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# Long Term Physical Aging of Amorphous Polymers

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## Abstract

The dynamic properties of amorphous polymers is investigated during long term aging by means of high resolution low frequency mechanical spectroscopy. Two polymers are considered in this work, namely atactic polystyrene and quenched amorphous poly(ethylene naphthalate). It is shown that during aging at temperature higher than that of secondary relaxation but lower than that of primary one (if tested at 1Hz), the strength of the secondary relaxation first increases and then decreases for long aging times. This phenomenon is explained on the basis of concepts of (i) the cohesion heterogeneity of the amorphous network at the nanometric scale and (ii) cooperativity of molecular motions responsible for the secondary relaxations.

*Keywords* secondary relaxation, amorphous polymers, glass transition, mechanical spectroscopy, physical aging, structural relaxation, cooperative motions

## 1. Introduction

Physical aging in the glassy state (or structural relaxation) is known to affect the physical properties of amorphous systems and amorphous polymers in particular. Although numerous studies have been devoted to the relationships between structural state and molecular mobility, a precise and general picture of the effects of aging on the different degrees of freedom in polymers is not known yet. Experimental and theoretical approaches of the aging effects on the  $\alpha$  (main) relaxation are main keys for the glass transition understanding. Moreover, the influence of structural state on the  $\beta$ ,  $\gamma$ ,  $\delta$ , ... (*i.e.* secondary) relaxation processes is of interest since the  $\beta$  relaxation is a major aspect of the glassy state physics. Actually, the  $\beta$  relaxation process was first proposed to originate from motions within 'islands of mobility' [1] and to be a specificity of the glassy state [2]. Such assumptions were studied and checked by dielectric spectroscopy on a set of molecular glasses and liquids [3]. More recently, the  $\beta$  relaxation was considered as the elementary motion for the more complex  $\alpha$  relaxation [4-6], thus inferring a relation with structural state and thus structural relaxation.

The aim of this work is to show that physical aging does influence the sub- $T_g$  relaxation process in a complex way when it shows a degree of cooperativity (*i.e.* when the activation parameters have no longer physical meaning in term of energy barrier). It is shown that the aging condition (temperature and duration) may result in specific aging effect on the secondary relaxation process.

## 2. Materials and techniques

### 2.1 Materials

Two amorphous polymeric materials were investigated in this work, namely atactic polystyrene (PS) and poly(ethylene naphthalene 2,6 dicarboxylate) (PEN for short). In the case of PEN, fast quenching from the liquid state was necessary to avoid crystallization.

The glass transition temperature  $T_g$ , assessed by DSC (heating rate 10 °C/min), is 95°C and 120°C (midpoint) for PS and PEN, respectively. The molecular weights  $M_n$  and  $M_w$  of PS are 93000 and 240000g/mol; and that of PEN are 22000 and 38000 g/mol.

### 2.2 Techniques

The dynamic shear modulus  $G^* = G' + jG'' = G \cdot \exp(j\phi)$  was measured using a high resolution mechanical spectrometer [7], **based on an inverted pendulum operated in the forced oscillation mode, and** working in the low frequency range ( $10^{-4}$  Hz up to 1 Hz), which allows to separate the secondary and main relaxation processes more clearly. The strain amplitude does not exceed  $10^{-5}$ . Such a low level ensures that the mechanical excitation does not modifies the structural state of the specimens. This mechanical spectrometer makes it possible to study the dynamic shear modulus by frequency and/or temperature scanning. **For constant frequency measurements, the heating rate was 1°C/min.**

The long term aging procedure in isothermal conditions was carried out in the spectrometer, **thus ensuring reliable results.**

In addition, calorimetric measurements (DSC model TA 2920) were performed to characterize the energy released on rejuvenation of aged specimens and estimate the so-called fictive temperature according to a procedure long ago proposed by **Moynihan *et al* [8].**

### 3. Experimental results

The aging effect was studied by monitoring the complex shear modulus by frequency scanning at constant temperature and also by temperature scanning at constant frequency.

