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

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1 **ABSTRACT**

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

22
23 **KEY WORDS.** Annealing, dynamic mechanical measurements, glass transition temperature,
24 mobile amorphous fraction, PTFE, relaxation, rigid amorphous fraction.

1 INTRODUCTION

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

15 Since its discovery by Plunkett in 1938, PTFE has been the topic of a comprehensive
16 literature supported by the necessity to determine the origin and the limits of its peculiar
17 behavior. If the semi-crystalline character of the polymer is universally accepted, the exact
18 value of the glass transition temperature (T_g) is still today subject to controversies. Indeed, the
19 reported values of PTFE's T_g range from -110 °C to 130 °C with intermediate values such as -
20 70 or -50 °C [5,6]. The difficulty to assess this critical temperature by calorimetry could be
21 considered as a first element responsible of this open debate [7]. At the same time, other
22 techniques currently used with polymers led to results that can be difficult to interpret. An
23 illustration of this complexity was encountered with viscoelastic measurements usually
24 convenient to evaluate the T_g of a polymer. In 1959, McCrum [8] registered the rheological
25 behavior of PTFE *versus* the temperature. The thermomechanical profile showed the presence

1 of four main relaxations that ranged between -200 °C and 380 °C. Characterizing the
2 rheological response of samples with distinct crystallinity degrees, this author showed that
3 two transitions were related to the crystalline fraction of the polymer. The first one located at
4 ca. 330 °C (T_m), was easily assigned to the polymer's melting point and that appeared
5 consistent with the sharp drop of the mechanical rigidity. The other one, observed in the 20-
6 30 °C range, was related to the reorganization of PTFE's crystalline structure. The two last
7 rheological transitions observed in the PTFE thermomechanical profile were qualified as
8 second order transitions. As their respective intensities were found to increase when the
9 crystallinity decreased, these transitions were assigned to the response of amorphous domains
10 [9]. But, the comparable amplitudes of their corresponding relaxation peaks did not allow the
11 authors to precise the exact nature of the mechanisms involved in these transitions. Prudently,
12 the relaxation observed at -110 °C (T_γ) was attributed to small sections of the macromolecule
13 whereas that registered at 130 °C (T_α) was assigned to large molecular segments. Later, Eby
14 and Sinnott [10] named these relaxations as Glass I and Glass II transitions, respectively, but
15 the authors did not explain the presence of two glass transitions in PTFE.

16 In 1963, Tobolsky *et al.* [11] suggested to consider the α transition centered at 110 °C
17 as the PTFE glass transition. The authors came to this conclusion after conducting the stress
18 relaxation experiments at temperatures higher than the polymer's melting point. Indeed, the
19 best description of the results was achieved from the Williams-Landel-Ferry equation in
20 which the T_g of the polymer was close to 110 °C. Indeed, the description of the experimental
21 data with this semi-empirical relation was judged satisfactory considering the value of PTFE
22 close to 110 °C. Using an experimental approach based on the measurement of the linear
23 thermal expansion coefficient at different temperatures, Araki [12] also proposed to set
24 PTFE's T_g at 123 °C (396 K) due to the discontinuity in the evolution of this parameter at this
25 temperature that resembled that currently observed during the glass transition of a polymer.

1 This author also reported the same conclusions after conducting stress relaxation tests [13].
2 Unfortunately, in both studies, the experiments were only carried out at temperatures above
3 room temperature. In other words, the domain where the γ process occurred itself was not
4 explored. After achieving the conduction of plasticization experiments on PTFE,
5 Starkweather [14] also suggested the assignment of α relaxation as a glass transition. In
6 particular, he observed that such a relaxation was able to shift with the volume fraction of
7 diluent while the position of γ relaxation was almost constant. Extending his researches to the
8 characterization of different semicrystalline fluoropolymers by thermally stimulated currents,
9 this author attributed the γ process of PTFE to localized and cooperative motions of a few CF_2
10 units. Consequently, the occurrence of this relaxation in the ac dielectric response of various
11 poly(TFE-*co*-HFP) random copolymers was consequently judged logical [15]. While
12 analyzing the relaxation behavior of PTFE in the temperature domain including the α process,
13 Wortmann [16] also considered this latter process as relevant of a glassy/amorphous
14 transition.

