

Drying of polymer varnishes: Solvent diffusion in glassy polymer films

A.C. Dubreuil, F. Doumenc, B. Guerrier, C. Allain

Laboratoire F.A.S.T., UMR 7608, bât 502, Campus Universitaire, F – 91405 Orsay cedex

Understanding the drying kinetics of polymer solutions is a major issue in numerous industrial processes. Indeed, most of lacquer, paint and varnish coatings are obtained by performing solvent evaporation from an initial dilute solution. Drying kinetics generally shows two distinct regimes: the first step is rapid and mainly governed by the exchanges between the solution and the environment. Then the solvent evaporation flux decreases strongly and kinetics becomes governed by the physico-chemical properties of the system. Solvent transport in the second step (polymer concentrated domain) involves several complex phenomena. First, the solvent/polymer diffusion coefficient decreases by several orders of magnitude when solvent concentration decreases. Moreover, since the glass transition temperature of a polymer solution depends on the solvent concentration, the film enters the glassy state during the drying. The solvent diffusion through the polymer matrix is then coupled with the relaxation of the viscoelastic stresses on the macromolecular chains and exhibits a non-fickian behaviour.

This study deals with the influence of the glass transition on solvent diffusion. A PMMA/PnBMA statistical copolymer film was chosen to perform a series of differential drying and swelling experiments for various solvent concentrations. A gravimetric technique was used, based on a quartz crystal microbalance placed in a controlled solvent vapour pressure chamber. The coupling between diffusion and viscoelastic behaviour is described with the "solubility" model that takes relaxation into account through a time variable boundary condition at the film/vapour interface. In the concentrated domain, the solvent/polymer diffusion coefficient was shown to decrease by about three orders of magnitude when solvent content decreases. Contrary to some authors, no slowing down in the evolution of the diffusion coefficient was observed when crossing the glass transition.

1 Introduction

Lacquer, paint and varnish coatings are commonly obtained in industrial processes by performing solvent evaporation from an initial dilute solution. Forced convection or radiant heating are used to heat the solution and drying kinetics is governed by strongly coupled heat and mass transfers. As shown in a previous study dedicated to polymer films (Guerrier et al., 1998), drying kinetics shows two distinct regimes. The first step is rapid and mainly governed by the exchanges between the solution and the environment, namely the heat and mass transfer coefficients. Then the solvent evaporation flux decreases strongly and kinetics is governed by the physico-chemical properties of the polymer/solvent system, i.e. the saturated vapour pressure and the mutual diffusion coefficient. These two quantities depend strongly on both temperature and concentration. For example, mutual diffusion coefficient varies typically from four orders of magnitude between the initial state (dilute solution) and the dry film (very concentrated domain). Given the Biot and the Lewis numbers in a typical industrial configuration, temperature gradient in the film can be neglected while very important concentration gradients appear. A modeling of the process has been developed with the assumption that the temperature of the film is always higher than the glass transition temperature. With this assumption the film can be viewed as a rubbery binary solution. This assumption is clearly valid at the beginning of the process, since the glass transition temperature of a polymer solution decreases rapidly as the solvent concentration increases. At the end of the drying, when the polymer concentration is very high, and above all at the end of the process when the film is cooled, it enters the glassy state. The solvent diffusion through the polymer matrix is then coupled with the relaxation of the viscoelastic stresses on the macromolecular chains and exhibits complex non-fickian behaviour. The influence of glass transition on solvent transport in a polymer solution has yet been studied but is still not well understood and several theoretical approaches have been developed. In order to go towards a complete modeling of glass transition occurring in drying and cooling in a real process, this paper deals with a preliminary study in the framework on solvent diffusion in glassy polymer. An experimental study of toluene diffusion in a

PMMA/PnBMA copolymer film has been performed. This copolymer was chosen because it is a component of usual industrial varnishes used for example in packaging and because the glass transition of the pure copolymer (without solvent) is about 75°C. When drying a toluene/copolymer film at room temperature, the solution crosses the glass transition when the solvent weight fraction becomes less than 0.12, and it was then possible to study solvent diffusion in the glassy domain.

The paper is organized as follows: a brief description of film preparation, experimental set-up and experimental procedure is given in section 2. The model of diffusion/relaxation used in this study is described in section 3. The set inversion method used to fit the data, qualitative analysis and quantitative results are given in section 4.