#### 3.1 PS

Figure 1 presents the complex evolution of the phase lag  $\varphi$  measured at a constant temperature (80°C, *i.e.* not far below  $T_g$ ) and constant frequency (0.316Hz) as a function of aging time at 80°C. During the shortest aging times, the decrease of the value of  $\varphi$  is attributed to the classical aging effect on the  $\alpha$  process inducing a reduction of the long range molecular motions. Nevertheless, it appears clearly that the  $\beta$  relaxation strength first increases for longer times and then decreases for ultra long term aging.

Figure 2 displays the associated evolution of the dynamical behavior of PS observed during aging at 80°C. The increase of the secondary relaxation strength is again clearly observed on aging. This observation also is confirmed by the comparison of isochronal measurements of the specimen *i*) after aging and *ii*) after erasing of thermal history as shown in Figure 3, where the enhancement of the  $\beta$  process on aging is underlined.

The structural relaxation was characterized by calorimetric measurement (heating and cooling rate =10°C/min) as shown in Figure 4. The overall effect of long term aging (86°C during 7 months) appears clearly by calculating the fictive temperature  $T_f$ . The fictive temperature of PS is decreased down to  $T_f=89^\circ\text{C}$  after long term aging, that is to be compared to  $T_f=100^\circ\text{C}$  after rejuvenation.

#### 3.2 PEN

In order to go a step further, another amorphous polymer was considered where the secondary and main relaxation processes are clearly separated, namely PEN as shown in Figure 5. Actually, there are two sub- $T_g$  relaxation processes in PEN, namely  $\beta$  and  $\beta^*$  (according to the usual nomenclature agreed in the case of PEN). Actually, the low temperature secondary process  $\beta$  can be separated into two individual components, namely  $\beta_1$  and  $\beta_2$ . These low temperature secondary processes correspond to localized motions of chain segments, since the activation entropy is rather low for both components. In addition, the  $\beta_2$  component was shown to be affected by the presence of adsorbed water. As a consequence, the  $\beta_1$  and  $\beta_2$  processes will not be considered further in this work. The  $\beta^*$  process in PEN is believed to be a true secondary relaxation process but with cooperative character, since the activation entropy is found to be about 200J/mol.K. Thus, the aging was carried out at intermediate temperature (105°C) *i.e.* between that of  $T_\alpha$  and  $T_{\beta^*}$ . It is observed that during the long term aging the strength of the secondary relaxation is first decreasing, then increases (Figure 6a), and then decreases at very long aging duration (Figure 6b). The upturn attributed to the  $\alpha$  relaxation is only visible on the reference state, and does not appear on the curves obtained after aging.

The evolution of the  $\beta^*$  relaxation strength during long term and ultra long term aging is summarized on Figure 6. It is obvious that the  $\beta^*$  relaxation strength goes through a maximum for an aging duration about  $3.10^4$  minutes.

#### 4. Discussion

It is shown that the  $\beta^*$  relaxation of PEN exhibits a behavior similar in many aspects to that of  $\beta$  relaxation in PS and the high temperature component of the  $\beta$  relaxation in BPA-PC [9], PEEK and PES [10].

Isothermal physical aging at an intermediate temperature, *i.e.* between  $T_{\beta(1\text{Hz})}$  and  $T_{\alpha(1\text{Hz})}$  appears to first increase the strength of the  $\beta$  relaxation, even if it slows down the dynamics of the  $\alpha$  process and eventually the  $\beta$  process.

In agreement with these previous findings, this study leads to the conclusion that with aging, the **domains of cooperatively rearranging regions responsible** for the main relaxation process evolve and transform into **domains of high mobility** for the less cooperative sub- $T_g$  relaxation motions (**that could correspond to 'islands of mobility'**[1-3,11]). For the longest aging times, the amorphous structure continues to evolve and the amplitude of the  $\beta$ -relaxation decreases again. In other words, **the rearranging regions where the  $\alpha$  and  $\beta$  relaxation processes develop** are different **but should be** related in the sense that structural relaxation induces a conversion of part of the molecules involved in the  $\alpha$  motions into active species responsible for the  $\beta$  (or  $\beta^*$ ) events.

