Aging in PMMA/Toluene Films

Hugues Bodiguel[a], Frédéric Doumenc[b] and Béatrice Guerrier[b]

[a]*Laboratory LOF (Rhodia, CNRS, University Bordeaux 1), 178 Avenue du Dr Schweitzer, F33608 Pessac, France*
[b]*Laboratory FAST (University Pierre et Marie Curie, University Paris Sud, CNRS) Building 502, Campus Universitaire, Orsay, F91405, France*

Abstract. Experimental results of aging behavior for a polymer solution, when the control parameter is the solvent vapor pressure above the film (i.e. the activity) and the observation is the solvent concentration, are presented. Various aging protocols have been performed and analyzed on the system Polymethylmethacrylate (PMMA)/Toluene.

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INTRODUCTION

Physical aging of glassy polymers is characterized by a slow evolution of the system physical properties with time, which depends on the whole sample history below the glass transition. In this paper we present experimental results of complex aging phenomena for a polymer solution, when the control parameter is the solvent vapor pressure above the film (i.e. the solvent activity) and the observation is the solvent concentration. We have used a Polymethylmethacrylate (PMMA)/Toluene solution at a temperature smaller than the glass transition temperature of the pure polymer. Then the film is swollen when the solvent concentration is high and glassy below a given solvent concentration. By changing the solvent vapor pressure above the film, it is possible to swell or dry the film and to study the glass transition induced by solvent desorption [1]. Aging behaviour for various protocols has been studied in a previous study [2,3]. A model joining up polymer thermodynamics theory [4] and glass relaxation models [5] allow to capture some of the of the observed phenomena, but fails in describing the specific kinetics observed when aging is followed by a short but deep quench. In this paper we report additional experimental results on this last point.
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EXPERIMENTAL

The polymer used was PMMA (Sigma-Aldrich) and the solvent Toluene. According to the suppliers, PMMA glass transition temperature is T_{gp}=395 K, the molecular weight is 350 000 g/mol and the polydispersity is between 4 and 5; Toluene has a 99.9% purity. The densities of PMMA and Toluene are 1170 kg/m^3 and 867 kg/m^3 respectively. Four samples have been used. The first one was obtained by slow drying of a PMMA/Methylethylketone solution, transferred onto a 38 µm thick aluminium substrate, and annealed at 373 K during a few days. Two others were spin cast onto silicon wafers using a PMMA/toluene solution, transferred onto 38 µm thick aluminium substrates, dried several days at ambient temperature and then dried 24 h in vacuum at 298 K. The last one was obtained in a similar way, excepted that the film was not supported on a substrate. Supported and non supported films are about 0.6 µm and 2.2 µm thick respectively. Note that for such film thickness no influence of the thickness on glass transition is expected.

The mass of the film in the presence of the solvent vapour was measured using a Hiden IGA balance. The measuring cell is filled with pure solvent vapour (no inert gas) whose temperature and pressure are accurately controlled: temperature is kept constant at T=298 K ± 0.05 - that is 97 K below the glass transition temperature of dry PMMA - and pressure P ranges from a few Pa (noted 0 Pa in the following) to 3.4×10^3 Pa with a stability ±2 Pa.

Assuming that the solvent vapour behaves as an ideal gas, the activity of the solvent is given by $a=P/P_{vs0}$ (where $P_{vs0}=3.79 \times 10^3$ Pa is the saturated vapour pressure of toluene at 298 K). In the following we use the activity as the control parameter to analyze the results. Before each run the pressure is maintained at or above a=0.9 (P>3.4×10^3 Pa) during 160 min. The polymer film is then largely swollen (containing about 50% of solvent which is well above the solvent concentration at the glass transition) and we can assume that it is molten and that the previous pressure history is erased. A first family of pressure cycles, called cycle I in the following, consists in decreasing the pressure down to a given activity a_{stop} (step "a" in Figure 1), keeping $a=a_{stop}$ during a waiting time t_{stop} (step "b" in Figure 1) and then increasing the activity again up to 0.9 (step "c" in Figure 1). A second family of pressure cycles is similar to the previous one at the beginning, i.e. the pressure is decreased to a given activity a_{stop} during a waiting time t_{stop}, but then the activity is decreased to zero and the sample is kept at zero pressure during t_0 before the increasing ramp [6]. Such a cycle, called cycle II in the following, is given in Figure 1 for $a_{stop}=0.396$, $t_{stop}=600$min and $t_0=60$min.