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

$$18 \quad 1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (\text{Eq. 1})$$

19 where w_1 and w_2 stand for the weight fraction of each monomer incorporated, while T_{g1} and
20 T_{g2} are assigned to the glass transitions of the corresponding homopolymers. A good
21 agreement between the experimental and calculated values was obtained considering that the
22 T_g of PTFE was close to -50 °C, *i.e.* an intermediate position between T_γ and T_α . Later, Boyer
23 [18] reported similar results. In different studies devoted to the rheological characterization of

1 perfluoropolyethers, Marchionni *et al.* [19,20] also suggested to consider PTFE's glass
2 transition temperature close to -75 °C.

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

16 Table 1 summarizes the different techniques used to assess the glass transition
17 temperature of PTFE. The uncertainty about the exact value of the PTFE's T_g may appear
18 surprising considering that this material received much attention by the scientific community
19 [26]. But, most studies were devoted to the description of its exceptional properties in
20 different fields related to physics and chemistry as mentioned above. Basic information such
21 as the exact nature of the molecular mechanisms at the origin of both γ and α relaxations were
22 regarded with less attention in spite of their usefulness. Thus, it was of interest to revisit
23 "basic" concept such as the glass transition of this polymer by using a novel approach
24 involving dynamic mechanical and aging tests. First, to go further in the description of the
25 rheological behavior of PTFE, the thermomechanical response of this material was registered

1 on a large temperature zone and for different values of the shearing frequency. Then, the
2 effects produced by a thermal treatment (annealing) on the polymer dynamic mechanical
3 properties were investigated. Finally, a real discussion was suggested by comparison of our
4 results with the data already published in separate articles to propose reliable structure-
5 properties relationships.

6 7 **Experimental**

8 **Material**

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

15 **Rheological characterization**

16 The different viscoelastic experiments were performed using a stress-controlled
17 dynamic rheometer (AR2000Ex model from TA). This apparatus was equipped with an
18 environmental testing chamber to allow the registering of the complex shear modulus $G^* =$
19 $G' + j G''$ under precise control of the temperature. The component G' , usually called “storage
20 modulus”, represents the mechanical rigidity of the sample (i.e. its elastic contribution). The
21 loss modulus G'' relates to the dissipated mechanical energy due to molecular motions in the
22 material. The behavior of the PTFE versus temperature was investigated from -150 °C up to
23 the molten state using rectangular torsion geometry. The different thermomechanical tests
24 were carried out at a heating rate of 3 °C min⁻¹ and at a fixed oscillating angular frequency ω
25 but ranging from 1 to 100 rad s⁻¹ to examine the influence of ω on the temperature position of

1 the different relaxation peaks. The reproducibility of the rheological results was checked by
2 repeating twice the analyses.