2 Experimental

2.1 Sample preparation

The statistical methyl methacrylate/n-butyl methacrylate (MMA/nBMA) copolymer was synthesized by radical polymerization. The copolymer monomer composition, measured by ^1H NMR, is 64% of MMA and 36% of nBMA. Toluene was used as solvent for sorption and desorption experiments. The polymer film was spin-cast directly onto the gold electrode of a piezoelectric quartz crystal. The thickness is 580 nm. The film was then annealed in a vacuum oven for 12 hours, at a temperature superior to the glass transition temperature of 50°C.

2.2 Experimental set-up and weight determination

The polymer film cast onto the quartz crystal resonator is located inside a vacuum chamber connected to a solvent reservoir (in which the solvent vapour pressure is equal to the saturated vapour pressure of pure solvent, ie. $P = 37.92$ hPa at $T = 25$ °C for toluene). The set-up relies on a quartz crystal resonator technique, known to be a very precise tool to determine the weight of thin films. When a film is cast onto one of the electrodes of a thickness-shear resonator, its acoustical resonance frequencies change due to the weight of the film. Using some assumptions, the film weight is deduced from the resonance frequencies shifts (Johannsmann et al., 1992). Because of the strong temperature-frequency coupling of the quartz crystal resonator, it is necessary to have a temperature control of the chamber. Using a thermostat the chamber temperature is adjusted to $T = 25 \pm 0.15$ °C (Bouchard et al., 1998).

Differential gravimetric experiments were performed to study solvent sorption and desorption in the copolymer films thanks to increments of solvent vapour pressure. Pressure steps are small (about 1 hPa) so that the film characteristics (mutual diffusion coefficient, viscoelastic properties...) can be assumed to be constant during an experiment. By varying the initial pressure of the pressure step, the evolution of the film behaviour with solvent concentration is studied. Pressure steps are obtained by suddenly opening the connecting valve between the main chamber and a secondary one. At the end of the step the pressure is kept constant with a PID regulation. Let us note that solvent vapour is the only gas present in the chamber, so that using the total pressure as the control parameter amounts to work with Dirichlet boundary condition on the upper surface of the film.

2.3 Experimental procedure

As soon as glassy state is concerned the experimental procedure that influences the whole film history must be carefully defined. In most of differential sorption or desorption experiments reported in the literature, pressure steps are performed one after the other, like "stairs". Another type of experimental procedure is used here: before each increasing step, the film is kept two hours at high pressure (about 33 hPa); the film is then very swollen and in the rubbery state, allowing the whole previous history to be "forgotten". Starting from this well defined rubbery state the pressure is lowered to the initial pressure of the sorption step. This initial pressure is maintained a few hours until a "quasi-equilibrium" is reached (i.e. diffusion is achieved and weight change due to relaxation is very small). Then the differential increasing pressure step is performed, the final pressure being maintained for about 5 to 10 hours, and is followed by a decreasing step of about the same amplitude (Dubreuil, 2001b). Several steps with initial pressure ranging from 10^{-3} hPa to 19.33 hPa (i.e. initial weight fraction ranging from 0 to 0.143) have been performed in these conditions.

3. Modeling

Many works have concerned diffusion of solvent in rubbery and glassy polymer films, and we just recall some main features. Deviation from fickian kinetics in the glassy state was observed by several authors when performing sorption or desorption experiments (cf. part I in Dubreuil, 2001b). Two coupled phenomena occur in non-fickian kinetics, solvent diffusion in the film and polymer matrix relaxation. The Deborah number is often used to compare the characteristic times of relaxation versus diffusion. Far above the glass transition temperature, relaxation is quasi instantaneous compared to diffusion and classical fickian kinetics is observed ($Deb \ll 1$). If Deb is $\gg 1$, macromolecular configuration evolution had no time to take place during a typical sorption experiment and fickian kinetics is also expected. Around the glass transition, Deb is about 1 and the coupling of the two phenomena leads to complex non-fickian kinetics. One possible description commonly used is to take the coupling between diffusion and relaxation into account through the boundary condition at the film/vapour interface only, which is expressed as: $c(z=e,t) = c_d + (c_\infty - c_d) [1 - \exp(-t/\tau_r)]$, where e is the film thickness, c_d is the pseudo-equilibrium concentration at the film/vapour interface (the asymptotic concentration if diffusion was the only mechanism), c_∞ the equilibrium concentration at $t=\infty$ and τ_r the characteristic relaxation time. Solvent diffusion through the film is described by a classical Fick law, with an impervious boundary condition at the quartz/film interface. This simple model was found to fit very well our data, and has the advantage to depend on four parameters only, c_d and D_{SP} (mutual diffusion coefficient in Fick equation) for diffusion and c_∞ and τ_r for relaxation.

