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## Molecular Mobility, Phase Transitions, Transformation Plasticity and Memory Effect in Poly(tetrafluoroethylene) (PTFE)

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**Résumé:** The dynamic mechanical behaviour of polytetrafluoroethylene is investigated by means of high resolution low frequency mechanical spectroscopy. Two relaxation processes are present. The  $\alpha$  process is located at 0.1Hz near 177K, and the  $\alpha'$  relaxation is close to 410K. Both processes are sensitive to the amorphous/crystalline microstructure. We show for the first time that the low temperature  $\alpha$  process is associated with a glass transition, whereas the  $\alpha'$  relaxation is to be related with defects motions in the disordered crystalline phase. Mechanical spectroscopy also show narrow peaks at the phase transitions (near 293 and 308 K). The study of deformation under a constant stress, during thermal cycles between 283 and 303K enabled us to show evidence of a transformation plasticity and a stress assisted memory effect related to the low temperature phase transition. Careful estimations are necessary to distinguish between the memory effect contribution and other superimposed deformations, due to elastic modulus changes, phase transformation dilatation, and thermal dilatation between 283 and 303K.

### 1. INTRODUCTION.

Polytetrafluoroethylene (PTFE) is a thermoplastic semicrystalline polymer. In spite of its widespread use, some of its elementary physical properties still remain unclear, such as the value of the glass transition temperature. The crystalline part of PTFE is complex as three crystalline phases can be found at ambient pressure. The corresponding phase transitions are located at about 293K and 308K. There also is a high pressure polymorph (III) and the phase diagram of PTFE is known [1-4]. In the low pressure phases of PTFE (I, II and IV) the chains are helical, but with different pitch length for each polymorph. Helicity defects in the form of reversal of handedness are believed to play a important role in the phase transitions mechanisms[5], and evidence of the dynamic features of these defects was shown by complementary spectroscopic techniques such as infrared absorption[6], Raman scattering[7,8] and NMR[9]. Thus, it appears that the molecular degrees of freedom likely to occur in the crystalline phases of PTFE are better known than the motions taking place in the amorphous phase, the effect of which have not been clearly identified.

The aim of this work is to contribute to the characterization of the dynamics in PTFE by low frequency spectroscopy, in order to establish the role of the amorphous phase. Moreover, the low temperature phase transition is shown to induce a transformation plasticity and a stress-assisted memory effect.

#### 1.1 Material.

The samples used in this work were obtained by compressing a highly crystalline powder (Hoechst TFM 1620) at ambient temperature at 30MPa. After the removal of the pressure, the temperature is increased at 1K/min up to 633K. An isothermal treatment is performed at 633K for 12 hours, and the temperature is decreased at 1K/min. The crystalline ratio of the obtained material is about 55%[10]. Films (0.5mm thick) could be cut in the sintered samples. Quenched samples were obtained by heating the films above the melting point and quenching in water at 285K. The microstructure of quenched and sintered samples is described in details elsewhere[10].

#### 1.2 Techniques.

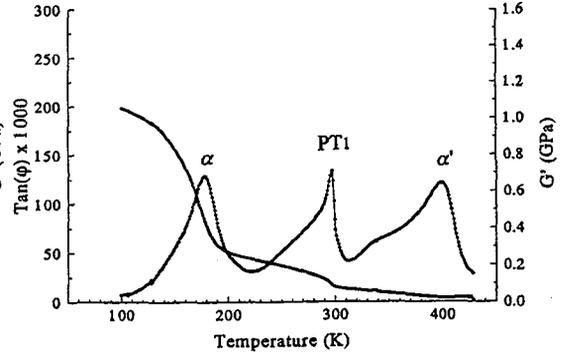
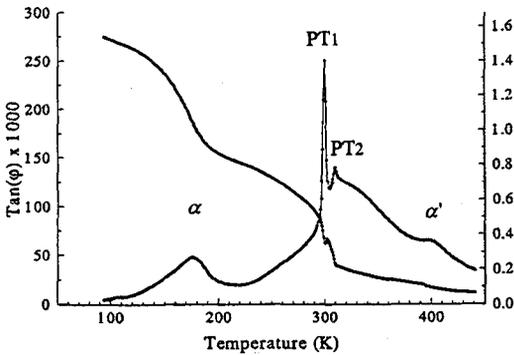
The dynamic mechanical behaviour of PTFE was investigated by means of a forced oscillation spectrometer[11]. This apparatus is specially designed to the study of films and fibers. This allows measurements on samples ( $0.35 \times 2 \times 10 \text{mm}^3$ ) with specific crystalline morphologies and limits the amplitude of thermal gradients within the samples. It gives the value of the complex shear modulus

$G^*(\omega\tau) = G' + iG''$  as a function of temperature and frequency, in the temperature-frequency window [100K-500K] . [10<sup>-4</sup>-1Hz].  $Tan(\phi)$  corresponds to the ratio  $G''/G'$ .