4 **Mechanical characterization**

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

8 **Physical treatment**

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

14 **Results and Discussion**

15 **Thermomechanical analyses of initial PTFE**

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

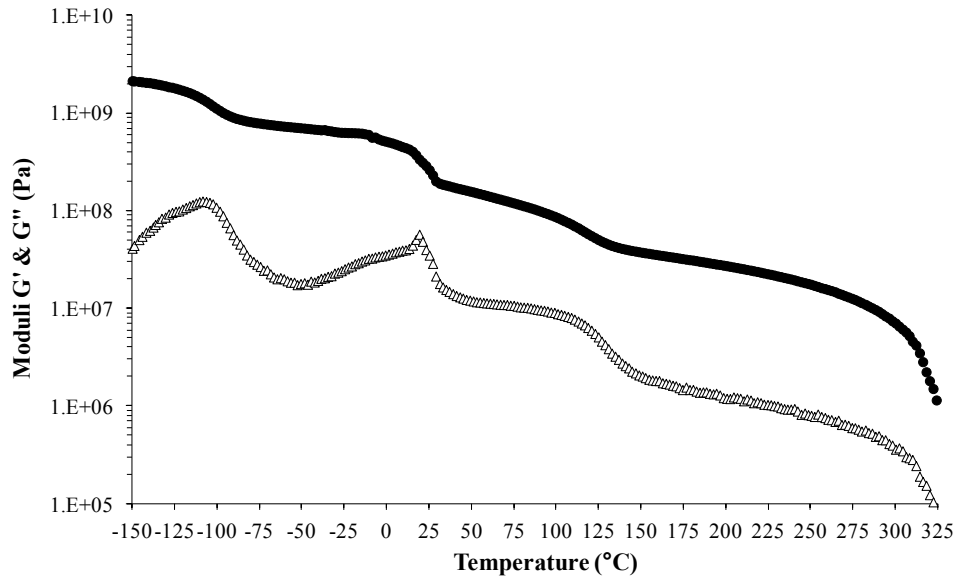
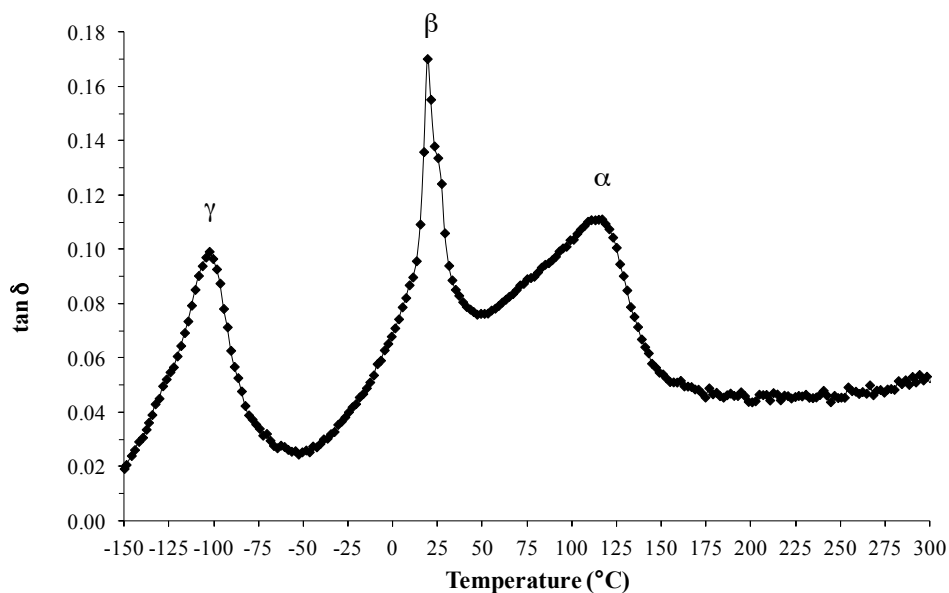


Figure 1. Thermomechanical analysis of PTFE with G': ● and G'': △ ($\omega = 1 \text{ rad/s}$)

Two transitions are well known and their interpretation does not suffer from any form of controversy. That observed from $-50 \text{ }^\circ\text{C}$ up to $32 \text{ }^\circ\text{C}$ 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 $19 \text{ }^\circ\text{C}$ and $30 \text{ }^\circ\text{C}$ [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 CF_2 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

1 temperature of 19 °C since the increase of the G'' curve from -50 °C reveals a progressive
2 growing in the local molecular mobility. The sudden drop between 20 °C and 30 °C of the
3 storage modulus curve agrees with the reported crystalline transition from triclinic to
4 hexagonal phase. Another universally accepted transition is reported above 320 °C where the
5 values of both moduli suddenly decrease. This phenomenon is characteristic of the polymer
6 melting as shown by the presence of an endothermic peak in PTFE calorimetric analysis [28].

7 Both γ and α relaxation peaks mentioned in the introduction can also be observed on
8 the G'' curve [14]. They appear in a clearer form by plotting the evolution of the loss factor δ
9 (defined by $\tan \delta = G''/G'$) versus the temperature (Figure 2) [8]. Named also “internal
10 friction”, this loss factor is really influenced by the nature and amplitude of molecular
11 motions [27]. The maxima of each relaxation peak are respectively taken down at $T_\gamma = -103$
12 °C and $T_\alpha = 116$ °C.



