Temperature cycling during the aging of a polymer glass

L. Bellon, S. Ciliberto, C. Laroche

Laboratoire de Physique - U.M.R. 5672
École Normale Supérieure de Lyon
46, allée d’Italie, 69364 Lyon Cedex 07, France

(received ; accepted )

PACS. 77.22Gm – Dielectric loss and relaxation.
PACS. 64.70Pf – Glass transitions.
PACS. 05.20–y – Statistical mechanics.

Abstract. – Temperature cycling is used to study aging properties of plexiglass (PMMA) dielectric constant. If a negative temperature cycle is applied during the aging time the relaxation dynamics is just delayed for a time equal to the cycle period. In contrast this time shifting procedure cannot be applied to positive temperature cycles. The analogies and differences with similar experiments done in other aging systems, such as spin glasses, orientational glasses and supercooled liquids, are discussed.

Introduction. – It is very well known that amorphous materials such as polymer solids present long relaxation time, when they are rapidly cooled from the liquid phase to any temperature below their glass transition temperature \( T_g \). This phenomenon which is known as aging has been widely studied in spin-glasses (SG), where remarkable theoretical and experimental progress have been achieved \[2, 3\]. In these systems many features of the relaxation dynamics have been understood by imposing temperature cycles to the samples. The response of the systems to these cycles has been interpreted with a hierarchical structure of the free energy landscape, which evolves with temperature \[3, 4\], or in a mean-field theoretical approach \[5\]. Very recently such a kind of experiments have been repeated in supercooled liquids (SL) \[6\] and in orientational glasses (OG) \[7\] by measuring the dielectric susceptibility of the sample. The relaxation dynamics turned out to be rather different from that of spin-glasses, and a domain growth interpretation \[8\] seems to be rather appropriate for OG and SL. Temperature cycling has been also applied in the study of polymer mechanical properties \[9\] but as far as we know no direct comparison to the previous systems has been done.

The purpose of this letter is just to describe a series of experiments where temperature cycling has been applied to the measurement of the dielectric constant of polymers, specifically of PMMA. The dielectric constant measurement is a common method to analyze aging properties of polymers. After presenting the results of our measurements, we will discuss differences and similarities between polymers and other aging systems.
Experiment. – To determine the dielectric constant, we measure the complex impendance of a capacitor whose dielectric is the PMMA sample. In our experiment a disk of PMMA of diameter 10cm and thickness 0.3mm is inserted between the plates of a capacitor whose vacuum capacitance is \( C_0 = 230 \text{pF} \). The capacitor temperature has a stability is 0.1K and it may be changed from 300K to 500K. Temperature quenches can be done at a rate of 3K/min.

The capacitor is a component of the feedback loop of a precision voltage amplifier whose input is connected to a signal generator. We obtain the real and imaginary part of the capacitor impedance by measuring the response of the amplifier to either to a white-noise or to a sinusoid. This apparatus allows us to measure the real and imaginary part of dielectric constant \( \varepsilon = \varepsilon_1 + i \varepsilon_2 \) as a function of temperature \( T \), of frequency \( \nu \) and time \( t \). The sensitivity of the measurement system is such that \( \varepsilon_2 \) as small as \( 4 \times 10^{-3} \varepsilon_1 \) can be measured at a frequency of 0.1Hz. We use this apparatus to study the aging properties of \( \varepsilon \) for \( 0.1 \text{Hz} < \nu < 20 \text{Hz} \) and \( 310K < T < 410K \). The glass transition temperature for PMMA is \( T_g \approx 388K \). The \( \alpha \) and \( \beta \) relaxation frequencies at \( T_g \) are for PMMA \( f_\alpha = 10^{-3} \text{Hz} \) and \( f_\beta \approx 2 \times 10^4 \text{Hz} \). These two frequencies, which are a decreasing function of \( T \), remain well outside the frequency range used in this experiment for \( 310K < T < T_g \). Therefore we probe the aging of \( \varepsilon \) well above \( f_\alpha \) and well below \( f_\beta \). The following discussion will focus on the imaginary part of the dielectric constant \( \varepsilon_2 \), but we could have chosen \( \varepsilon_1 \) as well as its behavior leads to the same results.

The measurement is performed in the following way. The sample is before heated till a temperature \( T_o = 410K \) which is higher than \( T_g \). After having left the sample at \( T_o \) for a few hours the temperature is rapidly decreased in about 15min at a temperature \( T_1 < T_g \). The temperature is then regulated by the oven. The zero of the aging time is taken at the instant, during the quench, when the sample temperature is equal to \( T_g \). A typical aging curve at 1Hz and \( T_1 = 365K \) is shown in fig.1 where \( \varepsilon_2 \) is plotted as a function of time. We clearly notice a logarithmic dependence on time of the dielectric constant after the first 10min from the quench. The logarithmic dependence on time of \( \varepsilon \) is observed in all the frequency range we have explored.