This suggests that an enhancement of  $\beta$  relaxation is occurring after a structural change when the characteristic size of the density fluctuations or '**cooperatively rearranging regions**' (structural size) is corresponding to the characteristic size of the implied molecular motions (dynamic size). As a result, such a complex phenomenon cannot be described with a 'quasi punctual' defect picture of amorphous matter [4].

Aging below  $T_g$  induces a decrease of the structural characteristic sizes, and a transient correspondence of structural and dynamic sizes for the  $\beta$ -relaxation can be observed when this process is close to the main relaxation and/or when it exhibits a cooperative character. This contrasts with the well known effects described by Johari [11].

Furthermore, it is interesting to address the spatial location of main and secondary processes at the nanometric scale. In fact the heterogeneous nature of the glassy structure was proposed a few years ago to explain the excess of vibrational density of states as shown by low frequency Raman scattering and inelastic neutron scattering [12]. According to this concept, cohesive domains (with size about 4 nm in polymers) are separated by less cohesive zones **that could be identified to the cooperatively rearranging regions**. It has been shown that the contrast within the network structure resulting from cohesive domains and soft zones is decreased by physical aging in a monotonous way, **the soft zones becoming more and more ordered**. Taking into account the complex effects of aging on  $\beta$  (or  $\beta^*$ ) processes, this means **the decrease of the cohesive contrast occurring within the soft zones is responsible for the conversion of part of the  $\alpha$  rearrangements of limited extension into secondary relaxation events exhibiting cooperative character**. This proposal could explain why the secondary relaxation strength goes through a maximum upon aging.

**Within the frame of the energy landscape, during the first step of the structural state evolution, the system can be understood as falling into a minimum presenting a large number of small energy barriers ( $\beta^*$  motions). Ultimately, after ultra long term aging, the system falls into a deeper minimum with higher energy barriers (the characteristic time of the  $\alpha$  processes is largely increased, and simultaneously, the strength of the  $\beta^*$  process is decreased).**

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## Captions for figures.

Figure 1.

Evolution of the phase lag  $\varphi$  at 80°C and 0.316Hz during aging of polystyrene. Ultra-long term aging measurements ( $\oplus$ ) indicates that the  $\beta$  relaxation strength goes through a maximum. The dotted line is drawn as a guide for the eye.

Figure 2.

Frequency scanning at 80°C of polystyrene showing the  $\beta$ -relaxation enhancement on aging.

Figure 3

Temperature scanning at constant frequency (1Hz) of polystyrene after aging 21 days at 80°C (solid circles) and subsequent rejuvenation due to fast cooling from  $T=125^\circ\text{C}$  after the first heating scan (open circles).

Figure 4.

Calorimetric measurements of PS on heating (at 10K/min). First scan: after aging 7 months at  $T_g-15^\circ\text{C}$ , second scan: quenched state.

Figure 5.

PEN mechanical relaxations measured on heating (1K/min) at 10Hz.

Figure 6a

PEN isochronals (0.316Hz) after aging at different times at 105°C showing the increase of the  $\beta^*$  relaxation amplitude after long term aging. The rising due to the  $\alpha$  relaxation appears only on the reference state curve. It does not appear on subsequent curves because (i) the  $\alpha$  relaxation dynamics is slower and (ii) the upper temperature of the scans was limited to the aging temperature (105°C) in order to avoid any change in the aging rate due to the measurements.

