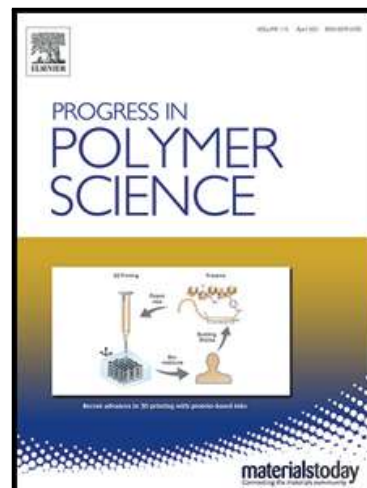


Why Does PTFE Still Matter? Revisiting Its  
Structure–Property–Performance–Applications Relationships Beyond  
the PFAS Debate

Saly Hawila , Jean-Pierre Habas , Bruno Ameduri

PII: S0079-6700(26)00096-1  
DOI: <https://doi.org/10.1016/j.progpolymsci.2026.102166>  
Reference: JPPS 102166



To appear in: *Progress in Polymer Science*

Received date: 2 November 2025  
Revised date: 30 July 2026  
Accepted date: 7 August 2026

Please cite this article as: Saly Hawila , Jean-Pierre Habas , Bruno Ameduri , Why Does PTFE Still Matter? Revisiting Its Structure–Property–Performance–Applications Relationships Beyond the PFAS Debate, *Progress in Polymer Science* (2026), doi: <https://doi.org/10.1016/j.progpolymsci.2026.102166>

This is a PDF of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability. This version will undergo additional copyediting, typesetting and review before it is published in its final form. As such, this version is no longer the Accepted Manuscript, but it is not yet the definitive Version of Record; we are providing this early version to give early visibility of the article. Please note that Elsevier's sharing policy for the Published Journal Article applies to this version, see: <https://www.elsevier.com/about/policies-and-standards/sharing#4-published-journal-article>. Please also note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2026 The Author(s). Published by Elsevier Ltd.  
This is an open access article under the CC BY-NC-ND license  
(<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

# Why Does PTFE Still Matter? Revisiting Its Structure–Property–Performance–Applications Relationships Beyond the PFAS Debate

**Saly Hawila, Jean-Pierre Habas\*, Bruno Ameduri\***

ICGM, Université de Montpellier, CNRS, ENSCM, Montpellier, France

Corresponding authors: jean-pierre.habas@umontpellier.fr - bruno.ameduri@enscm.fr

## **Abstract**

This review aims to present polytetrafluoroethylene (PTFE), its recent syntheses and processes, properties, applications, and its position in the per- and polyfluoroalkyl substances (PFAS) context. It is the most widely produced fluoropolymer, with production volumes increasing every year. In this review, this specialty polymer is described as endowing exceptional characteristics (chemical, thermal, UV, and aging resistance, waterproofness, rheological, mechanical, tribological, surface properties, and moisture vapor permeability). These outstanding features are well explained by numerous studies linking them to their crystallinity and packing structure, which are closely associated with a constantly evolving chemical synthesis process (fluorinated surfactants are no longer used nowadays). Moreover, the high molar mass of PTFE (several million  $\text{g}\cdot\text{mol}^{-1}$ ) prevents its penetration through the human membrane, in addition to its insolubility in all solvents, non-toxicity, and non-bioaccumulation, showing its safe behavior (i.e., biocompatible) and Food and Drug Administration (FDA) approval. Furthermore, although considered a PFAS, this material meets the 13 Organization for Economic Co-operation and Development (OECD) polymer of low concern (PLC) criteria and, so far, is not subject to regulatory restrictions. Because of such features, PTFE can be used in many advanced applications satisfying stringent requirements (in terms of durability, safety, operational efficiency, and sustainability). Then, PTFE is a must-have material in the medical field and in transportation (aerospace, aircraft, railway, and automotive). It is also essential in electronics, the Internet of Things, clean energy storage and conversion, and other high-tech applications, making it an irreplaceable material in many areas of daily life.