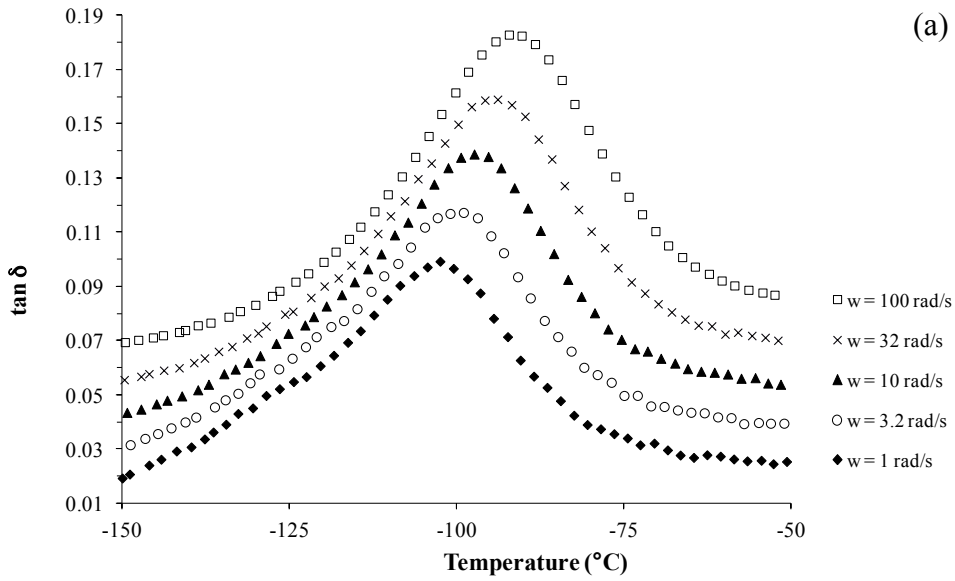
13
14 **Figure 2.** Evolution of the $\tan \delta$ of PTFE as a function of temperature

15
16 It is interesting to note that both relaxations also induce a significant decrease of the
17 storage modulus G' (Figure 1). This result is of first importance because it reveals that none

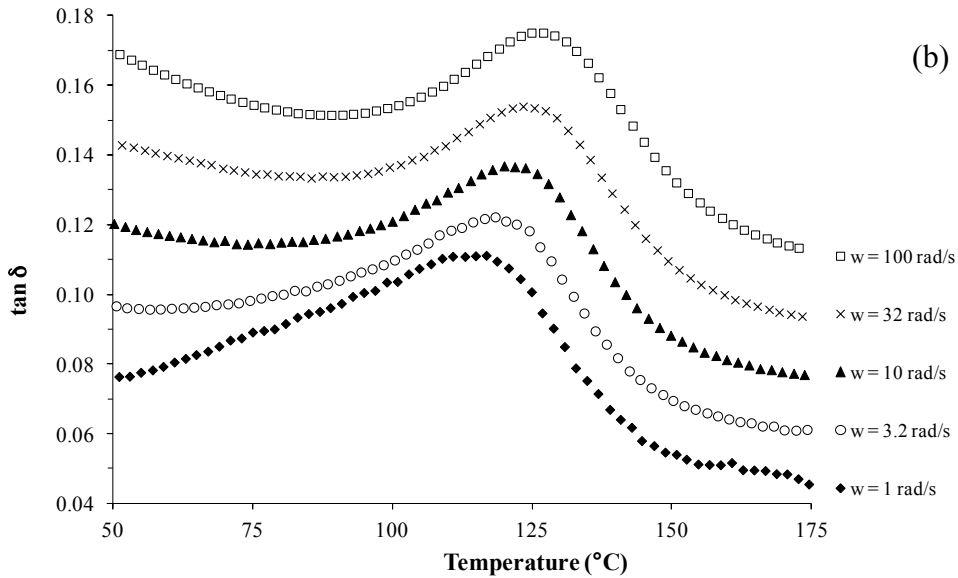
1 of these relaxations can be confused with “simple” rheological secondary relaxations. Indeed,
2 associated to local segmental motions in the polymer chain, secondary relaxations induce
3 mechanical losses that appear as rheological peaks on the curve characteristic of the
4 dissipative energy *i.e.* the loss modulus G'' . Due to its reduced amplitude, this phenomenon
5 has a poor effect on the G' modulus in contrast to the rheological evidence of the glass
6 transition temperature [29-34]. Indeed, in this latter process, the molecular dynamics is
7 usually characterized by cooperative motions of higher molecular segments which affect the
8 polymer mechanical rigidity [35,36]. Then, at this stage of that present discussion, PTFE
9 really seems to exhibit two glass transition domains as suggested by Eby and Sinnott [10]. But,
10 the existence of both transitions remains unexplained.

