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Where is the Glass Transition Temperature of Poly(tetrafluoroethylene)? A new approach by Dynamic Rheometry and Mechanical Tests

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ABSTRACT

Polytetrafluoroethylene (PTFE) has been used for many years in different application fields due to its outstanding chemical and physical properties. But, the value of its glass transition temperature is still today a matter of controversy and very different values are proposed in the literature. This paper proposes to answer to this scientific question using dynamic mechanical measurements. First, the viscoelastic properties of PTFE are described on a large temperature range and the influence of the shearing frequency is carefully investigated. Then, the effects produced by the polymer annealing on its thermomechanical behavior are detailed. This study comforts the idea that PTFE amorphous phase should be considered as comprised of two distinct regions. The first one named “mobile amorphous fraction” (MAF) is able to relax at low temperature ($T = -103 \, ^\circ C$). The other one is specific of the macromolecular segments present at the boundaries between crystalline and amorphous domains. Due to the close vicinity of the crystallites, these macromolecular segments present a more restricted mobility. The corresponding phase is designated as the “rigid amorphous fraction” (RAF) and its mechanical relaxation produces itself at higher temperature ($T = 116 \, ^\circ C$). Actually, this latter value is strongly dependent on the material crystallinity degree. In particular, it is shifted to higher temperature after occurrence of a recrystallization that is accompanied by a further reduction of the RAF’s dynamic. Instead, the characteristics of the MAF relaxation are poorly affected. Tensile tests also support that the “real” $T_g$ of the polymer is located at low temperature. All these results have been compared to those of the literature to propose a real scientific discussion and to understand the origin of somewhat contradictory interpretations.

KEY WORDS. Annealing, dynamic mechanical measurements, glass transition temperature, mobile amorphous fraction, PTFE, relaxation, rigid amorphous fraction.
INTRODUCTION

Fluorinated polymers are high value-added materials for various applications, due to their unique properties such as the thermal stability, the chemical inertness (to organic solvents, oils, water, acids and bases), the low values of the refractive index, permittivity, dissipation factor and water absorption, as well as excellent weather durability and resistance to oxidation. Hence, they can find relevant applications in many fields of high technology such as aeronautics, microelectronics, engineering, chemical industry, optics, textile finishing, automotive industry, houseware, chemical processing, medical devices, architectural fabrics, and wiring insulation [1-4]. Among these polymers, polytetrafluoroethylene, PTFE, is by far, the most produced and used macromolecule endowed with exceptional properties (low friction coefficient, poor wear resistance and abrasion resistance) [5]. PTFE has been produced by different companies such as Asahi, Daikin, DuPont, Dyneon, or Solvay Specialty Polymers under the Fluon®PTFE, Polyflon®, Teflon®, Hostaflon®, and Algoflon® tradenames, respectively [3-5], to name a few.

Since its discovery by Plunkett in 1938, PTFE has been the topic of a comprehensive literature supported by the necessity to determine the origin and the limits of its peculiar behavior. If the semi-crystalline character of the polymer is universally accepted, the exact value of the glass transition temperature ($T_g$) is still today subject to controversies. Indeed, the reported values of PTFE’s $T_g$ range from -110 °C to 130 °C with intermediate values such as -70 or -50 °C [5,6]. The difficulty to assess this critical temperature by calorimetry could be considered as a first element responsible of this open debate [7]. At the same time, other techniques currently used with polymers led to results that can be difficult to interpret. An illustration of this complexity was encountered with viscoelastic measurements usually convenient to evaluate the $T_g$ of a polymer. In 1959, McCrum [8] registered the rheological behavior of PTFE versus the temperature. The thermomechanical profile showed the presence
of four main relaxations that ranged between -200 °C and 380 °C. Characterizing the
rheological response of samples with distinct crystallinity degrees, this author showed that
two transitions were related to the crystalline fraction of the polymer. The first one located at
ca. 330 °C ($T_m$), was easily assigned to the polymer’s melting point and that appeared
consistent with the sharp drop of the mechanical rigidity. The other one, observed in the 20-
30 °C range, was related to the reorganization of PTFE’s crystalline structure. The two last
rheological transitions observed in the PTFE thermomechanical profile were qualified as
second order transitions. As their respective intensities were found to increase when the
crystallinity decreased, these transitions were assigned to the response of amorphous domains
[9]. But, the comparable amplitudes of their corresponding relaxation peaks did not allow the
authors to precise the exact nature of the mechanisms involved in these transitions. Prudently,
the relaxation observed at -110 °C ($T_\gamma$) was attributed to small sections of the macromolecule
whereas that registered at 130 °C ($T_\alpha$) was assigned to large molecular segments. Later, Eby
and Sinnott [10] named these relaxations as Glass I and Glass II transitions, respectively, but
the authors did not explain the presence of two glass transitions in PTFE.

