

**SOLVENT SORPTION IN GLASSY POLYMER FILMS
COUPLING BETWEEN SOLVENT DIFFUSION AND VISCOELASTIC RELAXATION**

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ABSTRACT

Swelling or drying of glassy polymer films exhibit complex kinetics. For such films local thermodynamic equilibrium is no more ensured at each time since the relaxation of the stresses induced by the volume variations involves slow rearrangements of macromolecular chains. A numerical comparison of two models is presented, as a function of the two pertinent parameters describing the coupling between solvent diffusion and polymer relaxation: the Deborah number that defines the ratio between the relaxation and diffusion characteristic times, and R the ratio between the “instantaneous” and “delayed” components of swelling. Then a numerical study of a global estimation method (SIVIA) is made, in order to estimate these parameters from weight uptake kinetics. The robustness of the estimation is analyzed according to R and the Deborah number.

INTRODUCTION

Diffusion of solvents or low molecular weight species in polymer films or membranes is the determining factor in many processes such as the drying of polymer coatings, membrane formation, drug release, etc. When the polymer film is rubbery, i.e. when its temperature is well above the glass transition temperature, solvent sorption (swelling) or desorption (drying) is usually described by Fick’s model, with a mutual diffusion coefficient varying with the solvent concentration. Indeed, in polymer solvent solutions, the diffusion coefficient changes of

several orders of magnitudes when the solvent volume fraction varies from 0.3 to 0 [1]. Swelling or drying kinetics is much more complex in the glassy domain: local thermodynamic equilibrium is no more ensured since the relaxation of the stresses induced by the volume variations involves slow rearrangements of macromolecular chains. The glass transition temperature of a solution, T_g , depends on the solvent content, increasing from the T_g of the pure solvent to the T_g of the pure polymer as the solvent concentration decreases. When drying a solvent/polymer solution at a fixed temperature (lower than the T_g of the pure polymer), the film becomes glassy for a given solvent mass fraction: during a drying experiment, the glass transition is not induced by a change in temperature but by the change in solvent concentration.

When the time scales characterizing diffusion and relaxation are comparable, it is well known that the kinetics is no more Fickian [2-9]. Figure 1 gives an example of different “anomalous” kinetics that can be observed in the glassy domain. This kinetics was obtained by performing gravimetry experiments on the system poly(methyl methacrylate)/methyl acetate [2]. The film is swelled by small successive increasing of the solvent vapor pressure above the film. For each step the solvent uptake is very small so that the diffusion coefficient may be assumed constant during the step. If the kinetics were Fickian the weight uptake versus $t^{1/2}$ would show an initially linear shape followed by an evolution towards an asymptotic value. On the contrary, the sorption curves of Figure 1 display the characteristic pattern

of solvent absorption in the glassy state observed when increasing the solvent content in the film: S-shaped (run S2R1), pseudo-Fickian (run S2R2) and two stages (run S2R3-S2R8).