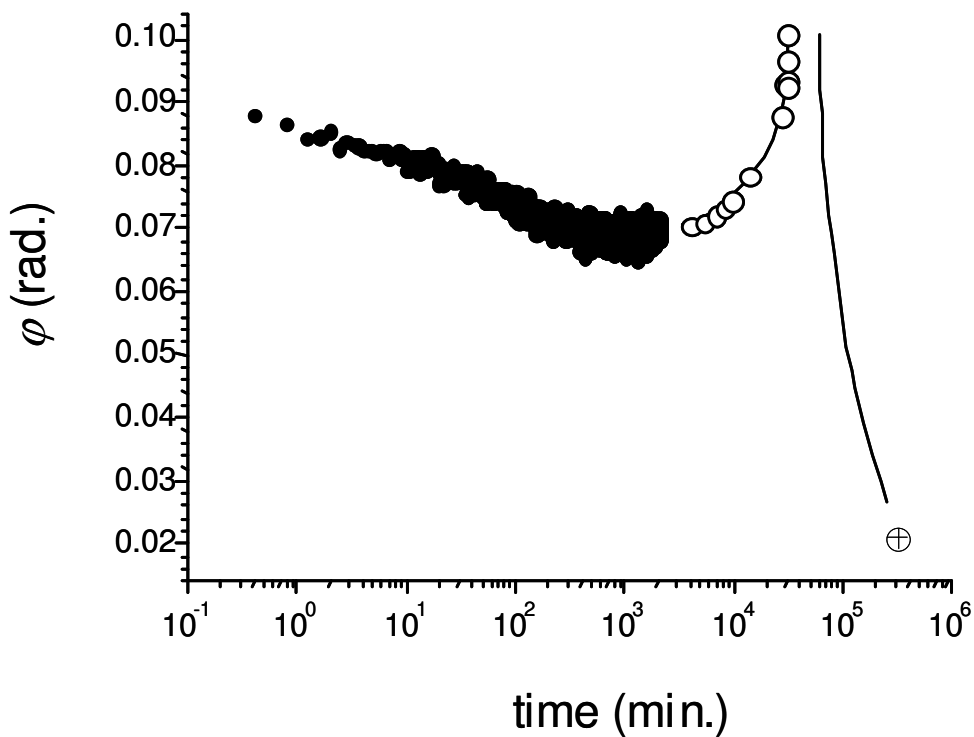
Figure 6b

PEN isochronals (0.316Hz) after aging at different times at 105°C showing the decrease of the  $\beta^*$  relaxation amplitude after ultra long term aging.

Figure 7

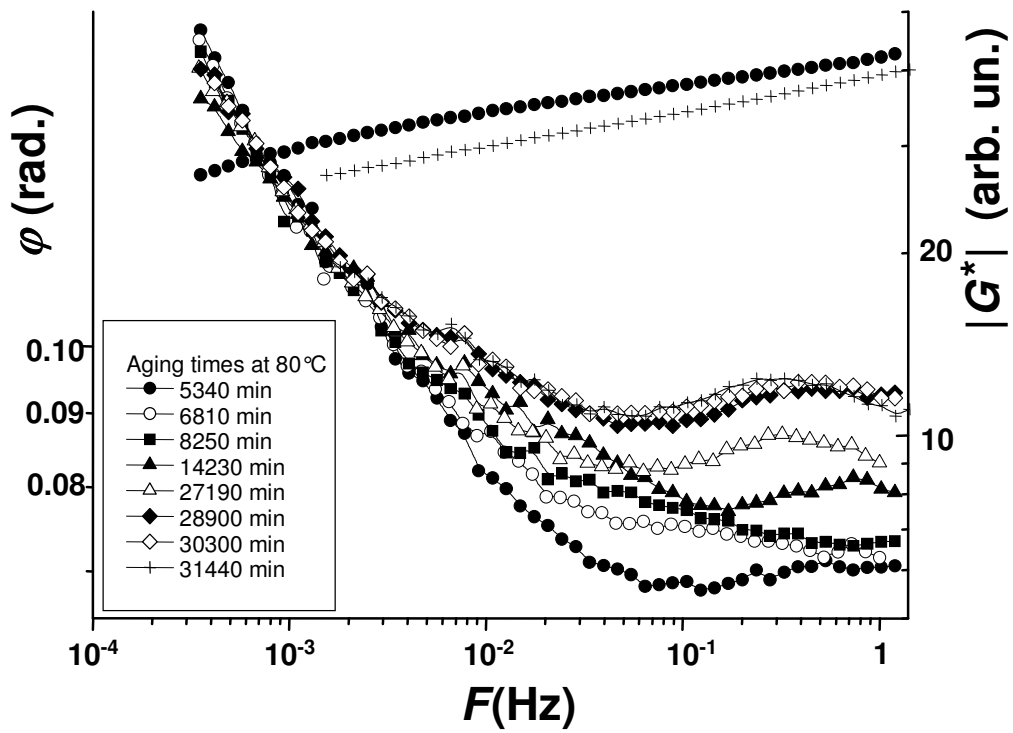
Evolution of the phase lag at 105°C and 0.316Hz during aging of PEN. The  $\beta^*$  relaxation strength goes through a maximum close to  $3 \cdot 10^4$  min.