In 1963, Tobolsky *et al.* [11] suggested to consider the $\alpha$ transition centered at 110 °C
as the PTFE glass transition. The authors came to this conclusion after conducting the stress
relaxation experiments at temperatures higher than the polymer’s melting point. Indeed, the
best description of the results was achieved from the Williams-Landel-Ferry equation in
which the $T_g$ of the polymer was close to 110 °C. Indeed, the description of the experimental
data with this semi-empirical relation was judged satisfactory considering the value of PTFE
close to 110 °C. Using an experimental approach based on the measurement of the linear
thermal expansion coefficient at different temperatures, Araki [12] also proposed to set
PTFE’s $T_g$ at 123 °C (396 K) due to the discontinuity in the evolution of this parameter at this
temperature that resembled that currently observed during the glass transition of a polymer.
This author also reported the same conclusions after conducting stress relaxation tests [13]. Unfortunately, in both studies, the experiments were only carried out at temperatures above room temperature. In other words, the domain where the \( \gamma \) process occurred itself was not explored. After achieving the conduction of plasticization experiments on PTFE, Starkweather [14] also suggested the assignment of \( \alpha \) relaxation as a glass transition. In particular, he observed that such a relaxation was able to shift with the volume fraction of diluent while the position of \( \gamma \) relaxation was almost constant. Extending his researches to the characterization of different semicrystalline fluoropolymers by thermally stimulated currents, this author attributed the \( \gamma \) process of PTFE to localized and cooperative motions of a few \( \text{CF}_2 \) units. Consequently, the occurrence of this relaxation in the ac dielectric response of various poly(TFE-co-HFP) random copolymers was consequently judged logical [15]. While analyzing the relaxation behavior of PTFE in the temperature domain including the \( \alpha \) process, Wortmann [16] also considered this latter process as relevant of a glassy/amorphous transition.

First divergence in the location of PTFE glass transition appeared with researches conducted by Durrell et al. [17]. These authors suggested to model the \( T_g \) evolution of a TFE copolymers series \textit{versus} their chemical composition using the Fox equation:

\[
\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad \text{(Eq. 1)}
\]

where \( w_1 \) and \( w_2 \) stand for the weight fraction of each monomer incorporated, while \( T_{g1} \) and \( T_{g2} \) are assigned to the glass transitions of the corresponding homopolymers. A good agreement between the experimental and calculated values was obtained considering that the \( T_g \) of PTFE was close to \(-50\,^\circ\text{C}\), \textit{i.e.} an intermediate position between \( T_{\gamma} \) and \( T_{\alpha} \). Later, Boyer [18] reported similar results. In different studies devoted to the rheological characterization of
perfluoropolyethers, Marchionni et al. [19,20] also suggested to consider PTFE’s glass transition temperature close to -75 °C.

Another research trend associated the low temperature γ relaxation (-110 °C) to the glass transition temperature of PTFE. Different experimental approaches were undertaken using mechanical, acoustical or thermodynamic techniques [21-23]. More recently, Rae and Dattlebaum [24] investigated the properties of PTFE in compression on a wide temperature zone and for different crystallinity degrees. Low-crystalline samples showed a little difference in their mechanical responses with strain-rate or temperature above -100 °C. A reverse situation was observed below this critical temperature interpreted as being close to the polymeric T_g. Fossati et al. indirectly led to the same conclusion in a study devoted to the sorption and permeation of hydrocarbons in a poly(TFE-co-perfluoromethylvinylether) copolymer, MFA [25]. Using PTFE as a material reference for their modeling, they used the common assumption that the polymer’s T_g was above room temperature. But, surprising results motivated the authors to examine the reverse situation. Under this latter assumption, a satisfactory representation of sorption data was obtained.