Repeating this experiment for various \( T_1 \) and \( \nu \) we find that the aging rate depends on this temperature and on frequency. The sample properties evolve faster when \( T_1 \) is close to \( T_g \). Specifically one can write \( \varepsilon_j(T_1, t, \nu) = A_j(T_1, \nu) - B_j(T_1, \nu) \log(t/t_o) \) with \( j = 1, 2 \) and \( t_o = 1h \). Here \( A_j \) is the value of \( \varepsilon_j \) at \( t = t_o \) It is found that \( A_j \) and \( B_j \) are functions of \( T_1 \)
The values of $A_2$ and $B_2$, measured at $\nu = 1Hz$, are plotted in fig.2(a) as a function of $T_1$. The imaginary part of $\varepsilon'$ increases at low and high temperature. The high temperature peak at about 400$K$ is related to the $\alpha$ relaxation ($f_\alpha \approx 1Hz$ at 400$K$), whereas the increase at small temperature is related to the $\beta$ relaxation[11]. Notice that $B_2$ is an increasing function of $T_1$ till a temperature $T_m$ close to $T_g$, and then goes down to 0 if $T_1 > T_g$. Indeed for a quench temperature larger than $T_g$ the sample can reach a thermodynamic equilibrium, so no aging is observed but only an exponential decay of $\varepsilon$ toward its stationary value.

The values of $A_2$ and $B_2$, measured at $T_1 = 366K$, are plotted in fig.2(b) as a function of $\nu$. The dependence on $\nu$ of $A_2$ is very weak in this frequency range. No relaxation peak is observed indeed $f_\alpha \approx 10^{-7}Hz$ and $f_\beta \approx 15kHz$ at 366$K$. $B_2$ is a slowly increasing function for $\nu \to 0$. Indeed aging is smaller at high frequencies than at low frequencies (a theoretical justification of such a behaviour can be found for example in ref.[2]).

In order to check for memory effects during the aging process, we have submitted the sample to temperature jumps around $T_1$. The following procedure has been used. After the quench from $T_o$ to $T_1$ the temperature is maintained at $T_1$ for $t_a = 2h$, and then suddenly changed to $T_2$. The sample temperature is regulated at $T_2$ for a time $\delta t = 4h$ and at time $t_b = t_a + \delta t$ once again changed to $T_1$. We will present separately the two cases $\Delta T = T_2 - T_1 < 0$ and $\Delta T > 0$. We show the results of the experiment at $\nu = 1Hz$ and $T_1 = 365K$ because this set of values give the best experimental accuracy in the analysis of the response of the system to a temperature perturbation. Indeed, looking at fig.2, one immediately sees that at this temperature and this frequency $B_2$ is large enough to have a large variation in a short time. Further $T_1$ is sufficiently far away from $T_g$ to make positive and negative cycles with the same amplitude, remaining always below $T_g$. The experiment have been done at other values of $T_1$ and $\nu$ but no differences on the response of the system to the temperature perturbation are observed.

Negative cycle ($\Delta T < 0$): a typical time history of the sample temperature is plotted in the inset of fig.2(a), with $T_1 = 365K$ and $T_2 = 343K$. The corresponding aging of $\varepsilon_2$ is compared in the figure with the standard aging curve at $T_1$. We clearly see that for $t > t_b$, when the...
Fig. 3. – (a) A temperature perturbation $\Delta T = -22K$ is applied at $t_a = 2h$ and switched off at $t_b = 6h$ (see inset : time history of the sample temperature). The corresponding time evolution of $\varepsilon_2$ at $\nu = 1Hz$ (continuous line) is compared with the standard relaxation curve (dashed line) at $T_1 = 365K$. The symbols ($\circ$) mark the evolution after the temperature perturbation (i.e. for $t > t_b$). (b) Same curves of a), but the points of the aging curve after the perturbation ($\circ$ – line) are now shifted of $\tau = -4h$ in order to superpose them with the standard aging curve.