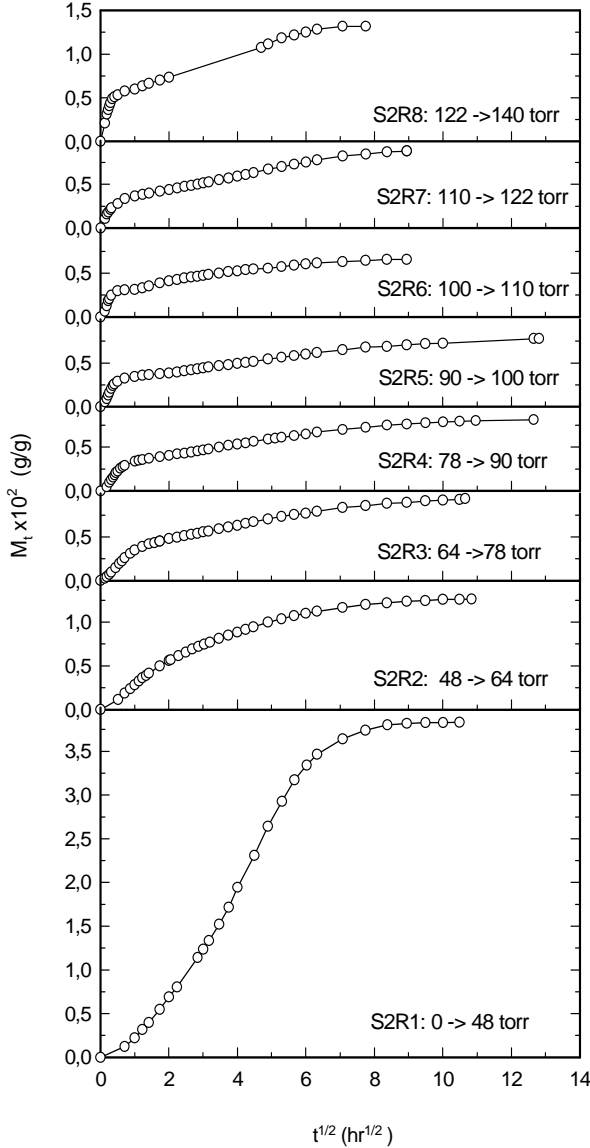


Figure 1: Series of successive absorption kinetics runs of MAc in PMMA at 30°C; weight uptake (g/g of dry polymer) as a function of $t^{1/2}$. (This graph was reproduced from [2])

Although numerous works have been devoted to the problem of non Fickian diffusion in the glassy domain, the involved phenomena are not yet completely understood. Moreover the quantitative interpretation of sorption or desorption experimental

kinetics is then complex, since the parameters that characterize diffusion and relaxation have to be estimated simultaneously. In the present paper a comparison is made between two models of sorption in the glassy state, for the purpose of getting a reliable phenomenological model simple enough to be suitable for estimation algorithms. Then the paper focuses on the estimation problem itself and analyses the robustness of the estimation according to the ratio of the characteristic times of diffusion and relaxation.

MODELING

Models: Several theoretical approaches have been proposed, none of them succeeding in fitting all the types of non-Fickian kinetics [3]. Several of these approaches take viscoelastic relaxation into account through a constitutive equation, where the viscoelastic behavior is approximated by a Maxwell model [5-7]. In the point of view considered in this paper, the effect of structural relaxations is treated mathematically by considering the temporal evolution of the polymer swelling as consisting of an “instantaneous” component plus a “delayed” component.

Petropoulos model (P): In the modeling approach of Petropoulos [8] the diffusion process is formulated in terms of a chemical potential gradient driving force, yielding

$$\frac{\partial c(x,t)}{\partial t} = \frac{\partial}{\partial x} \left(D_T \frac{c}{a} \frac{\partial a(x,t)}{\partial x} \right) \quad (1)$$

where c is the local solvent concentration, a is the corresponding activity, D_T is the thermodynamic diffusion coefficient. The solubility c/a is defined as a measure of the sorption capacity of the polymer at any given stage of the relaxation process. To model viscous relaxation process in a simple manner, a first order model is used and eq. (1) is supplemented with:

$$\frac{\partial c(x,t)}{\partial t} = \frac{\partial c_0}{\partial a} \frac{\partial a(x,t)}{\partial t} + \frac{1}{\tau_r} [c_\infty - c(x,t)] \quad (2)$$

Eq. (2) simply states that incremental penetrant uptake δc over a small time interval δt , can be separated into (i) an “instantaneous” (elastic) swelling, which is associated with a corresponding change in activity δa without relaxation, plus (ii) a “delayed” (viscous) part. The latter corresponds to

the amount of penetrant which can be accommodated in the swelling polymer, at constant activity, due to the extra sorption capacity generated by the relaxation process in time δt . Thus, two sorption isotherms are defined, an instantaneous one $c_0(a)$ for unrelaxed polymer, in addition to that of fully relaxed polymer $c_\infty(a)$. Calculations performed by an explicit finite difference numerical method have shown that the model can predict the basic features of non-Fickian kinetics observed in sorption experiments, with solvent uptake (a) small enough, where the diffusion coefficient and the relaxation time may be assumed constant (e.g. two-stage curves of Fig. 1), as well as (b) large enough to ensure a strong variation of both the diffusion coefficient and relaxation time during the sorption process (e.g. Case II kinetics) [8, 9].