Table 1 summarizes the different techniques used to assess the glass transition temperature of PTFE. The uncertainty about the exact value of the PTFE’s T_g may appear surprising considering that this material received much attention by the scientific community [26]. But, most studies were devoted to the description of its exceptional properties in different fields related to physics and chemistry as mentioned above. Basic information such as the exact nature of the molecular mechanisms at the origin of both γ and α relaxations were regarded with less attention in spite of their usefulness. Thus, it was of interest to revisit “basic” concept such as the glass transition of this polymer by using a novel approach involving dynamic mechanical and aging tests. First, to go further in the description of the rheological behavior of PTFE, the thermomechanical response of this material was registered
on a large temperature zone and for different values of the shearing frequency. Then, the
effects produced by a thermal treatment (annealing) on the polymer dynamic mechanical
properties were investigated. Finally, a real discussion was suggested by comparison of our
results with the data already published in separate articles to propose reliable structure-
properties relationships.

Experimental

Material

PTFE samples were kindly provided by Solvay Specialty Polymers and marketed
under the Algoflon® trademark. This neat polymer was received under a rectangular sheet that
was re-cut under rectangular tablets using automated saw working at low velocity. Typical
dimensions of the specimens were 40 mm x 8 mm x 1 mm. This geometry was judged well
suited for the viscoelastic characterization of the polymer in solid state. The same grade was
also received under dog-bone form for tensile tests (width of 10 mm and thickness of 4 mm).

Rheological characterization

The different viscoelastic experiments were performed using a stress-controlled
dynamic rheometer (AR2000Ex model from TA). This apparatus was equipped with an
environmental testing chamber to allow the registering of the complex shear modulus $G^* =
G' + j G''$ under precise control of the temperature. The component $G'$, usually called “storage
modulus”, represents the mechanical rigidity of the sample (i.e. its elastic contribution). The
loss modulus $G''$ relates to the dissipated mechanical energy due to molecular motions in the
material. The behavior of the PTFE versus temperature was investigated from -150 °C up to
the molten state using rectangular torsion geometry. The different thermomechanical tests
were carried out at a heating rate of 3 °C min$^{-1}$ and at a fixed oscillating angular frequency $\omega$
but ranging from 1 to 100 rad s$^{-1}$ to examine the influence of $\omega$ on the temperature position of
the different relaxation peaks. The reproducibility of the rheological results was checked by repeating twice the analyses.

**Mechanical characterization**

The tensile properties of PTFE were assessed using a universal material test machine from Zwick (model Z010) equipped with a 5 kN load cell. The tests were performed at ambient temperature at a constant speed of 5 mm/min according to ISO527 norm.

**Physical treatment**

To complete the scientific understanding of the rheological relaxations, some PTFE samples were exposed at the temperature of 105 °C in dry atmosphere for one month. The annealing effects on the polymer’s thermomechanical behavior were investigated using the same experimental conditions as previously described.

**Results and Discussion**

**Thermomechanical analyses of initial PTFE**

First rheological experiments were conducted on PTFE “as received” i.e. without any physical or chemical treatment. Figure 1 shows the evolution of the viscoelastic properties of the polymer as a function of temperature and at the constant angular frequency $\omega = 1$ rad/s. The evolution of the storage modulus $G' = f(T)$ agrees with that reported in the literature by McCrum [8] or Hintzer and Löhr [27]. Moreover, it describes a more extended temperature zone than that detailed in Starkweather’s work [14]. Undeniably, the thermomechanical profile can be qualified as being complex since four transitions are shown on the rheological curves.
Figure 1. Thermomechanical analysis of PTFE with G': ● and G": △ (ω = 1 rad/s)

