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Where is the glass transition temperature of poly(tetrafluoroethylene)? A new approach by dynamic rheometry and mechanical tests

Gérard Calleja [a], Alex Jourdan [b], Bruno Ameduri [a], Jean-Pierre Habas [a,]*

[a] *Institut Charles Gerhardt, Equipe «Ingénierie et Architectures Macromoléculaires», UMR CNRS 5253, CC 1702, Université de Montpellier 2, ENSCM, Place Eugene Bataillon, 34095 Montpellier, France*
[b] *AREVA – CH/DRD, BP 44-26701 Pierrelatte Cedex, France*

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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 ($T = -103$ °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 ($T = 116$ °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.

1. 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

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* Corresponding author. Tel.: +33 4 67 14 37 80; fax: +33 4 67 14 40 28.
E-mail addresses: gerard.calleja@gmail.com (G. Calleja), alex.jourdan@areva.com (A. Jourdan), bruno.ameduri@enscm.fr (B. Ameduri), jean-pierre.habas@univ-montp2.fr (J.-P. Habas).

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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 Sinnot [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 α 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 γ process occurred itself was not explored. After achieving the conduction of plasticization experiments on PTFE, Starkweather [14] also suggested the assignment of α 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 γ relaxation was almost constant. Extending his researches to the characterization of different semicrystalline fluoropolymers by thermally stimulated currents, this author attributed the γ process of PTFE to localized and cooperative motions of a few 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 α 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 versus their chemical composition using the Fox equation:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \tag{1}$$

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 °C, 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.