The pressure ramp rate is 25 Pa/min in all the performed cycles. This rate of pressure variation comes from a compromise between the duration of the experiment and the diffusion time inside the film. The characteristic time of a decreasing ramp being about 140 min and the film thickness 0.6 µm, the concentration gradient becomes non negligible if the diffusion coefficient is smaller than 10^{-16}m^2/s. That is less or of same order as the minimum value measured for PMMA/Toluene at very small activities [7] and we assume in the following that the diffusion time is always shorter than the time variation of the solvent content.
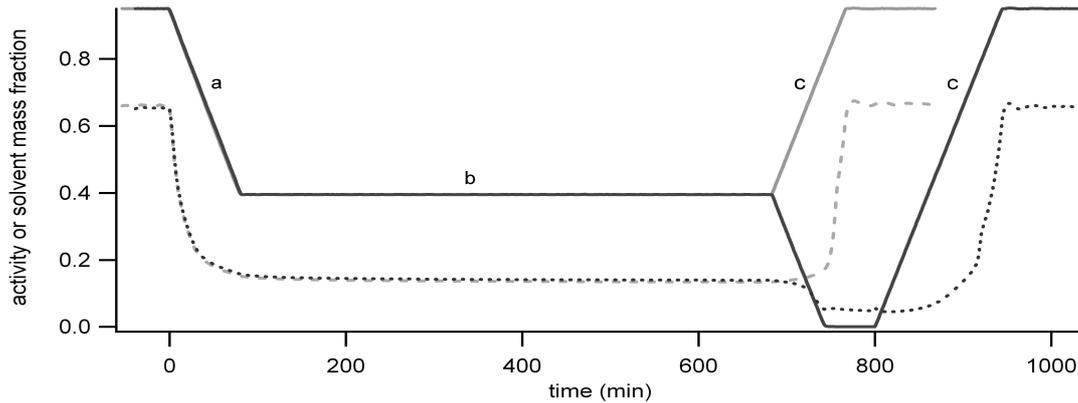

FIGURE 1. Aging protocol. Activity (continuous line) and solvent mass fraction (dotted lines) for cycle I (grey curves) and cycle II (black curves).

RESULTS

Desorption and resorption isotherms for an aging at a=0.396 and cycles I and II are compared in Figure 2. Starting from a high activity where the film is swollen and rubbery (the solvent mass fraction is about 0.45), the first part of the desorption curve (0.9>a>a_g) corresponds to the equilibrium isotherm of a rubbery polymer and can be described by a classical model such as the Flory-Huggins equation. Below the activity a_g, the desorption curve moves away from the equilibrium isotherm: the film is glassy and an excess of solvent is observed as the relaxation times are become too large for the material to follow the activity change. Then resorption occurs and the curve meets the equilibrium isotherm for an activity a_s greater than a_g (cf Figure 2).