4. Results

4.1 Solvent induced glass transition

Preliminary experiments consisting in desorption isotherms in quasi-equilibrium conditions (homogeneous concentration in the film) have been performed on the same copolymer to characterize the solvent induced glass transition at 25°C (Dubreuil et al., 2001a). The solubility curve (solvent weight fraction in the film versus the activity) shows the typical change of curvature for glass transition for a solvent weight fraction $\omega_{sg} = 0.12$. The corresponding pressure and activity (pressure in the chamber/saturated vapour pressure of toluene) are $P_g = 16.68$ hPa and $a_g = 0.44$.

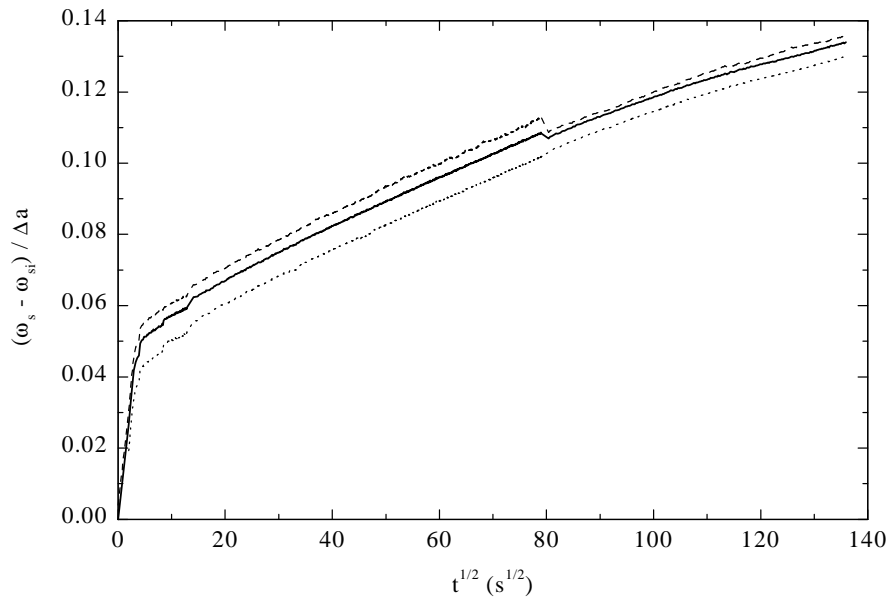


Figure 1: Kinetics of sorption for a pressure step 10.7 – 13.2 hPa (initial solvent weight fraction $\omega_{si} = 0.081$), surrounded by two bounding curves (dotted lines) taking the measurements uncertainties into account. These three curves are arbitrarily set to zero at the beginning of the step.

4.2 Kinetics

An example of kinetics of sorption is given in Figure 1, for a pressure step 10.7 – 13.2 hPa. The abscissa is $t^{1/2}$ and the ordinate is $(\omega_s - \omega_{s_i})/\Delta a$, where ω_s is the solvent weight fraction, ω_{s_i} the initial solvent weight fraction and Δa the activity change during the step. In this representation, fickian kinetics shows a linear increase at short times and then a saturation toward an asymptotic value at large times. As expected for an experiment performed at a low pressure corresponding to the glassy domain, the kinetics is clearly non-fickian and close to the so-called "pseudo-fickian" kinetics, with a linear part at short times followed by a slower increasing of $(\omega_s - \omega_{s_i})/\Delta a$. Good reproducibility in the results have been obtained, except for the steps at 10^{-3} hPa which were not taken into account for the quantitative estimation of the diffusion coefficient.

4.3 Experimental errors

Quartz microbalance is theoretically a very precise tool but several phenomena affect weight determination. First, resonance frequencies of a quartz depend on temperature (Lu and Czanderna, 1984). In the vacuum and around 25°C, preliminary measurements have been done on several blank quartz; an overestimate of the sensitivity is about -10^{-6} kg/m²/°C.

The pressure effect on resonance frequencies was also investigated. This effect has three sources: viscous drag of the gas, pressure dependence of the elastic constants of the quartz itself, and sorption or desorption of physisorbed molecules on the quartz surface (Lu and Czanderna, 1984). The systematic error due to pressure effects increases as pressure increases, from about 10^{-7} kg/m²/hPa at very low pressure up to $2.5 \cdot 10^{-6}$ kg/m²/hPa around 37 hPa (overestimations obtained from experiments on blank quartz).