Deformation measurements in uniaxial compression conditions were performed by means of an INSTRON 1185 equipped with a 100kN cell and a thermostated chamber. The samples used were cylinders with lengths of about 20mm, and diameters close to 10mm, in order to avoid buckling and barrelling effects.

**2. MOLECULAR MOBILITY.**

The dynamic mechanical behaviour of sintered and quenched samples are shown by figure 1a and 1b respectively.

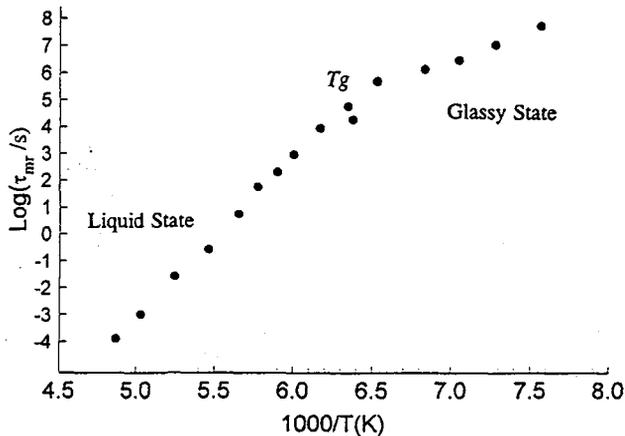


**Figure 1a.** Dynamic behaviour of PTFE in the sintered state at 0.1Hz (fixed frequency) and  $dT/dt=1K/min$ .

**Figure 1b.** Dynamic behaviour of PTFE in the quenched state. (same experimental conditions as figure 1a)

**2.1. Relaxation processes.**

Several relaxation processes can be observed. A low temperature relaxation ( $\alpha$ ) is close to 170K at 0.1Hz. A higher temperature process ( $\alpha'$ ) is located at about 410K at the same frequency. Both processes are affected by a thermomechanical treatment, as they are better defined in the case of the quenched sample. This feature is not sufficient to identify the location of motions responsible for each relaxation, because quenching both increases the amount of amorphous phase and the disorder in the crystalline phase. To go a step further, frequency scans were performed in isothermal conditions for both relaxations. The  $\alpha$  relaxation exhibited an approximate simple thermorheological behaviour and the Arrhenius diagram deduced from the shift factors of the master curve is shown by figure 2.



**Figure 2.** Arrhenius diagram of PTFE for the  $\alpha$  relaxation process, and showing the glass transition  $T_g$  (at 10<sup>5</sup>s).

On the contrary, it was not possible to perform the same analysis on the  $\alpha'$  process because the frequency scans could not be shifted to the same pattern in the entire temperature domain

investigated. This feature seems a characteristic of this complex  $\alpha'$  process[12], possibly it is partly due to structural evolution during the measurements, as we observed that some successive frequency scans recorded at the same temperature were not superimposable.

The Arrhenius diagram of the  $\alpha$  process is very typical of a glass transition phenomenon, as the isostructural (low temperature) and the metastable (high temperature) states can be localized. The temperature interval between the two domains is centred near 157K, which yields the value of the glass transition temperature of PTFE at the time scale of  $10^5$ s [13]. This diagram also enables us to compare the glass transition of PTFE with that of other polymers and glass forming systems studied under the same experimental conditions. PTFE exhibits a 'strong' behaviour, as the value of the slope of the arrhenius diagram in reduced coordinates,

$$m = \frac{d \text{Log}_{10}(\tau_{rm})}{d(T_g/T)} = \frac{Ea}{R \cdot T_g \cdot \text{Ln}(10)}$$