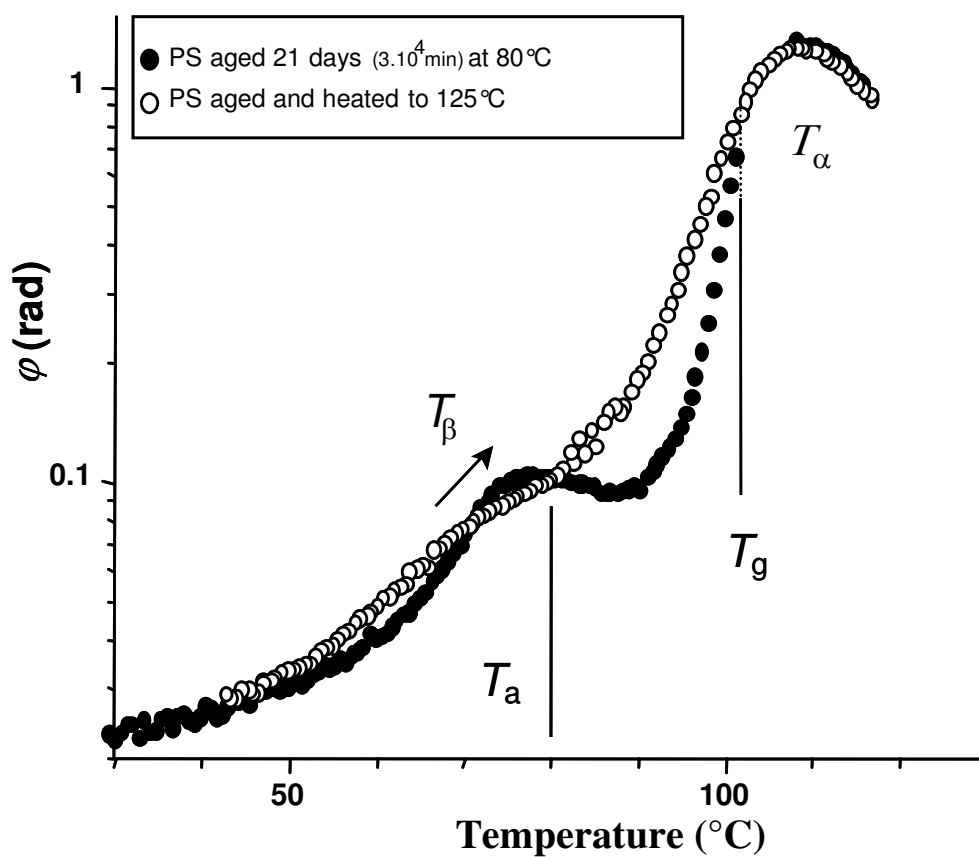


Etienne et al, Figure 1.