Another uncertainty comes from the limitation of the validity domain of the theoretical models of quartz microbalances (cf. part II in Dubreuil, 2001b). A typical example is given in Figure 1 for $t^{1/2} = 80$ s^{1/2}. At this time the model used to estimate the film weight from the frequencies shifts was changed, which gives a small deviation of the curve.

4.4 Global estimation method

Given these various systematic errors that can be bounded but not enough accurately determined to allow corrections, a specific estimation method has been developed to analyse the experimental data. Indeed, classical least square optimization was not suitable to estimate the four parameters of the solubility model, since quartz microbalance method induces systematic errors due to pressure and temperature effects while least square optimization is relevant for random errors. Moreover, when diffusion and relaxation are coupled, the problem is badly conditioned, i.e. close kinetics can be obtained by quite different parameter sets. To overcome this difficulty, we have used a "global" optimization method that aims to estimate all the parameter sets " $\mathbf{p}=(c_d, c_\infty, D_{SP}, \tau_r)$ ", that give kinetics that are compatible with the experimental one. Using the upper-bound of the different experimental uncertainties, we have first defined two bounding curves $m_{\min}(t)$ and $m_{\max}(t)$ surrounding the experimental one $m(t)$, such that the real kinetics should lie between these two bounds. To analyse kinetics we are interested only to weight variation from the beginning of the step and $m_{\min}(t)$, $m_{\max}(t)$ and $m(t)$ are arbitrarily set to zero at the beginning of the step. One example of these bounding curves is detailed in Figure 1. They have been evaluated using the pressure and temperature measurements and the characterisation of the uncertainties detailed in section 4.3. As can be seen, the errors effects are not symmetric since the direction of variation is known. We then look for all the parameter sets " \mathbf{p} " that give kinetics included between the two bounding curves.

The optimization method is detailed in (Walter and Pronzato, 1997) and we just give the main features of the algorithm. First, a large initial *a priori* variation domain is chosen for each parameter, leading to an initial box (dimension=4). An iterative procedure divides this initial box into smaller boxes that are partitioned in feasible, unfeasible and ambiguous elements. A box is said feasible (unfeasible) if all its quadruplets " \mathbf{p} " give kinetics $m(t)$ that are included (that are not included) between the two bounding curves for the whole measurement horizon. Other boxes are said ambiguous. Because $m(t)$ is monotonic versus the four parameters when excluding overshoot phenomena, it is possible to characterize each box easily by computing the kinetics $m(t)$ associated with the extreme values of the box. Unfeasible boxes are eliminated and feasible ones are stored in a file.

Ambiguous boxes are divided into two smaller ones and the procedure is repeated until the ambiguous domain is small enough. This method has the great advantage to give well defined feasible domain for the four parameters, without favouring any specific solution. It is however computer time consuming (a few hours on a Pentium III 500 MHz for the analysis of one kinetics).

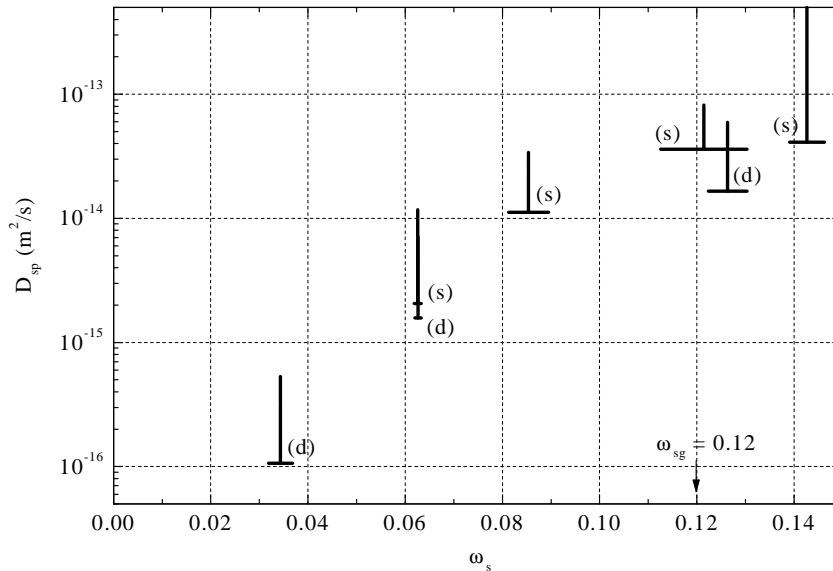


Figure 2: Evolution of the mutual diffusion coefficient D_{SP} with the solvent weight fraction ω_s . Vertical lines correspond to feasible variation domains issued from the set inversion method and horizontal lines to solvent weight fraction domains covered during sorption (s) or desorption (d) steps.