Two transitions are well known and their interpretation does not suffer from any form of controversy. That observed from -50 °C up to 32 °C is named β and currently related to the crystalline transitions that produce themselves in PTFE [25]. Indeed, X-ray experiments have already shown in the past that such a thermoplastic polymer can exhibit three solid phases at atmospheric pressure with two first-order crystal-crystal transitions that occur at 19 °C and 30 °C [24,28]. The first one is known to be characteristic of the transition from a highly ordered triclinic structure to a hexagonal crystal. More precisely, the macromolecule slightly untwists since it passes from a 13/6 helical conformation (13 CF₂ groups are equally spaced in 6 turns) to a 15/7 helix. The second crystalline transition corresponds to the evolution to a pseudohexagonal crystal due to the further untwisting and that is accompanied by a rise in the crystalline cell from 13 to 15 carbon atoms. In rheology, the differentiation of these crystalline transitions is more difficult because they produce themselves in neighboring temperature zones. Nevertheless, the width and the asymmetry of the relaxation peak in the temperature range associated to these crystalline changes seem to be consistent with the presence of two transitions. The former one seems to prepare itself well before the critical
temperature of 19 °C since the increase of the G” curve from -50 °C reveals a progressive growing in the local molecular mobility. The sudden drop between 20 °C and 30 °C of the storage modulus curve agrees with the reported crystalline transition from triclinic to hexagonal phase. Another universally accepted transition is reported above 320 °C where the values of both moduli suddenly decrease. This phenomenon is characteristic of the polymer melting as shown by the presence of an endothermic peak in PTFE calorimetric analysis [28].

Both γ and α relaxation peaks mentioned in the introduction can also be observed on the G” curve [14]. They appear in a clearer form by plotting the evolution of the loss factor δ (defined by tan δ = G”/G’) versus the temperature (Figure 2) [8]. Named also “internal friction”, this loss factor is really influenced by the nature and amplitude of molecular motions [27]. The maxima of each relaxation peak are respectively taken down at Tγ = -103 °C and Tα = 116 °C.

![Figure 2](image-url)

**Figure 2.** Evolution of the tan δ of PTFE as a function of temperature

It is interesting to note that both relaxations also induce a significant decrease of the storage modulus G’ (Figure 1). This result is of first importance because it reveals that none
of these relaxations can be confused with “simple” rheological secondary relaxations. Indeed, associated to local segmental motions in the polymer chain, secondary relaxations induce mechanical losses that appear as rheological peaks on the curve characteristic of the dissipative energy *i.e.* the loss modulus $G''$. Due to its reduced amplitude, this phenomenon has a poor effect on the $G'$ modulus in contrast to the rheological evidence of the glass transition temperature [29-34]. Indeed, in this latter process, the molecular dynamics is usually characterized by cooperative motions of higher molecular segments which affect the polymer mechanical rigidity [35,36]. Then, at this stage of that present discussion, PTFE really seems to exhibit two glass transition domains as suggested by Eby and Sinnot [10]. But, the existence of both transitions remains unexplained.

Then, to investigate further the characteristics of $\gamma$ and $\alpha$ processes, another series of thermomechanical analyses were performed on new PTFE samples in the solid state to analyze more deeply the influence of the value of the shearing angular frequency on the position of each relaxation. As shown in Figures 3a and 3b, both $\gamma$ and $\alpha$ mechanical peaks occur at higher temperatures when $\omega$ is increased.
Figure 3. Influence of the shearing angular frequency $\omega$ on the position of $\gamma$ and $\alpha$ peaks measured on $\tan \delta = f(T)$ and represented by (a) and (b) series, respectively.

The evolution of the temperatures taken at the maximum of each relaxation peak can be described using the model proposed initially by Glasstone, Laidler and Eyring [57] to detail the effect of the temperature on the diffusion phenomena:
where $R$ stands for the gas constant (8.32 J/mol/K), $T$ (K) the absolute temperature at which the maximum of $G''$ is observed for the corresponding angular frequency $\omega$ (rad/s), $E_a$ the activation energy (kJ/mol) and $A$ the preexponential factor (rad/s). In other words, two apparent activation energies can be calculated from the plot of $\log \omega$ versus the inverse of the temperature taken at the maximum of each corresponding peak (Figure 4).

**Figure 4.** Evidence for the Arrhenius dependence of $T_\gamma$ and $T_\alpha$ temperatures as a function of the shear angular frequency $\omega$.