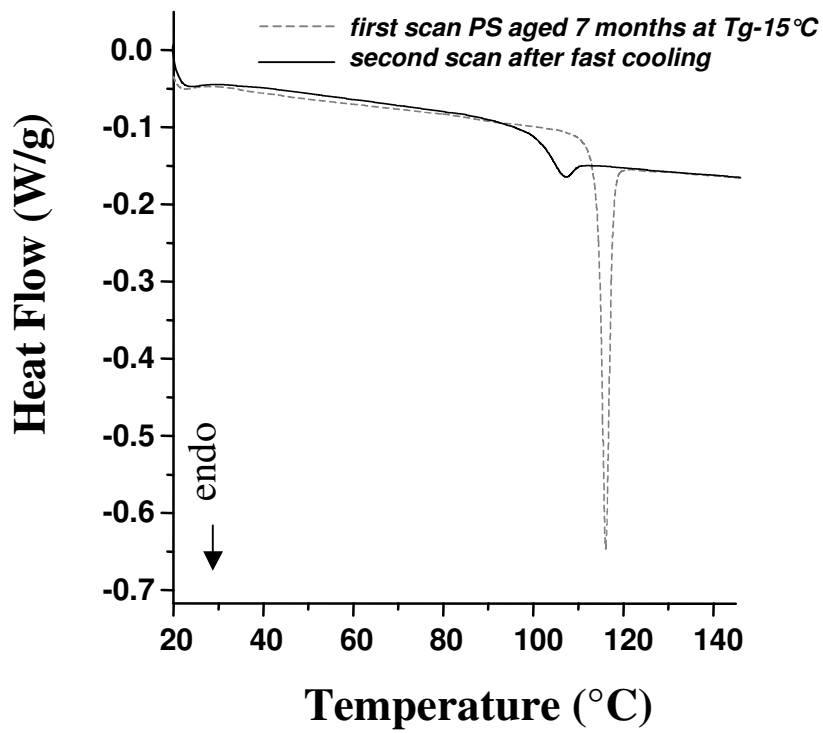
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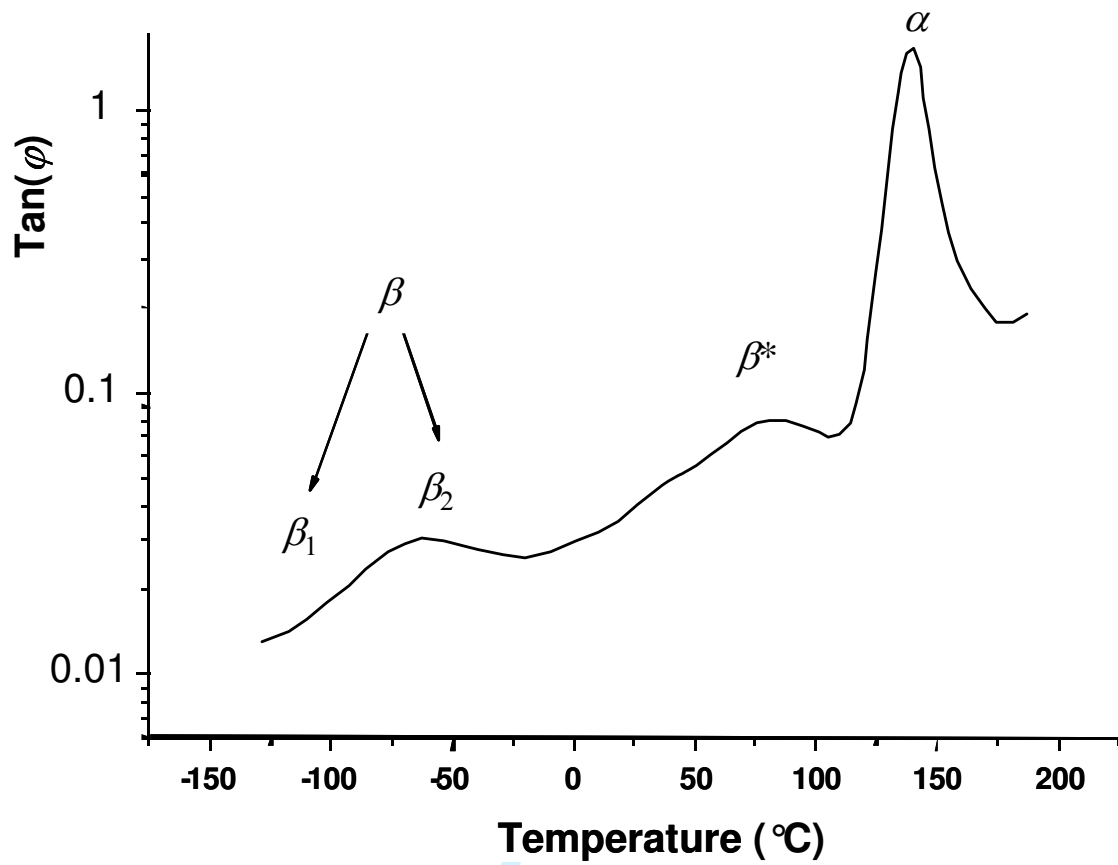
Etienne et al, Figure 2.