Fig. 4. – (a) A temperature perturbation $\Delta T = +15K$ is applied at $t_a = 2h$ and switched off at $t_b = 6h$ (see inset : time history of the sample temperature). The corresponding time evolution of $\varepsilon_2$ at $\nu = 1Hz$ (continuous line) is compared with the standard reference relaxation curve (dashed line) at $T_1 = 365K$ (b) The perturbed aging curve (continuous line) is compared with the shifted reference curve (dashed line) with $\tau = 16h$ (see [2]). The time shifting procedure does not work this time.

temperature comes back to $T_1$ the corresponding aging curve is different from the standard one at $T_1$. However in fig.4(b) we show that it is possible to superpose the two curves, by applying a time shift $\tau = -4h$ to the values of $\varepsilon_2$ measured after the cycle at $T_2$ (i.e. for $t > t_b$). We see that after the shifting procedure the time behavior is the same with and without temperature modulation: there is a memory effect of the previous history of the sample.

As suggested by the behavior of $B_2$ for low temperatures, aging is slower at $T_2$ than at $T_1$ : we notice that for this experiment the time shift $\tau$ is very close to $-\delta t$, as if nothing had happened during the cooler period. In fact we expected $\tau$ to be a function of $\Delta T$, with $\tau \to 0$ when $\Delta T \to 0$. So we repeated this temperature cycling experiment for various $\Delta T$. 
The surprising result of these measurements is that for all perturbations ($T_1 = 365K$ and $\Delta T = -32, -30, -22, -12$ and $-5K$) except the smallest one, $\tau \simeq -\delta t \cdot (1 \pm 0.1)$ and the only evidence of $\tau$ vanishing to zero is $\tau = -0.66\delta t$ for $\Delta T = -5K$. The systems acts as if aging at any temperature $T_2$ a bit below $T_1$ during the cycle was almost useless when back to $T_1$.

Positive cycle ($\Delta T > 0$) : the results of a measurement with $\Delta T > 0$ are shown in fig.4. If we were to define a shifting time $\tau$ for this experiment, we would expect it to be positive as aging is faster at higher temperature. Indeed, the values of $\epsilon_2$ after the cycle are under the standard aging curve in fig.4(a). Thus they correspond to an older reference sample. But as one can see in fig.4(b), the best time shift of the experimental data to superpose it to the standard aging curve doesn’t lead to a good approximation.

A positive cycle cannot be summarized by a time shift : if aging has been accelerated by the temperature perturbation, its behavior after the cycle is not equivalent to a redefinition of the time origin for the standard curve.

Comparison with other temperature cycling experiments. –

The results of these temperature cycling measurements are rather different from those of SG [3], or SL [6] experiments, but quite similar to the OG [7] measurements. Let us study separately again the two cases $\Delta T < 0$ and $\Delta T > 0$.

When a negative temperature cycle is applied to any of the former systems, the common trend for long time after the cycle is a delay of the aging process. For both SG and OG, a backward time shift $-\tau \leq \delta t$ can be applied to the aging curve after the cycle in order to superpose it with the standard aging curve, exactly as in our experiment. But for both systems, the short time behavior after the perturbation had to be discarded since a fast contribution to the aging dynamics gives an overshoot of the aging curve. This effect, which can be understood in a mean-field theory framework for SG [5], is absent or at least really weak in PMMA.

In SL, this “short time” behavior (undershoot of the aging curve this time) is in fact dominant for a time of the same order of the perturbation duration. That’s why Leheny and Nagel [6] give no estimation of $\tau$ since the delay of the aging process for long times is not the main consequence of the cycle. Again PMMA is very different since the time shift applies to any time $t > t_b$.

When a positive temperature cycle is applied to SG or OG, these systems tend to “forget” their previous history (no data of positive cycle for SL is available to our knowledge). PMMA definitely doesn’t behave as SG for positive cycle, but it is quite close to OG, where the long time behavior would corresponds to a different cooling rate (and therefore a different final equilibrium state) rather than a different time origin. Indeed we checked that a slower cooling leads to smaller values of $\epsilon_2$ so that for the same age a slowly cooled sample looks older than a rapidly quenched one. The relative amplitude of this rate dependence is comparable to the one of OG [10, 13].

Conclusion. – We have described the results of a temperature cycling experiment on the aging of the dielectric constant of PMMA. We have shown that in PMMA, as in OG and SG, the dynamics is quite different for positive and negative temperature cycles. The negative pulses produces just a time delay in the evolution whereas the positive pulses have the tendency to reinitialize the aging. The main difference between the OG and SG dynamics and that of the PMMA is in the the presence of an overshoot after the negative cycles in OG and SG. These overshoots are absent in PMMA. Furthermore in PMMA the values of $\epsilon$ strongly depend on the cooling rate as in the OG, which is not the case for SG.