Long and Richman model (LR): the (LR) model [10] can be viewed as a simplified version of the (P) model, the relaxation being taken into account at the interface only: each volume element in the bulk is assumed to be at the thermodynamical equilibrium and the classical formulation for Fickian diffusion is employed to describe the solvent diffusion through the film:

$$\frac{\partial c(x,t)}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c(x,t)}{\partial x} \right) \quad (3)$$

where D is the mutual diffusion coefficient. The effect of the relaxation is introduced by making the surface concentration a function of time in the same way as in the (P) model (first order model). Then, assuming a perfect activity step eq. (2) can be integrated yielding to the following boundary condition:

$$c(x=l, t > 0) = c_0 + (c_\infty - c_0) \left[1 - \exp\left(-\frac{t}{\tau_r}\right) \right] \quad (4)$$

From the theoretical point of view, the Petropoulos model (P) gives a better description of the relaxation phenomena involved during swelling than the Long and Richman (LR) more simple approach.

Two dimensionless quantities are involved in these models: the Deborah number that compares the characteristic times of diffusion and relaxation: $Deb = \tau_r/\tau_d$, with $\tau_d=l^2/D$; and R , the ratio between the

instantaneous and delayed component of the solvent concentration: $R = c_0/c_\infty$. A very small Deb corresponds to the rubbery Fickian case, when relaxation phenomena are instantaneous on the diffusion time scale so that the system is in local thermodynamic equilibrium. On the contrary a very large Deborah leads to two stages kinetics (the two phenomena are well separated) or even to Fickian kinetics if the second stage is not sensitive on the time scale of the experiment. More complex kinetics is obtained for intermediate values, depending on both Deb and R .

Comparison: Figures 2a, 2b and 3 give the comparison of the two models for $Deb = 1$ or 10 and $R = 0.1$ or 0.5 . The dimensionless time is $t^*=t/\tau_d$ and the dimensionless weight uptake is $\Delta M^*=[M(t)-M(t=0)]/[M_\infty-M(t=0)]$. The (LR) model always gives more rapid kinetics, which is expected since the solubility delay is limited to the boundary condition. The less accurate agreement is obtained for $Deb=1$ and $R=0.1$, when the two phenomena are strongly coupled and when the solvent uptake due to relaxation is dominant (Figure 3). The influence of Deb and R is resumed in Figure 4. As can be seen, the error is maximum around $Deb=0.3$ and increases when R decreases, i.e. when the relaxation is dominant. However this difference is always small (less than 10%) which makes possible the use of the (LR) model.

From the numerical point of view, the Long and Richman model is simpler since relaxation effect is introduced through a boundary condition only and not in the equation describing solvent diffusion inside the film. The cpu time needed to simulate a sorption experiment is then much more smaller than with the Petropoulos model. Such a simplification is very useful when iterative optimization methods are used to estimate unknown parameters from experimental data. Indeed, identification algorithms imply the simulation of the sorption kinetics a great amount of times, which requires a simulation model with small cpu.

ESTIMATION

Experimental sorption kinetics is obtained by making a step of pressure vapor above the film and recording the weight uptake. Inevitably the experimental duration \mathcal{H} is finished so that the equilibrium value c_∞ can have been not reached at the end of the experiment if τ_r is large. The general

estimation problem then consists in estimating the four parameters “ τ_r , τ_d , c_0 , c_∞ ”.

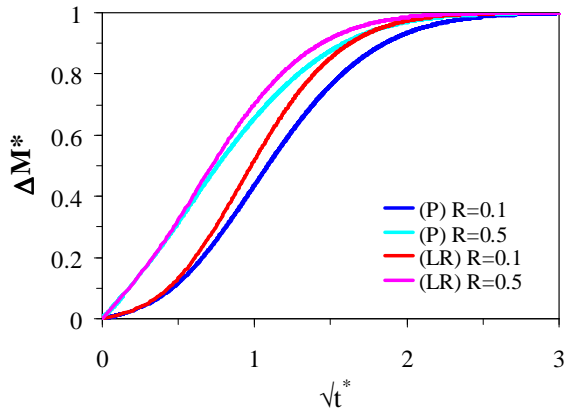


Figure 2a

Comparison of (P) and (LR) models for Deb=1
Weight uptake as a function of $t^{*1/2}$