This result is currently observed for secondary transitions and this may be contradictory with previous remarks. Indeed, one of $\gamma$ or $\alpha$ relaxations is suspected to be associated with the glass transition of the polymer. Then, in this case, the corresponding temperature ($T_\gamma$ or $T_\alpha$) would more likely obey the William–Landel–Ferry (WLF) equation [37]. Actually, due to the limited evolution of the angular frequency value, it was not possible to discriminate which
kind of law the most appropriate. The exploitation of the results according Arrhenius
dependence gives the respective activation energy: $E_\gamma = 105$ kJ/mol and $E_\alpha = 444$ kJ/mol.
These latter values are in the same order of magnitude as that proposed for the
characterization of PTFE from dielectric spectroscopy [15,38]. Besides this theoretical
treatment, it is interesting to note that the change in frequency did not induce any shoulder
formation or peak dissociation. This means that $\gamma$ and $\alpha$ processes are governed by specific
major molecular mechanisms.

**Characterization of PTFE after annealing at $T = 105$ °C**

Figure 5 depicts the evolution of the dynamic mechanical properties, namely tan $\delta$, of
a PTFE sample after annealing at the temperature of 105 °C for 72 hours. This temperature
was fixed at a value comprised in the temperature domain associated to the $\alpha$ relaxation. To
make possible a better understanding of the changes induced by the thermal treatment, the
thermomechanical response of the “initial” polymer is also drawn.

![Figure 5](image_url)

**Figure 5.** Non-isothermal tan $\delta$ curves of the initial PTFE (solid line) and after annealing at
105 °C for 3 days (dotted line).
While the annealing step produced little effects on the $\gamma$ relaxation, it induced more significant changes on both position and shape of the other rheological peaks. First, the $\beta$ peak that is characteristic of different crystalline transitions in the PTFE undeniably exhibits higher amplitude. Nevertheless, the temperature associated to the maximum is unaffected. Second, the $\alpha$ relaxation peak is shifted to higher temperature after annealing: $T\alpha$ value increased from 116 °C up to 124 °C. In addition, at the same time, the melting enthalpy assessed by DSC also increased from 31 J/g to 37 J/g.

The higher enthalpy of fusion seems to reveal that the annealing step has induced an increase of the polymer crystallinity. This hypothesis is coherent considering also the growing intensity of the transition $\beta$. In fact, the phenomenon described here points out the “crystal perfection” already observed in different semi-crystalline polymers [39,42]. This mechanism seems perfectly valid with PTFE. Indeed, from X-ray diffraction technique, Jain and Vijayan [43] investigated the effects produced by a thermal aging conducted at $T = 150$ °C on PTFE structure and they showed an increase of the polymer’s degree of crystallinity. Similar results were also obtained by Yamamoto and Hara [44] for an exposure temperature close to $T\alpha$.

The understanding of the evolution of both $\gamma$ and $\alpha$ peaks must be highlighted now. A reduction of their amplitude was expected as reported by McCrum [8] who assigned these relaxations to polymer amorphous phase. But, in this present work, the main noticeable change is the increase of $T\alpha$. A possible mechanism is to imagine that the expansion of the crystalline phase is accompanied by a reduction of the molecular mobility of the amorphous domains located in the close vicinity of the crystallites [45]. In other words, the $\alpha$ process is only characteristic of the mechanical relaxation of these constrained amorphous areas and the
higher \(T_\alpha\) rise is the direct consequence of the inner stresses increase due to the development of crystalline zones.

Our hypothesis seems consistent with results of various surveys in which many semicrystalline polymers should be considered as three-phase systems [46-50]. In this approach initially used to explain the discrepancies between the degrees of crystallinity obtained from different techniques (calorimetry, X-ray diffraction, NMR or Raman spectroscopy), the amorphous phase is modeled as made of two distinct domains. The first one is named “mobile amorphous fraction” (MAF) and corresponds to the classical representation of macromolecular chains randomly arranged in space. The second one is defined as “rigid amorphous fraction” (RAF) and is associated with the interphase between the crystalline and the mobile amorphous phase. The existence of this intermediate interfacial region is justified by the continuation across the phase boundaries of the macromolecules (Figure 6). Due to its particular position, the RAF is characterized by a molecular mobility that is intermediate between that of MAF and crystalline domains. It can be reasonably believed that this description is applicable to the case of PTFE represented schematically in Figure 6: if the \(\alpha\) relaxation is assigned to the RAF, the \(\gamma\) relaxation is likely to be characteristic of the MAF. Considering that the main glass transition temperature of the polymer is defined as being characteristic of the amorphous phase of the “perfect” glass, the PTFE’s \(T_g\) must be taken at the value characteristic of the MAF, i.e. at \(T_\gamma = -103 \, ^\circ\text{C}\).
Figure 6. Schematic illustration of PTFE structure.