4.5 Mutual diffusion coefficient in the glassy domain

For each sorption and desorption steps the set inversion method was used to analyse the data. The evolution of the mutual diffusion coefficient with the solvent weight fraction is given in Figure 2. The results are presented in the following way: the vertical line corresponds to the feasible variation domain issued from the set inversion method. When no upper bound was obtained, the vertical line is drawn up to the graph frame. The horizontal line corresponds to the solvent weight fraction domain covered during the step. As can be seen, the variation in solvent weight fraction during a step is very small (often smaller than 0.01), which validates the assumption of differential sorption or desorption. The symbols (s) and (d) mean sorption and desorption respectively. The value of the solvent weight fraction corresponding to the glass transition, $\omega_{sg}=0.12$, is noted on the graph. Most of the results correspond to the glassy domain.

The quantitative analysis confirms the results observed on the kinetics: the estimated diffusion coefficients corresponding to sorption and desorption are close (Dubreuil, 2001b). Moreover, in the glassy domain, the mutual diffusion coefficient decreases strongly when the solvent concentration decreases: between two and three orders of magnitude for a 0.09 change in ω_s . Similar results were obtained by Boom and Sanoupolou on the system PMMA/methylacetate (Boom and Sanoupolou, 2000). On the contrary, Billovits and Durning observed a large difference in the D_{SP} variations between the rubbery and glassy domains, obtaining a nearly constant diffusion coefficient in the glassy domain for the system PS/ethylbenzene (Billovits and Durning, 1994). Sun and Lee obtain also a "plateau" in the glassy domain for the system PHEMA/water (Sun and Lee, 1996). This "plateau" was interpreted by the authors as the consequence of large slow down in free volume decrease, due to the glass transition.

These different behaviours show that the influence of glass transition on the diffusion coefficient is a complex problem and that the respective influences of the system nature, the experimental procedure and the distance to the glass transition is still not deeply understood.

5. Conclusion

A detailed analysis of differential swelling and drying kinetics has been performed for a PMMA/PnBMA copolymer in the glassy domain. Special care was given to the treatment of the experimental uncertainties and a specific global estimation method was used to analyse the data. Contrary to some authors, we have not observed a large slowing down in the evolution of the diffusion coefficient in the glassy state. Further works will extend this study to non-differential steps, closer to industrial configuration, and to the influence of copolymer composition on diffusion behaviour.

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References

- G.F. Billovičs and C.J. Durning, Linear viscoelastic diffusion in the poly(styrene)-ethylbenzene system: Comparison between theory and experiment, *Macromolecules*, vol. 27, pp. 7630-7644, 1994.
- J.P. Boom and M. Sanopoulou, Interval sorption kinetics in the system poly(methylmethacrylate)-methylacetate, *Polymer*, vol. 41, pp. 8641-8648, 2000.
- C. Bouchard, B. Guerrier, C. Allain, A. Laschitsch, A.-C. Saby and D. Johannsmann, Drying of glassy polymer varnishes: A quartz resonator study, *J. Appl. Polym. Sci.*, vol. 69, pp. 2235-2246, 1998.
- A.-C. Dubreuil, B. Guerrier, C. Allain and D. Johannsmann, Glass transition induced by solvent desorption for statistical MMA/nBMA copolymers – Influence of copolymer composition, *Polymer*, vol. 42, pp. 1383-1391, 2001a.
- A.-C. Dubreuil, Séchage de films polymères : Etude du couplage entre la diffusion et la transition vitreuse - Application à des copolymères PMMA/PnBMA, PhD thesis, université Paris VI, Paris, France, 2001b.
- B. Guerrier, C. Bouchard, C. Allain, C. Bénard, Drying kinetics of polymer films, *AIChE J.*, vol. 44(4), pp. 791-798, 1998.
- D. Johannsmann, K. Mathauer, G. Wegner and W. Knoll, Viscoelastic properties of thin films probed with a quartz crystal resonator, *Physics Review B*, vol. 46, pp. 7808-7815, 1992.
- C. Lu and A.W. Czanderna, *Applications of piezoelectric quartz crystal microbalances*, Elsevier, Amsterdam, 1984.
- Y.M. Sun and H.L. Lee, Sorption/desorption properties of water vapour in poly(2-hydroxymethyl methacrylate): 1. Experimental and preliminary analysis, *Polymer*, vol. 37(17), pp. 3915-3919, 1996.
- E. Walter and L. Pronzato, *Identification of parametric models from experimental data*, Springer-Verlag, London, 1997.