11 Then, to investigate further the characteristics of γ and α processes, another series of
12 thermomechanical analyses were performed on new PTFE samples in the solid state to
13 analyze more deeply the influence of the value of the shearing angular frequency on the
14 position of each relaxation. As shown in Figures 3a and 3b, both γ and α mechanical peaks
15 occur at higher temperatures when ω is increased.

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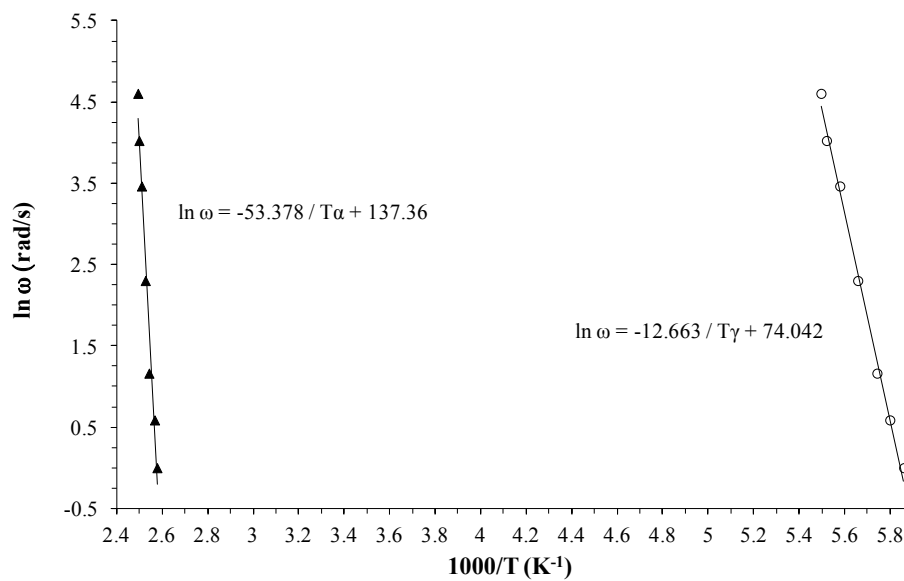
3 **Figure 3.** Influence of the shearing angular frequency ω on the position of γ and α peaks
 4 measured on $\tan \delta = f(T)$ and represented by (a) and (b) series, respectively.

5

6 The evolution of the temperatures taken at the maximum of each relaxation peak can
 7 be described using the model proposed initially by Glasstone, Laidler and Eyring [57] to
 8 detail the effect of the temperature on the diffusion phenomena:

1
$$\omega = A \exp(E_a / RT) \quad (\text{Eq. 2})$$

2 where R stands for the gas constant (8.32 J/mol/K), T (K) the absolute temperature at which
 3 the maximum of G'' is observed for the corresponding angular frequency ω (rad/s), E_a the
 4 activation energy (kJ/mol) and A the preexponential factor (rad/s). In other words, two
 5 apparent activation energies can be calculated from the plot of $\log \omega$ versus the inverse of the
 6 temperature taken at the maximum of each corresponding peak (Figure 4).



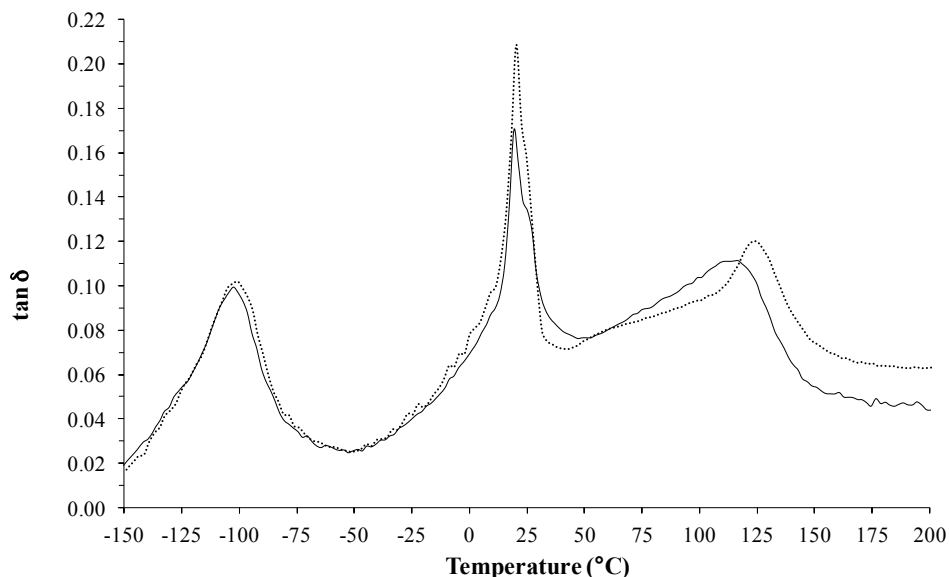
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 8 **Figure 4.** Evidence for the Arrhenius dependence of T_γ and T_α temperatures as a function of
 9 the shear angular frequency ω .

