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Atomistic packing models for experimentally investigated swelling states induced by CO₂ in glassy polymers

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Introduction

Gas induced changes of glassy polymers, manifested as “swelling” or “plasticization”, influence the molecular mobility of the polymer chains as well as their amorphous packing structure. These changes can have drastic influences on properties important for applications, e.g. the long time performance of gas separation membranes [1], or the stability and reliability of construction and barrier materials. In the present study we describe our attempt to develop molecular packing models of representative un-swollen and swollen states for several polymers corresponding to experimental measurements of gas sorption on these materials and also the respective dilation effects.

Results and Discussion

The concentration of sorbed gas in a polymer film sample was measured gravimetrically using an electronic high-pressure microbalance in a temperature controlled air bath. Complementary to the gas sorption, the characteristics of the swelling/dilation behavior of the polymer/gas systems including the associated plasticization and relaxational processes were investigated using a gas pressure dilatometer based on a capacitance distance sensor.

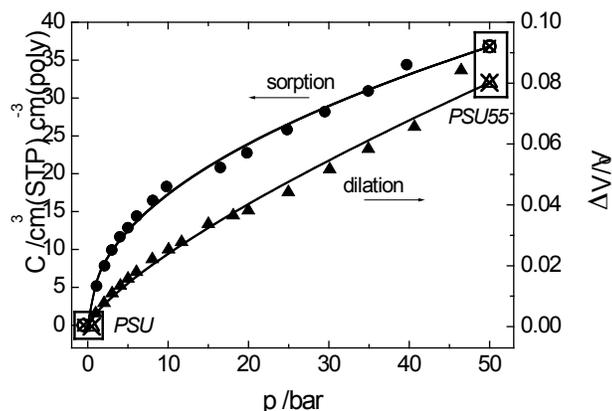


Fig. 1. Experimental sorption and dilation isotherms for PSU/CO₂/35°C: ● sorption isotherm, dilation isotherm (24 h). The pure and the 50 bar CO₂ swelling states chosen for construction of the model are marked (□, □). The lines represent a fit with a two parameter function $C(p) = ap^b$.

As example, in Fig. 1 sorption isotherm data for CO₂ in polysulfone are presented together with respective dilation values determined after a time of 24 h at each pressure step. Due to the difference in characteristic time-scales of the experimentally observed phenomena (minutes to hours for Fickian diffusion, relaxation) and typical atomistic simulations (several nanoseconds) it is not possible to simulate the relaxation effects directly in time with the modeling techniques

used in this study. Therefore for selected reference states (as marked in Fig. 1) atomistic bulk models were realized employing the amorphous cell module of the *InsightII/Discover* software [2]. The applied basic techniques of packing and equilibration are completely described elsewhere, e.g. [3,4]. The obtained models were characterized with respect to their structural features, such as free volume distribution, chain dynamics and gas sorption behavior. As demonstrative example Fig. 2 shows representative slices of about 4 Å thickness of several packing models for PSU. Here, the differences between the un-swollen state and a swollen state are already qualitatively visible. (the model *PSU* was build by packing a polymer chain of 5078 atoms, i.e. 94 repeat units, into a simulation box).

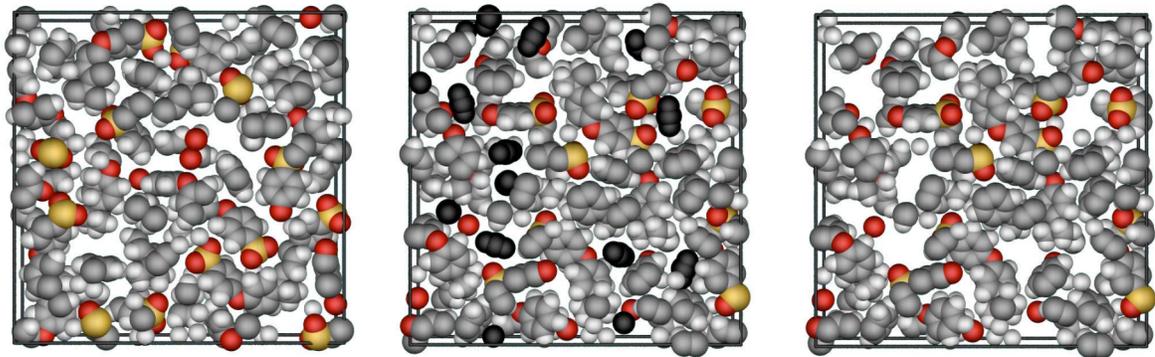


Fig. 2: Representative slices taken from atomistic packing models for polysulfone corresponding to the un-swollen state (PSU, left) and the swollen state (PSU55, center) with the CO₂ molecules colored black and the swollen matrix with the CO₂ molecules removed (PSU55m, right).

The model *PSU55* for the swollen state corresponds to the experimental situation of a PSU sample under 50 bar CO₂ pressure (build by packing the same chain but with additional 55 CO₂ molecules into the box). The volume dilation of about 6% (corresponding to an increase of length of the simulation box of about 1.6%) is only hardly to be seen. But, if we compare the free volume regions of the swollen matrix (model *PSU55m*, CO₂ molecules removed), the significant increase of the free volume is clearly to be seen. In the presentation the comparison will be also made quantitatively, e.g. by considering respective free volume size distributions.

The contribution will demonstrate with several examples the future potential of a close collaboration between experiment and molecular simulation in order to better understand gas-induced structural changes in polymeric membrane materials on a molecular level.

References

- [1] T. Visser, G.H. Koops, M. Wessling, On the subtle balance between competitive sorption and plasticization effects in asymmetric hollow fiber gas separation membranes, *Journal of Membrane Science* 253 (2005) 265–277.
- [2] Polymer User Guide, Amorphous Cell Section, Version 4.0.0p+; Molecular Simulations Inc.: San Diego, CA, 1999.
- [3] D. Hofmann, L. Fritz, J. Ulbrich, C. Schepers, M. Böhning, Detailed-atomistic molecular modelling of small molecule diffusion and solution processes in polymeric membrane materials, *Macromol. Theory Simul.* 9 (2000) 293-327.
- [4] M. Heuchel, D. Hofmann, P. Pullumbi, Molecular Modeling of Small-Molecule Permeation in Polyimides and Its Correlation to Free-Volume Distributions, *Macromolecules* 37 (2004), 201-214.