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A novel multiscale method for the prediction of the volumetric and gas solubility behavior of high-T_g polyimides

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ABSTRACT

A multiscale method for the evaluation of the fluid solubility in glassy polymers with high glass transition temperature T_g is presented and applied to the case of two polyimides, Ultem and Kapton. The method adopts Molecular Dynamics (MD) to simulate the polymer pressure–volume–temperature (pVT) behavior at temperatures above T_g not experimentally accessible. Such values are used to obtain the polymer parameters for the Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) Equation of State (EoS) required to calculate the gas solubility in the polymers below T_g with the Non Equilibrium PC-SAFT model. The MD-simulated polymer density values agree with the experimental and simulated data available, and the solubility calculated with the Non Equilibrium model represents correctly the experimental values for CH_4, N_2, O_2 and CO_2 sorption in Ultem, and the CO_2 and SO_2 solubility in Kapton at different temperatures. The approach can be applied to other high-T_g glassy polymers.

1. Introduction

The description of gas and vapor solubility in high-T_g glassy polymers, and of polyimides in particular, is relevant for many practical applications, from membrane separations [1,2] to packaging [3,4], and from sensors development [5,6] to medical applications [7,8].

Whereas many macroscopic thermodynamic models based on equations of state (EoS) [9–19] or activity coefficient approaches [20–23] are available to evaluate the properties of rubbery polymers, the description of sorption in glassy polymers is still frequently based on empirical tools, such as the dual mode solubility model [24], containing adjustable parameters that depend on the gas–polymer couple as well as on temperature, pressure and history of the glassy polymer [25].

The Non Equilibrium Thermodynamics for Glassy Polymers (NET-GP) [26–29] is a rigorous macroscopic theory able to predict the solubility of fluids in glassy polymers reliably and accurately with a negligible consumption of CPU time. This approach, combined with an equation of state theory, such as the Lattice Fluid (LF) [9–12], Statistical Associating Fluid Theory (SAFT) [13–16], or Perturbed Hard Sphere Chain (PHSC) [17–19], gives rise to the corresponding non equilibrium models named NELF, NE-PHSC and NE-SAFT [26–29], respectively.

The characteristic parameters required by the model are those of the specific equation of state chosen, and, for the penetrants, they are normally retrieved fitting liquid–vapor (LV) equilibrium data, while for polymers, pressure–volume–temperature (pVT) data above T_g are required. Such data are available in the literature for medium or low-T_g polymers [30], whereas for high-T_g glassy polymers they are often impossible to measure. An alternative route to retrieve EoS parameters in such cases is to fit a set of gas solubility data in the glassy polymer with the NE-EoS model [31]: such procedure however is not as predictive and general as the one previously described.

The prediction of gas solubility in glassy polymers can also be performed with a fully atomistic approach, by means of Molecular Dynamics (MD) or Monte Carlo (MC) methods. The approaches available are the grand canonical Monte Carlo (GCMC) [32], Gibbs Ensemble Monte Carlo (GEMC) [33], Widom test particle insertion [34], staged particle deletion (SPD) [35], and direct particle deletion (DPD) [36–38] methods. These tools provided interesting results as reported in the literature for the prediction of gas solubility in glassy polyimides [39,40] even if their agreement with the experimental results is poorer than that obtained in a molten or rubbery system, and requires longer equilibration times. Furthermore, if the

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penetrant induces swelling and rearrangement of polymer chains, preswollen polymer packing models might be required in order to improve the simulation [37,41–43].

In the present work, the molecular simulation of the glassy polymer structure is carried out above T_g, where the mobility of the chains is much higher and equilibration is achieved faster. The values of polymer density in this range, which are largely inaccessible experimentally, are suitable to obtain the EoS parameters required to model the polymer sorption behavior below T_g by the NET-GP theory. The procedure is applied to polyimides but it can be extended to any other glassy material.

In the literature, few works were devoted to the obtainment of EoS parameters with molecular simulations [44–48]. In particular, Fermeglia and Pricl [44] evaluated the PHSC parameters A^* and V^* with molecular mechanics and a graphical algorithm, while E^* was obtained from MD simulations of monomers in the gas state. In the same work, the LF EoS close-packed state density and pressure, ρ^* and p^*, were obtained by extrapolating to 0 K density and cohesive energy density curves obtained by NpT-MD simulations in the equilibrium state, following the definition of such parameters. The T^* was obtained inserting p^* and ρ^* and a simulated set of pVT data into the EoS expression. In practice, such type of approach uses molecular simulations to evaluate, more or less directly, the EoS parameters based on their definition, which is a theoretically sound methodology.