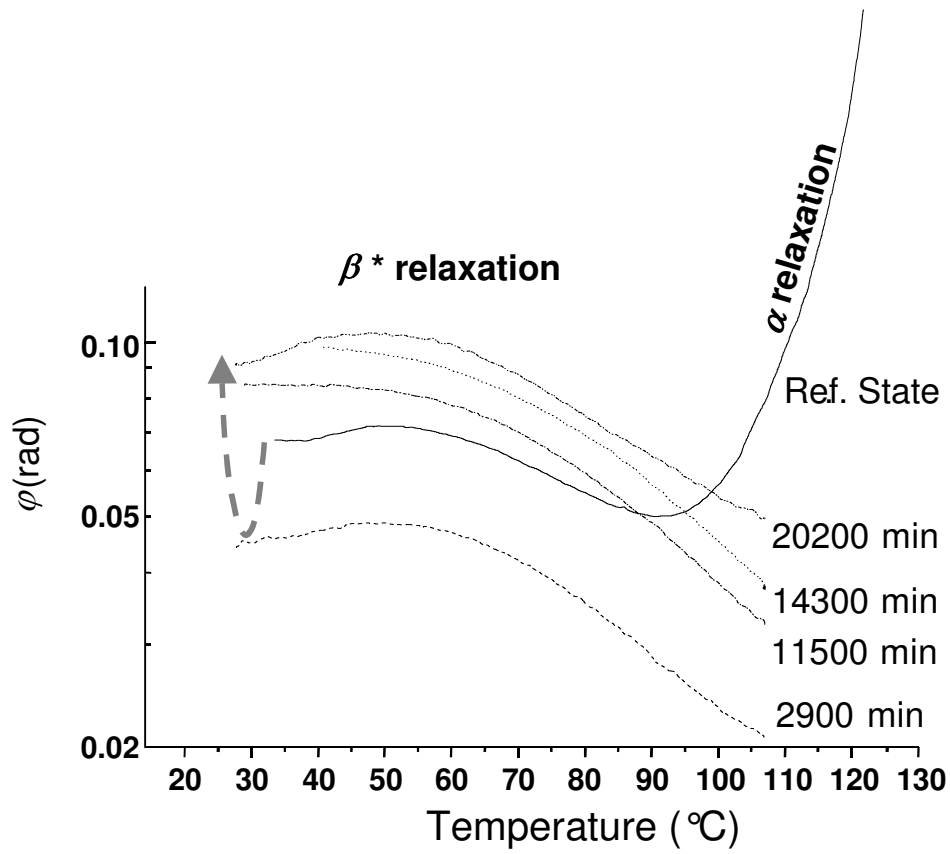
Etienne et al, Figure 3.



Etienne et al, Figure 4.