(1): mobile amorphous phase; (2): rigid amorphous phase; (3): crystalline phase

Dividing PTFE according to three phases also agrees with the researches conducted by Dlubek et al. [52]. These authors investigated the local free volume of PTFE and its copolymer based on TFE and perfluoro(propyl vinyl ether), PFA, on a large temperature scale. Comparing the results of pressure-volume-temperature experiments with data obtained by positron annihilation lifetime spectroscopy, they led to the conclusion that a fraction of the amorphous phase was restricted in its segmental mobility due to the incorporation of polymer chains into the crystals. Indeed, they proposed to split the amorphous phase into two different subdomains with specific properties according to an approach that resembles the MAF and RAF concepts described above. After exploitation of their PVT experiments, they evaluated the volumetric glass transition temperature of PTFE lower than -85 °C. However, these authors did not mention any volume transition in the vicinity of 130 °C. This first result seems consistent with our own assignment of the γ relaxation as being the rheological evidence of
PTFE’s glass transition. Another information raised from Dlubek’s work points out that the constrained amorphous phase which is formed during the polymer crystallization from the melt is characterized in the first times by a smaller specific free volume compared to the MAF. But, the restricted segmental mobility in the RAF limits the contraction of the corresponding domains and finally the RAF presents a larger free volume than that specific of the MAF. To our opinion, this finding should be analyzed considering Starkweather’s work [14] that reports the effects of PTFE exposure versus different fluids (hexafluoropropylene dimer, perfluorodimethylcyclohexane, chloroform…). In this latter research, the α peak assessed by DMA was the only one affected by the chemical treatment. Its shift to lower temperature region was interpreted as significant of the polymer plasticizing due to the fluid diffusion in the polymer matrix. Consequently, Starkweather proposed to interpret the α relaxation as a characteristic of the polymer’s glass transition. But, the same evolution can also be considered as a pure consequence of the higher free volume of the RAF compared to the MAF. Indeed, the liquid is likely to diffuse in an easier way in the constrained amorphous phase plasticizing the corresponding macromolecular segments.

Other key elements seem to support our interpretation of both γ and α rheological relaxations. The tensile behavior of PTFE can be regarded as an additional response. Figure 7 illustrates that PTFE presents a ductile character at room temperature with a breaking strain that exceeds 400%. This feature that is responsible of the inadequate use of PTFE in structural functions seems to be consistent with the assignment and centering of the polymer’s glass transition at Tγ. Indeed, under this hypothesis, the classical amorphous macromolecular segments are likely to present a mobility high enough to induce the polymer's ductility at ambient temperature.
Figure 7. Tensile behavior of PTFE measured at 25 °C with the displacement velocity of 5 mm/min.

Another interesting point to take into account is the polymer T\textsubscript{g} value evaluated using the semi-empirical method proposed by Van Krevelen [54]. According to this approach, the chemical structure of the polymer can be split into elementary chemical groups characterized by specific contribution Y\textsubscript{i} and molar mass M\textsubscript{i}. Then, the polymer’s T\textsubscript{g} is calculated from the ratio of the summation of the elementary Y\textsubscript{i} by the sum of the individual weight M\textsubscript{i} according Eq. 3:

$$T_g = \frac{\sum Y_i}{\sum M_i}$$

(Eq. 3)

The value of Y\textsubscript{CF2} obtained from different fluorine-derivated polymers was evaluated to 10500 K g/mol whereas M\textsubscript{CF2} worths 50 g/mol. The final calculation led to PTFE’s T\textsubscript{g} close to 210 K i.e. -63 °C. Although this value does not correspond exactly to that assessed for the T\textsubscript{γ}, it seems to support the idea for which the PTFE’s glass transition is located at very low temperature. Actually, it is important to keep in mind that the T\textsubscript{g} is a practical parameter.
to define the temperature domain where the glass transition is centered. Indeed, this latter domain can be 50 K wide due to the continuous contribution of the different macromolecular segments [55-56].