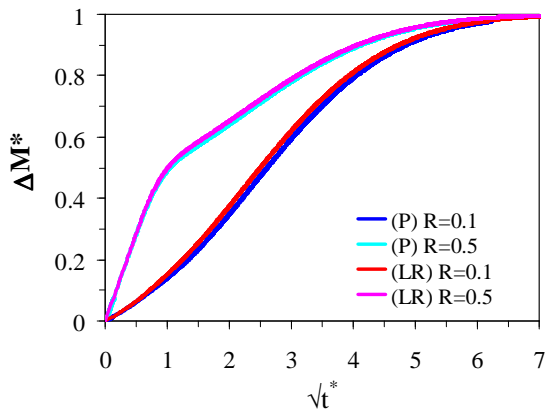


Figure 2b

Comparison of (P) and (LR) models for Deb=10
Weight uptake as a function of $t^{*1/2}$

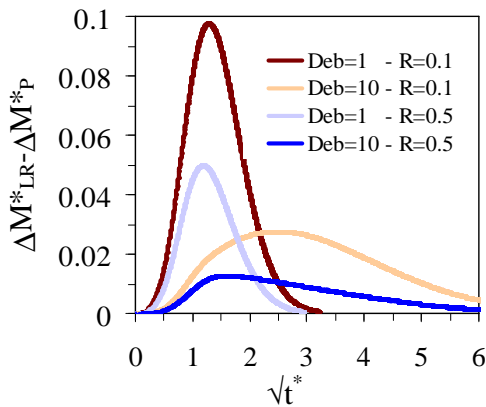


Figure 3

Difference between the (P) and (LR) models

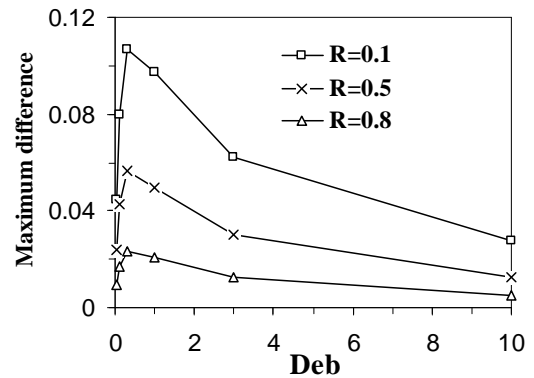


Figure 4

Maximum difference between the (P) and (LR)
models as a function of Deb

SIVIA estimation algorithm: Classical least square optimization is not suitable to analyze experimental data for that problem. Indeed, when diffusion and relaxation are coupled, the problem is badly conditioned, i.e. close kinetics can be obtained with quite different parameters sets [11]. To overcome this difficulty we use a global optimization method, the set inversion method [12]. The aim is to estimate all the parameter sets “ τ_r , τ_d , c_0 , c_∞ ” that give kinetics lying between two a priori bounding curves of the experimental kinetics. These bounding curves are first fixed (before estimation) taking into account the various experimental errors.

The optimization method is detailed in [12] and we just give the main features of the SIVIA algorithm (Set Inversion Via Interval Analysis). First, a large a priori variation domain is chosen for each parameter, leading to an initial box in the parameters space (dimension=4). An iterative procedure divides this initial box into smaller and smaller boxes that are partitioned in feasible, unfeasible and ambiguous boxes. A box is said feasible (unfeasible) if all its quadruplets give kinetics lying (not lying) between the two bounding curves. Other boxes are said ambiguous. Because the kinetics is monotonic versus the four parameters (overshoot phenomena are excluded) – at a given time, the weight uptake is an increasing function of c_0 and a decreasing function of R , τ_r , τ_d – it is easy to characterize each box by computing the theoretical kinetics associated with the extreme values of the box. After

elimination of the unfeasible boxes and selection of the feasible ones, the ambiguous boxes are divided into smaller ones and the procedure is repeated until the ambiguous domain is small enough.

This method has the great advantage to give well-defined uncertainty domain for the four parameters, without favoring any specific solution. All the quadruplets that give a kinetics included in the two bounding curves are obtained. One dimension projections give the maximum variation domain for each parameter. The method is however computer time consuming (a few hours on a Pentium IV computer for the analysis of one weight kinetics). Let us underline that the resolution of the (LR) model itself uses an analytical solution and takes less than one second. The use of the (P) model would then not be possible with such a global estimation method.