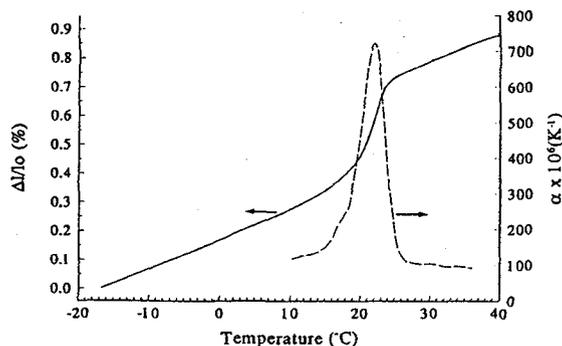
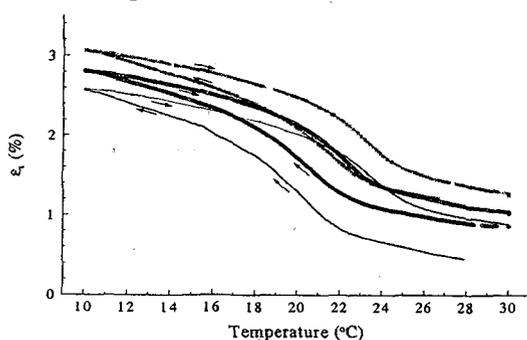
is close to 50 (at  $\tau_{rm}=10^5$ s) whereas for aromatic polymers like PES or PPS, this value is about 150 [14]. Vinylic polymers like PMMA and PVC also exhibit a more 'fragile' behavior, with values for  $m$  close to 160 and 170 respectively[15]. Strong liquids often exhibit a very small increment of  $C_p$  at the glass transition, which is the case for PTFE but also for the amorphous copolymers of PTFE (ex: Teflon AF). Moreover, the absence of lower temperature secondary  $\beta$  relaxation, which seems a characteristic of strongest liquids (ex silica) is confirmed for PTFE [16]. At last, a connection must be made between PTFE and PIB, as the strong behaviour of both polymers is related to a symmetrical, smooth and compact repeat unit [17].

## 2.2. Phase transitions.

Figure 1 also show the ambient temperature phase transitions of PTFE. The temperature locations of these narrow peaks are independent of frequency, but their amplitude classically increase with decreasing frequency. In the sintered sample, the two phase transitions are well defined. The first phase transition (PT1) exhibits a softening effect as a decrease in  $G'$  can be observed. The quenched samples do not show the second phase transition, and the PT1 is located at lower temperatures with no softening effect. Consequently, the crystalline structure induced by quenching promotes the formation of the high temperature phase (I), which is known to exhibit both higher intramolecular and intermolecular disorder than the lower temperature polymorphs (II,IV)[18-19].

## 3. MEMORY EFFECTS AND TRANSFORMATION PLASTICITY.

The effects of a constant stress during thermal cycles is illustrated by figure 3a, and should be compared with the deformation recorded with negligible stress during a dilatometric experiment (figure 3b). The temperature range of the thermal cycles is centred on the phase transformation occurring at 293K.



**Figure 3a.** Deformation cycles measured in compression mode ( $\sigma=8\text{MPa}$  at  $dT/dt=0.2\text{K/min}$ ) for a sintered PTFE sample. ( $\bullet$ ): First cycle; ( $\circ$ ):second cycle and ( $\times$ ): third cycle  
**Figure 3b.** Dilatometric curve of a sintered sample mode ( $\sigma=8\text{MPa}$  at  $dT/dt=0.2\text{K/min}$ ) for a sintered PTFE showing the thermal and phase transformation dilatations ( $\Delta\epsilon=0.5\%$  between 283 and 303K)

The amplitude of each deformation cycle is about 2%, and is much higher than the sum of thermal dilatation and phase transformation dilatation (0.5%) between 10°C (283K) and 30°C (303K). It is also necessary to take into account the change in the value of the elastic modulus  $E$ , which induces a change in deformation  $\Delta\epsilon_E$  given by

$$\Delta\epsilon_E = \sigma \frac{E(10^\circ\text{C}) - E(30^\circ\text{C})}{E(10^\circ\text{C}) E(30^\circ\text{C})}$$

This component is close to 0.35% for  $\sigma=8\text{MPa}$ . We associate the missing deformation (about 1.2%) to a memory effect. A similar value is found in tensile mode experiments. Moreover, It can be observed that the deformation cycles of figure 3a shift to higher deformation values. This effect is not due to creep because before the thermal cycles, the sample was submitted to the stress  $\sigma$  at 303K during a time long enough to reach a stationary regime, where the deformation does not increase significantly. The observed shifts between the cycles are thus considered as plastic (unrecoverable) components due to the phase transformation process occurring at low temperature. The behavior of PTFE bears many common aspects with shape memory alloys, such as (i) the linear increase of the transformation plasticity deformation with strain and (ii) the levelling of the memory shape deformation with applied strain  $\sigma$ . [20,21].

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