If we first compare the softening behaviour for the two cycles I, the softening activity a_s is all the high as the aging time is large. This phenomenon is well accounted by the model that we presented in a recent communication [3]. More surprising is the isotherm corresponding to the cycle II. Aging time (600 min) is followed by a short stay at a=0, which greatly changes the softening behaviour. Indeed, the system softens even faster than after an aging of only a few minutes with cycle I.
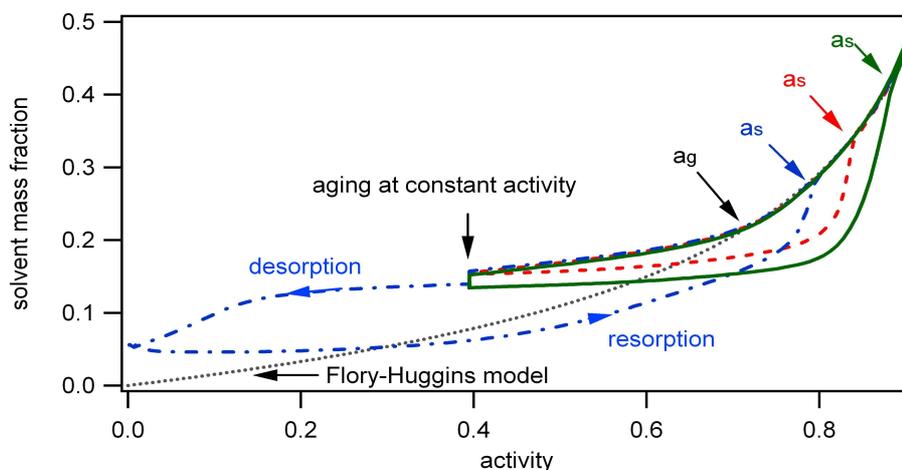
FIGURE 2. Desortion and resorption isotherms. Aging activity is 0.396. For cycles I, aging time is 4min (red dotted line) and 603 min (green continuous line). For cycle II, aging time is 600 min and t_0 (time at a=0) is 60 min (blue mixed dotted line).

The specific behaviour of cycles II was obtained for other experiments and does not depend on the sample preparation (c.f. experimental section) as shown in Figure 3 where results for various samples and various aging times are shown. Hopefully these experimental results will bring new insights on the problem of glassy state dynamics and call for theoretical developments.
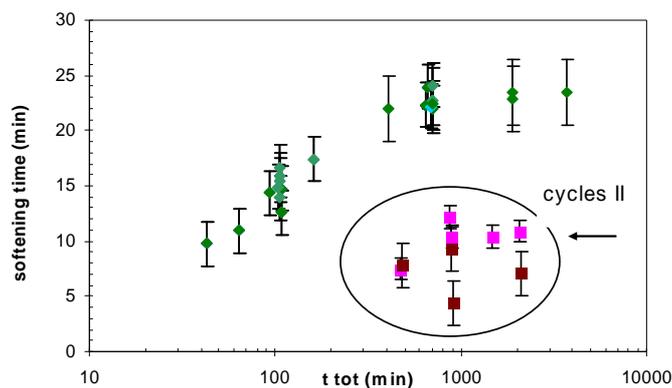

FIGURE 3. Softening time ([as-ag]/[da/dt], where da/dt=6.6×10^{-3}min^{-1}] as a function of the total time elapsed below the glass transition. Green diamonds correspond to cycles I, pink (supported films) and brown (non supported films) squares correspond to cycles II.

ACKNOWLEGMENTS

REFERENCES

1. Y. Zheng and G.B. McKenna, *Macromol.* **36**, 2387 (2003).
2. F. Doumenc, B. Guerrier and C. Allain, *EuroPhys.Lett.* **76**, 4, 630 (2006).
3. F. Doumenc, H. Bodiguel and B. Guerrier, submitted to *EPJ-E,* (2008).
4. L. Leibler and K. Sekimoto, *Macromol.* **26**, 6937 (1993).
5. J.M. Hodge, *J. of Non-Crystalline Solids* **169**, 211 (1994).
6. L. Bellon, S. Ciliberto and C. Laroche, *Eur. Phys. J. B* **25**, 223 (2002).
7. A.C. Dubreuil, F. Doumenc, B. Guerrier and C. Allain, *Macromol.* **36**, 5157 (2003).