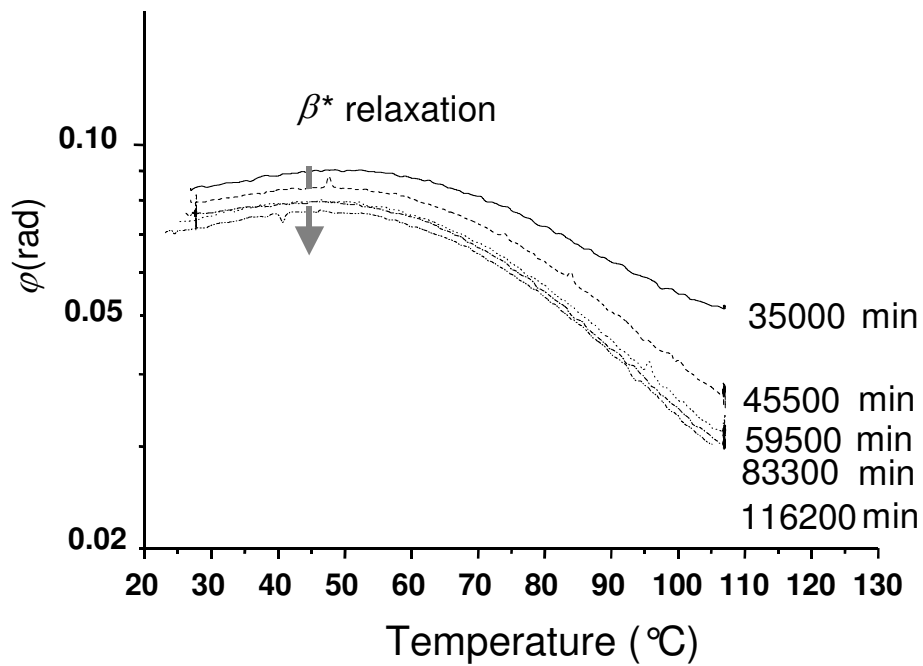


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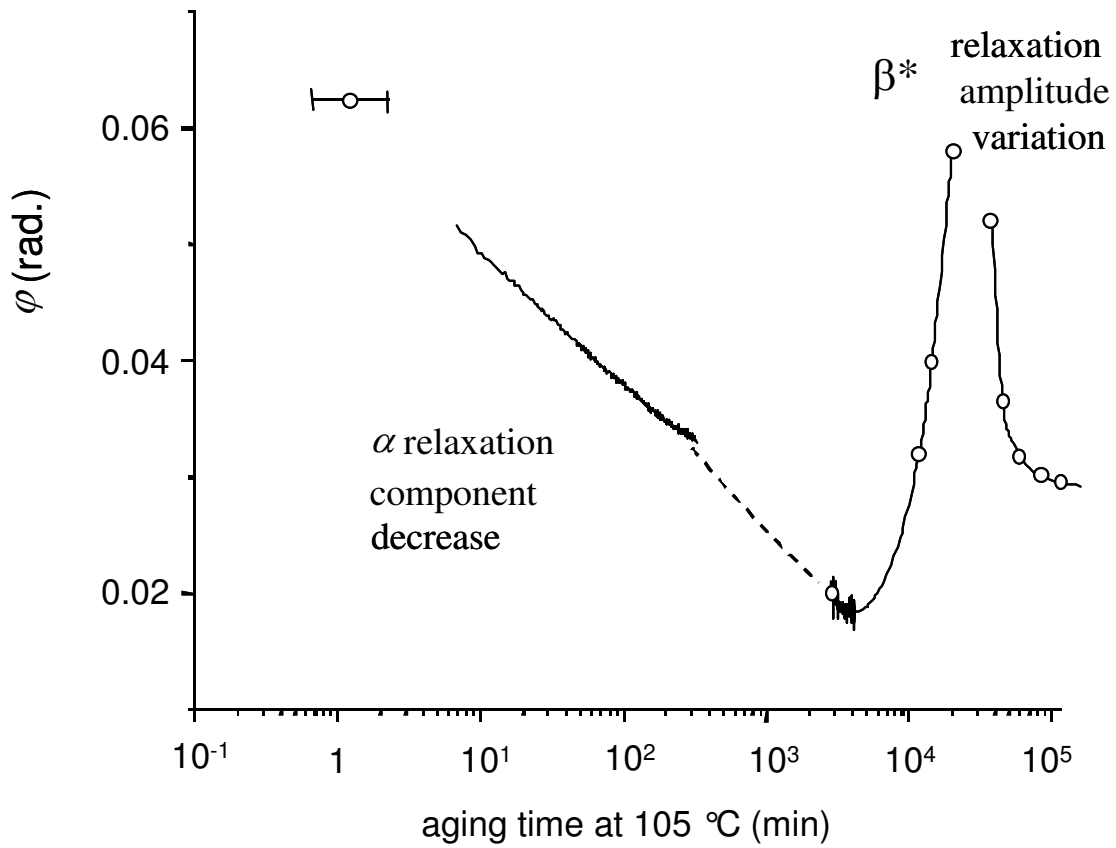
Etienne et al, Figure 6a.

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Etienne et al, Figure 6b.

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Etienne et al, Figure 7.

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