10
 11 This result is currently observed for secondary transitions and this may be contradictory with
 12 previous remarks. Indeed, one of γ or α relaxations is suspected to be associated with the
 13 glass transition of the polymer. Then, in this case, the corresponding temperature (T_γ or T_α)
 14 would more likely obey the William–Landel–Ferry (WLF) equation [37]. Actually, due to the
 15 limited evolution of the angular frequency value, it was not possible to discriminate which

1 kind of law the most appropriate. The exploitation of the results according Arrhenius
2 dependence gives the respective activation energy: $E_\gamma = 105$ kJ/mol and $E_\alpha = 444$ kJ/mol.
3 These latter values are in the same order of magnitude as that proposed for the
4 characterization of PTFE from dielectric spectroscopy [15,38]. Besides this theoretical
5 treatment, it is interesting to note that the change in frequency did not induce any shoulder
6 formation or peak dissociation. This means that γ and α processes are governed by specific
7 major molecular mechanisms.

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

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



14
15 **Figure 5.** Non-isothermal $\tan \delta$ curves of the initial PTFE (solid line) and after annealing at
16 105 °C for 3 days (dotted line).

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While the annealing step produced little effects on the γ relaxation, it induced more significant changes on both position and shape of the other rheological peaks. First, the β 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 α relaxation peak is shifted to higher temperature after annealing: T_{α} 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 β . 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_{α} .

The understanding of the evolution of both γ and α 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_{α} . 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 α process is only characteristic of the mechanical relaxation of these constrained amorphous areas and the

1 higher T_{α} rise is the direct consequence of the inner stresses increase due to the development
2 of crystalline zones.

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

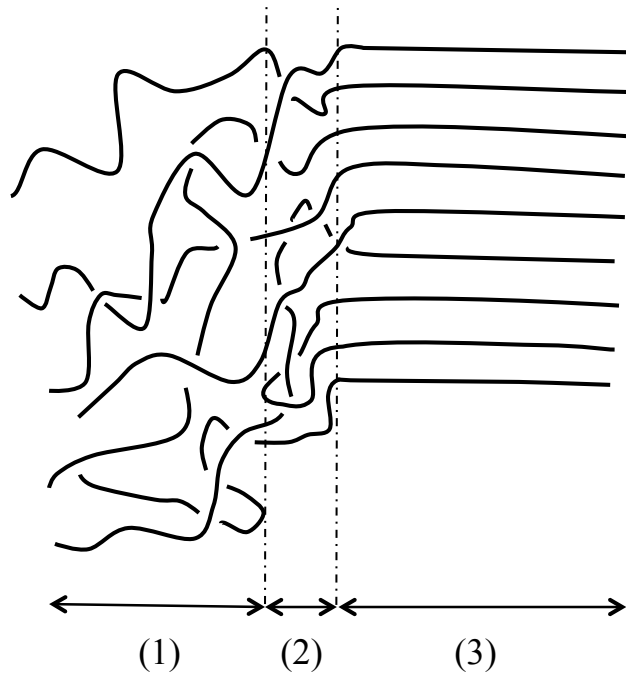


Figure 6. Schematic illustration of PTFE structure.

