. Indeed the amorphous phase of a semicrystalline polymer is often treated as a crosslinked structure, in which the crystallites constrain the bonded noncrystalline portion of the macromolecules just like covalent crosslinks in rubbery materials [39,40].

Interestingly, the model which best represents the experimental CO_2 solubility in the systems analyzed by Bonavoglia et al. [33] is the Nonequilibrium Lattice Fluid Model (NELF), which considers the amorphous domains to be in a hindered, non equilibrium state with a density value different from the one evaluated in the equilibrium state at the same temperature and pressure. Surprisingly such approach offered the best description of solubility in the amorphous phase of the semicrystalline polymers even above T_g and therefore in the rubbery equilibrium state.

Such findings seem to indicate that the constraining effect of the crystallites leads the amorphous phase to an apparent nonequilibrium behavior, assuming different values of density and chemical potential with respect to the equilibrium value at the same temperature and pressure, also above T_g.

In this work we adopt a different modeling approach, which does not require the constrained amorphous phase to be in a non equilibrium state. In particular we propose an equilibrium approach based on an equation of state (EoS) model, coupled to a suitable set of constraints in the phase equilibrium expression, to represent the behavior of the semicrystalline polymer. We assume that the crystalline phase imposes an isotropic stress on the amorphous phase, which can be quantified as a thermodynamic pressure, p_c, in addition to the pressure applied by the fluid phase p. The solubility of the gas in the constrained amorphous phase is then calculated by solving the phase equilibrium problem between the gas and the solid phase, using the equilibrium equation of state model for the density of the gas–polymer mixture and the chemical potential expression. It is noteworthy that the chemical potential of the penetrant in the gaseous phase is calculated at the temperature of the gas–polymer system and pressure of the gaseous phase. On the contrary, the chemical potential of the gas in the solid phase is evaluated at the same temperature and at the total pressure prevailing in the amorphous solid phase, which is, according to the present assumptions, equal to $p + p_c$. The constraint pressure p_c is treated as an adjustable parameter, but it will be shown that its value does not depend on the penetrant type and decreases with increasing temperature, in agreement with its physical meaning.

The use of an additional pressure as constraint to account for the reduced mobility of the polymer macromolecules in presence of crystallites has been first developed by Memari and coworkers, and applied to the study of gas solubility in LDPE. An extra constraint pressure was applied to the amorphous portion of a polyethylene system in a simulation scheme based on the Monte Carlo method, in order to represent correctly the gas solubility, which is otherwise overestimated [41,42]. This technique allowed Memari et al. to obtain reliable results in terms of pure and mixed gas solubility in PE below T_m with penetrant-independent values of the extra pressure.

In this work, we expanded that idea, following the same representation of the mechanical constraint by means of pressure, although the use of classical thermodynamic tools allows for an accurate estimation of solubility with a much lower consumption of computer time with respect to molecular simulation approaches, with a fast solution of the phase equilibrium problem. Moreover, the present approach, as it will be demonstrated in the following, allows to correlate quantitatively the extra pressure to the crystallinity degree of the polymer and to the temperature, offering a rigorous but rather simple and general tool for the evaluation of solubility of fluids in semicrystalline solids.

2. Model description

Equation of state models are often able to provide an accurate and reliable description of thermodynamic properties of polymer–fluid mixtures. Several approaches have been applied to the case of molten polymers, such as PE or PP above their melting temperatures, and they often showed remarkable results. Among the others, it is worthwhile to recall the Lattice Fluid representation of polymeric mixtures adopted by the Sanchez Lacombe equation of state [34,35], or the Statistical Associating Fluid Theory (SAFT) in its different modifications [32,43–45].

2.1. Sanchez Lacombe equation of state

In the present work, the Sanchez Lacombe model is employed to describe the thermodynamic properties of the mixtures formed by the different penetrants with the molten polymers, or with the amorphous phase of the semicrystalline ones. An accurate description of the model can be found in the original works by Sanchez and Lacombe [34,35], but the main features are here briefly recalled for the sake of clarity.

In the Sanchez Lacombe framework, polymer macromolecules are considered as a set of beads on a lattice, and the polymer chains are mixed randomly with penetrant molecules. Unlike the Flory Huggins model [46], the SL EoS considers also configurations with empty sites in the lattice, so that free volume exists in the polymer–penetrant mixture, and volume changes upon mixing penetrant and polymer molecules are allowed. The description of each component is provided by three independent parameters: the characteristic pressure p_i^*, related to the cohesive energy density of component i in the close-packed state (liquid at 0 K), the corresponding mass density ρ_i^*, and the characteristic temperature T_i^*, which is associated to the depth of the potential energy well. These three parameters can be determined from experimental data of pure components, such as saturated vapor pressure or pressure-volume-temperature measurements. The main equations of the SL EoS are systematically illustrated in Table 1, which also includes the main parameters and mixing rules. It is noteworthy that the only binary parameter is the binary interaction coefficient k_{ij}, which accounts for deviations of the polymer–penetrant energetic interactions from the geometric mean rule.

The SL EoS characteristic parameters for penetrants and polymers considered in this work are retrieved from specific collections available in the technical literature, and are reported in Table 2.