The main question is to find the more suitable model which can describe these observations. On a first approximation our results could be qualitatively explained by the aging models based on a free energy landscape with a temperature dependent hierarchical structure. This
rather qualitative model has been constructed to account for the general behavior of spin glasses. It seems to be adapted to our experiment. The sensitivity of the PMMA free energy landscape on temperature can be estimated using the dependence on temperature of the delay time for the negative temperature cycles. As no change in \( \tau \) has been observed for \( \Delta T > 5K \) we can claim that one should change temperature of at least 5K in order to strongly modify the PMMA landscape and its time evolution.

Recently two other models have been proposed \[5, 8\]. One \[5\] is based on a mean field approximation of a continuous spin system \[14, 15\]. This model explains quite well the SG dynamics and the presence of overshoot but as pointed out by the authors it cannot be applied to OG \[5\]. The second model \[8\] is based on thermally activated domain growth accounts for the experimental results of OG. Based on the similar cooling rate dependence of the OG and PMMA dielectric values one could probably conclude that the model of ref. \[8\] is more suitable to describe PMMA aging. New insights to this problem should be given by performing other perturbation procedures like those recently applied to OG and SG \[16, 17\].

***

We acknowledge useful discussion with J. Kurchan. This work has been supported by the ”Programme Thématique Matériaux” de la Région Rhône-Alpes.

REFERENCES

[1] L. C. Struick, Physical aging in amorphous polymers and other materials, (Elsevier, Amsterdam) 1978.
[2] For a recent review see for example Jean-Philippe Bouchaud, Leticia F. Cugliandolo, Jorge Kurchan, Marc Mezard, in Spin-glasses and random fields, A. P. Young Ed., (World Scientific) 1997, and references therein.
[3] M. Lederman, R. Orbach, J. M. Hammann, M. Ocio, E. Vincent, Phys. Rev. B, 44 (1991) 7403; E. Vincent, J. P. Bouchaud, J. M. Hammann, E. Lefloch, Phil. Mag. B, 71 (1995) 489; C. Djuberg, K. Jonason, P. Nordblad., cond-mat/9810314 (1998).
[4] J. M. Hammann, F. Lefloch, E. Vincent, M. Ocio, J. P. Bouchaud, Random magnetism and high temperature superconductivity, edited by Beyermann, Huang Liu and Mac Laughlin eds., (World Scientific) 1994.
[5] L. F. Cugliandolo, J. Kurchan., cond-mat/9812229 1998.
[6] R. L. Leheny, S. R. Nagel, Phys. Rev. B, 57 (1998) 5154.
[7] F. Alberici, P. Doussineau, A. Levelut, Europhysics Lett., 39 (1997) 329.
[8] F. Alberici-Kious, J.P. Bouchaud, L.F. Cugliandolo,P. Doussineau, A. Levelut, Phys. Rev. Lett., 81 (1998) 4987.
[9] J. Y. Cavaillé, S. Etienne, J. Perez, L. Monnerie, G. P. Johari, Polymer., 27 (1986) 686.
[10] In fact, \( A_i \) and \( B_i \) are also functions of the cooling rate. In PMMA, \( \epsilon_2 \) changes of about 25%, when the cooling is changed by two orders of magnitude. More details will be given elsewhere. All our measurements where performed here with the same rate of \(-3K/min\).
[11] N. G. McCrum, B. E. Read, G. Williams, Anelastic and Dielectric Effects in Polymeric Solids, (Dover 1991)
[12] The value of \( \tau \) is found by a best fitting procedure which minimizes the difference for \( t > t_b \) between the perturbed aging curve and the shifted reference curve \( \epsilon_2^{ref}(t) = A^{ref}_2 - B^{ref}_2 \log(t + t_0) \), where \( ref \) stands here for reference curve.
[13] F. Alberici, P. Doussineau, A. Levelut, J. Phys. I, 7 (1997) 329.
[14] M. Mézard, G. Parisi, J. Phys. I, 2 (1991) 1705.
[15] L. F. Cugliandolo, J. Kurchan, Phys. Rev. Lett., 71 (1993) 173.
[16] K.Jonason, E. Vincent, J. Hamman, J. P. Bouchaud, P. Nordblad, Phys. Rev. Lett., 81 3243 (1998) 3243; P. Doussineau, T. de Lacerda-Aroso, A. Levelut, Europhysics Lett., 46 (1998) 401.
[17] L. Bellon, S. Ciliberto, C. Laroche, *cond-mat/9906162*, (1999).
temperature $T_1$ (K)

$A_2(T_1, \nu=1\text{Hz})$

$B_2(T_1, \nu=1\text{Hz})$

(a)
A_2(T=366K, \nu) = 366K, \nu

B_2(T=366K, \nu)

(b)