Test problems:

To analyze the quality of the estimation according to Deb and R on one hand, and the influence of the use of the simplified (LR) model on the other hand, the following test procedure was chosen:

-Test 1: in a first step the (LR) model was used to generate pseudo experimental kinetics (weight versus time) for different values of Deb and R. The two bounding curves were obtained by assuming a constant error of ± 0.01 on ΔM^* . The SIVIA estimation algorithm was then used on these data. The model used to generate the data being the same than the one used in SIVIA, this first test aims to characterize the more or less good conditioning of the inverse problem, according to Deb and R.

- Test 2: in a second step the (P) model was used to generate the pseudo data and the SIVIA algorithm, using the (LR) model, was applied on these data (also assuming a constant error of ± 0.01 on ΔM^*). The influence of the use of the simplified (LR) model in the estimation algorithm is analyzed by comparing the results obtained with tests 1 and 2.

All the tests have been performed with $\tau_d=1$, $R=0.5$ and $\mathcal{H} > 4 \max(\tau_d, \tau_r)$.

Results and discussion:

The results of tests 1 and 2 are given in Figures 5, 6 and 7. For each Deborah number, the grey (test 1) and red (test 2) vertical bars give the total admissible domain for the diffusion time (Figure 5), the normalized relaxation time (i.e. the ratio of the estimated τ_r to the true τ_r , Figure 6) and R (Figure 7). All the combinations of the parameters are of course not possible and a more detailed analysis would need

the use of the projections of feasible domains on spaces of dimension 2 or 3, but this is beyond the scope of this paper. The three figures point out that the estimation problem is badly conditioned for small Deborah numbers: when Deborah is smaller than one, the information brought by kinetics data is not rich enough to get an accurate estimation of the parameters that characterize diffusion and relaxation: Numerically the experimental weight uptake may be ensured by a great number of combinations of relaxation and diffusion phenomena, while the kinetics stays between the two bounding curves previously defined: $|\Delta M(t)^*_{\text{estimated}} - \Delta M^*(t)| < 0.01$. Let us note that this difficulty may be overcome by decreasing the film thickness. Indeed, the diffusion time is proportional to the square of the film thickness while the relaxation time does not depend on it.

Concerning the influence of the (LR) approximation, the comparison of tests 1 and 2 confirms the results already obtained in the modeling section: For this value of R the admissible domains of the different parameters are shifted when using the (LR) model in the estimation algorithm, but the shift is less than about 20% when Deb is greater than 1.

CONCLUSIONS

Estimation of coupled diffusion and relaxation phenomena in glassy polymer films is possible as long as the Deborah number is large enough. More detailed analysis, to be published later, would need to study the influence of R, \mathcal{H} and the error magnitude.

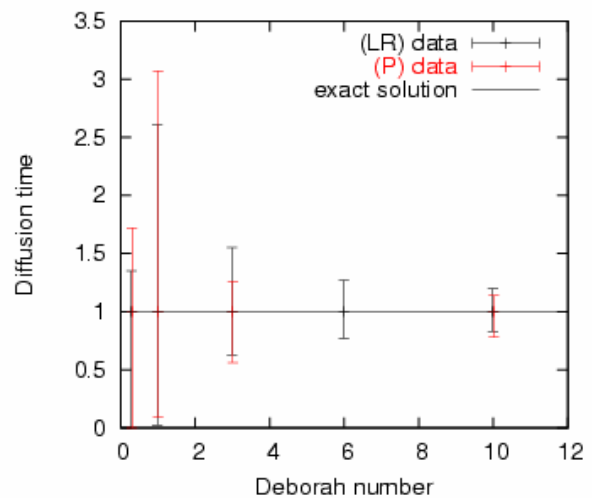


Figure 5

Estimated diffusion times for test 1 (grey) and test 2 (red), for different Deb.