CONCLUSION

This paper aims at bringing a new insight in the definition and location of PTFE’s glass transition temperature. To answer to this scientific question, we have chosen to use dynamic mechanical measurements to study and interpret the nature of the different molecular mechanisms at the origin of the different thermomechanical relaxations. As the β peak is universally accepted as being representative of crystalline transitions in the polymer, most of our work has been devoted to the investigation of γ and α relaxations that have been found controversial in the literature. Our first results underlined that both rheological processes were accompanied by an important decrease of the polymer rigidity. Actually, they were identified as characteristic of segmental molecular motions of large amplitude. No confusion was possible with secondary relaxations based on localized molecular motions. Some researchers already proposed to relate both γ and α relaxations to the amorphous phase of PTFE considering that their respective amplitudes were reduced by an increase of the polymer crystallinity favored by low cooling rates from the molten state. However, in our study, the annealing of the polymer at $T = 105 \, ^\circ C$ made it possible a better discrimination of these relaxations. Indeed, this heat treatment was assessed as responsible of the occurrence of a cold crystallization in the polymer matrix. Moreover, this latter phenomenon induced the shift of the α peak to higher temperatures whereas the γ relaxation remained unaffected. This differentiation led us to consider that the amorphous phase of PTFE should be divided into two sub-categories. The first one was defined as specific of the rigid amorphous fraction (RAF) located at the vicinity of the crystallites. The second one, named MAF, was described
as being composed of the remaining amorphous segments characterized by a higher molecular mobility. Consequently, the $\alpha$ relaxation was assigned to the rigid amorphous phase while the $\gamma$ process observed at lower temperatures (-110 °C) was attributed to the mobile amorphous fraction. Different information were precised to support our interpretation. First, the displacement of the $\alpha$ peak observed after annealing was explained as being representative of the further reduction of the macromolecular mobility at the immediate vicinity of the crystallites due to the cold crystallization. Second, the high mechanical ductility of PTFE at ambient temperature seemed another consistent key element to locate the polymer’s glass transition temperature in the region where the $\gamma$ process was observed. Third, the concept of dividing PTFE according to three phases was also found in the literature that reports the characterization of this polymer by PVT measurements. Finally, the same approach was judged helpful to explain already published results about the effects produced by PTFE exposure versus fluorinated fluids on its thermomechanical behavior.

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CAPTIONS

Figure 1. Thermomechanical analysis of PTFE with G': ● and G": △ (ω = 1 rad/s).

Figure 2. Evolution of the tan δ of PTFE as a function of the temperature.

Figure 3. Influence of the shearing angular frequency ω on the position of γ and α peaks measured on tan δ = f(T) and represented by (a) and (b) series, respectively.

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Table 1: Different approaches used to assess the $T_g$ of PTFE with the attached corresponding values.

<table>
<thead>
<tr>
<th>Technique</th>
<th>$T_g$ value (°C)</th>
<th>Author</th>
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<tbody>
<tr>
<td>Dynamic mechanical analysis (DMA)</td>
<td>-110</td>
<td>McCrum [8]</td>
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<tr>
<td></td>
<td>+130</td>
<td>Starkweather [14]</td>
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<td>Wortmann [16]</td>
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<td>Steady or transient rheometry</td>
<td>+110</td>
<td>Tobolsky [11]</td>
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<td>Araki [13]</td>
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<tr>
<td>Mechanical measurements</td>
<td>-110</td>
<td>Woodward and Sauer [21]</td>
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<td>Rae and Dattelbaum [24]</td>
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<td>Dilatometry (CTE)</td>
<td>+123</td>
<td>Araki [12]</td>
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<td>Durrell [17]</td>
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<td>Marchionni [19,20]</td>
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<td>Kvacheva and Perepechko [22]</td>
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<tr>
<td>Permeability measurement</td>
<td>&lt; 20</td>
<td>Fossati [25]</td>
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