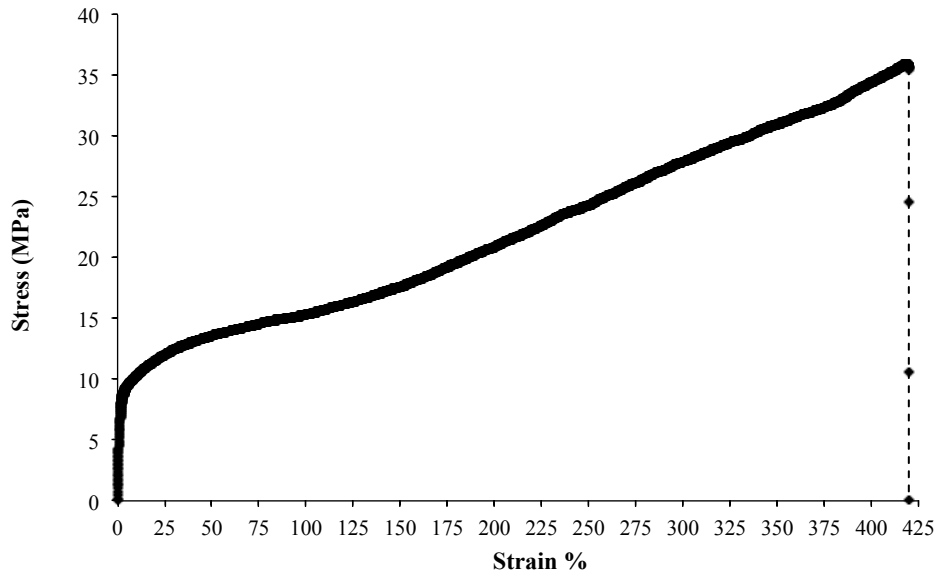
(1): mobile amorphous phase; (2): rigid amorphous phase; (3): crystalline phase

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 $-85\text{ }^{\circ}\text{C}$. However, these authors did not mention any volume transition in the vicinity of $130\text{ }^{\circ}\text{C}$. This first result seems consistent with our own assignment of the γ relaxation as being the rheological evidence of

1 PTFE's glass transition. Another information raised from Dlubek's work points out that the
2 constrained amorphous phase which is formed during the polymer crystallization from the
3 melt is characterized in the first times by a smaller specific free volume compared to the
4 MAF. But, the restricted segmental mobility in the RAF limits the contraction of the
5 corresponding domains and finally the RAF presents a larger free volume than that specific of
6 the MAF. To our opinion, this finding should be analyzed considering Starkweather's work
7 [14] that reports the effects of PTFE exposure *versus* different fluids (hexafluoropropylene
8 dimer, perfluorodimethylcyclohexane, chloroform...). In this latter research, the α peak
9 assessed by DMA was the only one affected by the chemical treatment. Its shift to lower
10 temperature region was interpreted as significant of the polymer plasticizing due to the fluid
11 diffusion in the polymer matrix. Consequently, Starkweather proposed to interpret the α
12 relaxation as a characteristic of the polymer's glass transition. But, the same evolution can
13 also be considered as a pure consequence of the higher free volume of the RAF compared to
14 the MAF. Indeed, the liquid is likely to diffuse in an easier way in the constrained amorphous
15 phase plasticizing the corresponding macromolecular segments.

16 Other key elements seem to support our interpretation of both γ and α rheological
17 relaxations. The tensile behavior of PTFE can be regarded as an additional response. Figure 7
18 illustrates that PTFE presents a ductile character at room temperature with a breaking strain
19 that exceeds 400%. This feature that is responsible of the inadequate use of PTFE in structural
20 functions seems to be consistent with the assignment and centering of the polymer's glass
21 transition at T_γ . Indeed, under this hypothesis, the classical amorphous macromolecular
22 segments are likely to present a mobility high enough to induce the polymer's ductility at
23 ambient temperature.

24



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Figure 7. Tensile behavior of PTFE measured at 25 °C with the displacement velocity of 5 mm/min.

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Another interesting point to take into account is the polymer T_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_i and molar mass M_i . Then, the polymer's T_g is calculated from the ratio of the summation of the elementary Y_i by the sum of the individual weight M_i according Eq. 3:

9

$$T_g = \frac{\sum_i Y_i}{\sum_i M_i} \quad (\text{Eq. 3})$$

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11

The value of Y_{CF_2} obtained from different fluorine-derivated polymers was evaluated to 10500 K g/mol whereas M_{CF_2} worths 50 g/mol. The final calculation led to PTFE's T_g close to 210 K i.e. -63 °C. Although this value does not correspond exactly to that assessed for the T_g , 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_g is a practical parameter

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1 to define the temperature domain where the glass transition is centered. Indeed, this latter
2 domain can be 50 K wide due to the continuous contribution of the different macromolecular
3 segments [55-56].