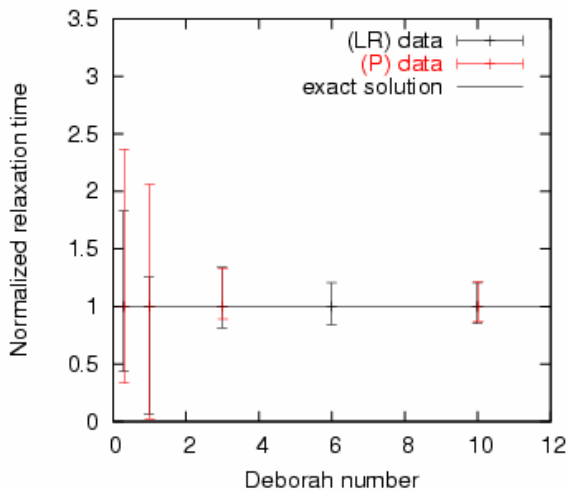


Figure 6

Estimated relaxation times for test 1 (grey) and test 2 (red), for different Deb.

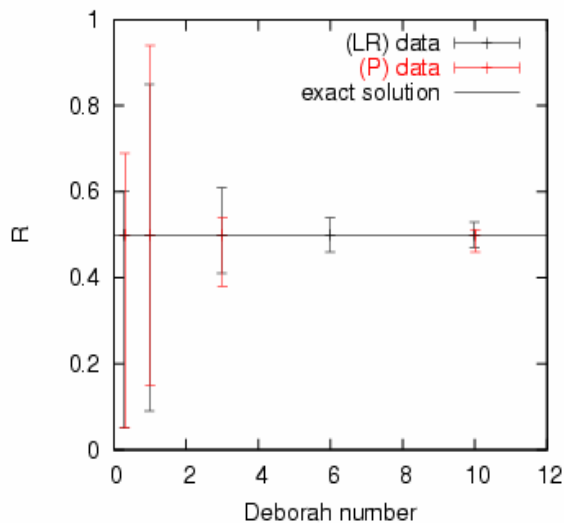


Figure 7

Estimated R for test 1 (grey) and test 2 (red), for different Deb.

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REFERENCES

1. Neogi, P., 1996, *Diffusion in Polymers*, Dekker, New-York.
2. Sanopoulou, M, and Boom, J.P, 2000, Interval sorption kinetics in the system poly(methyl methacrylate)-methyl acetate, *Polymer*, **41**, pp.8641-8648.
3. Sanopoulou, M, and Petropoulos, J.H, 2001, Systematic analysis and model interpretation of micromolecular non-Fickian sorption kinetics in polymer films, *Macromolecules*, **34**, pp.1400-1410.
4. Dubreuil, A.C, Doumenc, F, Guerrier, B, and Allain, C, 2003, Mutual diffusion in PMMA/PnBMA copolymer films - Influence of the solvent induced glass transition, *Macromolecules*, **36**, pp.5157-5164.
5. Thomas, N, and Windle, A, 1982, A theory of case II diffusion, *Polymer*, **23**, pp.529-542.
6. Durning, C, 1985, Differential sorption in viscoelastic fluids, *J. Polym. Sci.*, **23**, pp.1831-1855.
7. Edwards, D.A, and Cohen D.S, A mathematical model for a dissolving polymer, 1995, *AICHE J.*, **41**, pp.2345-2355
8. Petropoulos, H. P, 1984, Interpretation of anomalous sorption kinetics in polymer-penetrant systems in terms of a time dependent solubility coefficient, *J. Pol. Sci., Polym. Phys. Ed.*, **22**, pp.1885-1900.
9. Sanopoulou, M, Stamatialis, D.F, and Petropoulos, J.H., 2002, Investigation of Case II diffusion behavior. 1. Theoretical studies based on the relaxation dependent solubility model, *Macromolecules*, **35**, pp.1012-1020.
10. Long, A, and Richman, D, 1960, Concentration gradients for diffusion of vapors in glassy polymers and their relation to time dependent diffusion phenomena, *J. Am. Chem. Soc.*, **82**, pp.513-519.
11. Dubreuil, A. C, Doumenc, F, Guerrier, B, Johannsmann, D, and Allain, C, 2003, Analysis of the solvent diffusion in glassy polymer films using a set inversion method, *Polymer*, **44**, 2, pp.377-387.
12. Walter, E, and Pronzato, L, 1997, *Identification of parametric models from experimental data*, London, Springer.