In this type of methods, however, one relies on the evaluation of a small number of parameters obtained by extrapolation, which can be rather markedly affected by the statistical fluctuations of simulated curves. Moreover, the extrapolation to reference states, such as the absolute zero in the LF model, assumes that the behavior simulated in certain conditions holds true also in the reference state. One has also to consider that the characteristic parameters correspond closely to their definition only if the EoS model represents faithfully the physical behavior of the substance, which is true in the case of simple macromolecules (e.g. polyolefins) but not in the case of complex structures with several functional groups such as polyimides. Finally, in such approach, the algorithms used are not generally valid for any EoS, because they depend on the specific definition of the parameters in the model chosen.

Therefore, in this work we obtained the EoS parameters by regression on the entire set of MD-simulated pVT polymer data above T_g. Such method potentially has several advantages over the previously published ones: (i) it reduces the effect of statistical fluctuations, because the parameters are evaluated on a large number of simulated values; (ii) the procedure is the same for any EoS model chosen and does not require extrapolation to reference states; (iii) it resembles exactly the method used in the case in which experimental data pVT data in the melt state are available, thus the parameters are fully comparable to the ones obtained in the “usual” way for other polymers; (iv) it uses only the average volume obtained in the simulations, which is inherently less affected by unrealistic configurations that may locally appear in the packing models than other simulated quantities; (v) the parameters obtained in this way are able to provide an accurate representation of the pure polymer behavior, whether or not the EoS model chosen represents accurately the polymer structure and its parameters match with their definition. And finally, (vi) the practical decoupling of the parameter determination for the macroscopic EoS model from the used atomistic simulation of pVT polymer data allows also the application of other simulation techniques, e.g. Monte Carlo methods.

The procedure is not limited by the use of information about the polymer volume only: indeed, thermal expansibility and compressibility are ultimately related to energetic properties such as the cohesive energy density CED and solubility parameter δ [49,50], so that a set of pVT data contains all the information required by the EoS models to represent pure substances.

2. Materials

Polyetherimide (trade name Ultem® 1000) was selected to test the approach: despite its high T_g value (around 490 K), some experimental pVT data are available in the rubbery region [30] for a direct comparison with MD values, as well as a number of gas sorption isotherms to be compared with the NET-GP calculations [51–54].

The second polyimide studied is poly(4,4′-oxydiphenylenepyromellitimide) (trade name Kapton® H): for such polymer no clear T_g value is available,[1] and experimental density [30] as well as gas sorption [55–61] data exist only in the glassy range.

3. Modeling details

3.1. Molecular simulation methods

The molecular simulations were carried on by Dr. Matthias Heuchel of Helmholtz-Zentrum Geesthacht Centre for Materials and Coastal Research in Teltow within the framework of the bilateral project Italy-Germany Vigoni “Multiscale prediction of gas solubility in high performance polymers” (2009–2011).

The atomistic representation of the two polymers followed typical approaches in computational simulation of polymers. For both polymers (see structures of the repeating units in Fig. 1), three independent atomistic packing models, formed by a single chain of 73 repeat units for Ultem (4970 atoms) and 115 for Kapton (4487 atoms), were created with the Materials Studio software by Accelrys using the universal COMPASS force field [63,64]. The stepwise procedure to create well-equilibrated atomistic packing models (initial packing at low density with the *Amorphous Cell* routine [65,66], force field parameter and density scaling by a cycle of minimization and MD-steps, simulated annealing, and final relaxation with long NpT-MD simulations) is described in detail e.g. in Ref. [41] and it was already applied to describe the atomistic behavior of several glassy polymers with respect to free volume or solubility properties [40,41,67,68].

All molecular dynamics simulations were run with the Discover software package by Accelrys on 4- to 8-CPU nodes of a 92 CPU RadHat Linux cluster. The integration time step was 1.0 fs with the Verlet velocity algorithm. The van der Waals and Coulomb energy terms were summed up by the group based method. The cut-off distance was 15.5 Å. Pressure and energy tail corrections were added to all energy evaluations. In order to overcome the limitations due to the long relaxation times of glassy polymers at room temperature, the initial polymer packing models were created directly at a hypothetical rubbery state at $T = 900$ or 1000 K (at $p = 1$ bar). The fact that, at these temperatures, the “real” polymer might be already degraded does not affect the validity of the proposed approach. The advantage of such procedure, which has been already exploited by different authors [69,70], is that the mobility of the chains is much higher at this temperature, resulting in faster relaxation processes. Initial guess densities at this temperature (1.06 g/cm^3 for Ultem at 900 K, and 1.19 g/cm^3 for Kapton at 1000 K) were evaluated on the basis of a group contribution method (*Synthia*) [71], and have to be considered only as indicative values required to start packing the chain. The actual

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[1] Most studies locate the T_g of Kapton® H between 620 and 690 K according, mainly, to mechanical measurements, as discussed in Ref. [61]; Wrasidlo however performed calorimetric measurements up to 770 K observing no glass transition but rather evidences of thermal degradation [62].