4 5 CONCLUSION

6 This paper aims at bringing a new insight in the definition and location of PTFE's glass
7 transition temperature. To answer to this scientific question, we have chosen to use dynamic
8 mechanical measurements to study and interpret the nature of the different molecular
9 mechanisms at the origin of the different thermomechanical relaxations. As the β peak is
10 universally accepted as being representative of crystalline transitions in the polymer, most of
11 our work has been devoted to the investigation of γ and α relaxations that have been found
12 controversial in the literature. Our first results underlined that both rheological processes were
13 accompanied by an important decrease of the polymer rigidity. Actually, they were identified
14 as characteristic of segmental molecular motions of large amplitude. No confusion was
15 possible with secondary relaxations based on localized molecular motions. Some researchers
16 already proposed to relate both γ and α relaxations to the amorphous phase of PTFE
17 considering that their respective amplitudes were reduced by an increase of the polymer
18 crystallinity favored by low cooling rates from the molten state. However, in our study, the
19 annealing of the polymer at $T = 105$ °C made it possible a better discrimination of these
20 relaxations. Indeed, this heat treatment was assessed as responsible of the occurrence of a cold
21 crystallization in the polymer matrix. Moreover, this latter phenomenon induced the shift of
22 the α peak to higher temperatures whereas the γ relaxation remained unaffected. This
23 differentiation led us to consider that the amorphous phase of PTFE should be divided into
24 two sub-categories. The first one was defined as specific of the rigid amorphous fraction
25 (RAF) located at the vicinity of the crystallites. The second one, named MAF, was described

1 as being composed of the remaining amorphous segments characterized by a higher molecular
2 mobility. Consequently, the α relaxation was assigned to the rigid amorphous phase while the
3 γ process observed at lower temperatures (-110 °C) was attributed to the mobile amorphous
4 fraction. Different information were precised to support our interpretation. First, the
5 displacement of the α peak observed after annealing was explained as being representative of
6 the further reduction of the macromolecular mobility at the immediate vicinity of the
7 crystallites due to the cold crystallization. Second, the high mechanical ductility of PTFE at
8 ambient temperature seemed another consistent key element to locate the polymer's glass
9 transition temperature in the region where the γ process was observed. Third, the concept of
10 dividing PTFE according to three phases was also found in the literature that reports the
11 characterization of this polymer by PVT measurements. Finally, the same approach was
12 judged helpful to explain already published results about the effects produced by PTFE
13 exposure *versus* fluorinated fluids on its thermomechanical behavior.

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- 10

1 **CAPTIONS**

2
3 **Figure 1.** Thermomechanical analysis of PTFE with G' : ● and G'' : △ ($\omega = 1$ rad/s).

4 **Figure 2.** Evolution of the $\tan \delta$ of PTFE as a function of the temperature.

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

7 **Figure 4.** Evidence for the Arrhenius dependence of T_γ and T_α temperatures *versus* the shear
8 angular frequency ω .

9 **Figure 5.** Non-isothermal $\tan \delta$ curves of the initial PTFE (solid line) and after annealing at
10 105 °C for 3 days (dotted line).

11 **Figure 6.** Schematic illustration of PTFE structure.

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

13 **Figure 7.** Tensile behavior of PTFE measured at 25 °C with the displacement velocity of 5
14 mm/min.

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

Technique	T_{rg} value (°C)	Author
Dynamic mechanical analysis (DMA)	-110	McCrum [8]
	+130	Starkweather [14] Wortmann [16]
Steady or transient rheometry	+110	Tobolsky [11]
		Araki [13]
Mechanical measurements	-110	Woodward and Sauer [21]
		Rae and Dattelbaum [24]
Dilatometry (CTE)	+ 123	Araki [12]
Thermally stimulated currents (TSC)	+130	Sauer [15]
Calorimetry and Thermodynamics	-50	Durrell [17]
	-110	Lau [23]
Calculation	-50	Boyer [18]
	-75	Marchionni [19,20]
Acoustic	-110	Kvacheva and Perepechko [22]
Permeability measurement	< 20	Fossati [25]

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