**Keywords:** applications; chemistry; fluorinated polymers; physical properties; PTFE; structure-properties relationships.

## Table of contents

|                                                               |                              |
|---------------------------------------------------------------|------------------------------|
| 1. INTRODUCTION.....                                          | 5                            |
| 2. SYNTHESIS .....                                            | 6                            |
| 3. THERMAL PROPERTIES OF PTFE .....                           | 13                           |
| 4. RHEOLOGY AND PROCESSING OF PTFE: GOVERNING MECHANISMS..... | 24                           |
| 5. MECHANICAL PROPERTIES OF PTFE.....                         | 40                           |
| 6. TRIBOLOGICAL AND SURFACE BEHAVIOR OF PTFE .....            | 51                           |
| 7. SURFACE, WETTABILITY, AND ADHESION.....                    | 71                           |
| 8. ELECTRICAL AND DIELECTRIC PROPERTIES OF PTFE .....         | 76                           |
| 9. APPLICATIONS .....                                         | 91                           |
| 10. HEALTH CONTEXT: IS PTFE HAZARDOUS? .....                  | 100                          |
| 11. FATE OF PTFE AT END OF LIFE .....                         | 107                          |
| 12. LIMITS, CHALLENGES, PROSPECTS AND OUTLOOKS .....          | 120                          |
| CONCLUSIONS .....                                             | 121                          |
| REFERENCES .....                                              | ERROR! BOOKMARK NOT DEFINED. |

## Abbreviations

**AlN** aluminum nitride

**BNNB-G** glycine-functionalized boron nitride nanobarbs

**BfR** German Agency for Risk Assessment

**CAGR** Compound Annual Growth Rate

**CEPA** Canadian Environmental Protection Act

**CTFE** chlorotrifluoroethylene

**CTE** coefficient of thermal expansion

**CT** computed tomography

**CF** carbon fibers

**CNTs** carbon nanotubes

**CIR** Cosmetic Ingredient Review

**DTG** derivative thermogravimetric curve

**DLP** digital light processing

**E<sub>a</sub>** activation energies

**ePTFE** Expanded PTFE

**EWG** Environmental Working Group

**ETFE** poly(ethylene-*co*-tetrafluoroethylene) copolymer

**ECTFE** poly(ethylene-*co*-chlorotrifluoroethylene) copolymer

**ECHA** European Chemicals Agency

**FKM** poly(vinylidene fluoride-*co*-hexafluoropropylene) copolymer

**FDA** Food and Drug Administration

**GWP** global warming potential

**GF** glass fibers

**hBN** Hexagonal boron nitride

**HSP** Hansen Solubility Parameters

**ILSS** interlaminar shear strength

**MAF** mobile amorphous fraction

**mPTFE** modified polytetrafluoroethylene

**MRI** magnetic resonance imaging

**MPs** microplastics

**OECD** Organization for Economic Co-operation and Development

**ODP** ozone depletion potential

**PCTFE** Poly(chlorotrifluoroethylene)

**PFAS** per- or polyfluoroalkyl substance

**PFOA** perfluorooctanoic acid

**PFOS** perfluorooctanesulfonic acid

**PFSA** perfluorosulfonic acid

**PLC** polymer of low concern

**PE** polyethylene

**PEGDA** polyethylene glycol diacrylate

**PTFE** poly(tetrafluoroethylene)

**PEMFCs** Proton Exchange Membrane Fuel Cell



**PVDF** poly(vinylidene fluoride)

**PVF** poly(vinyl fluoride)

**PFIB** perfluoroisobutylene

**PFSA** perfluoroalkyl sulphonic acid

**REACH** Registration, Evaluation, Authorization and Restriction of Chemicals

**RAF** rigid amorphous fraction

**SR-PTFE** self-reinforced PTFE

**THz** terahertz

**TFE** tetrafluoroethylene

**T<sub>g</sub>** glass transition temperature

**TG-MS** thermogravimetric–mass spectrometric

**T<sub>m</sub>** melting temperature

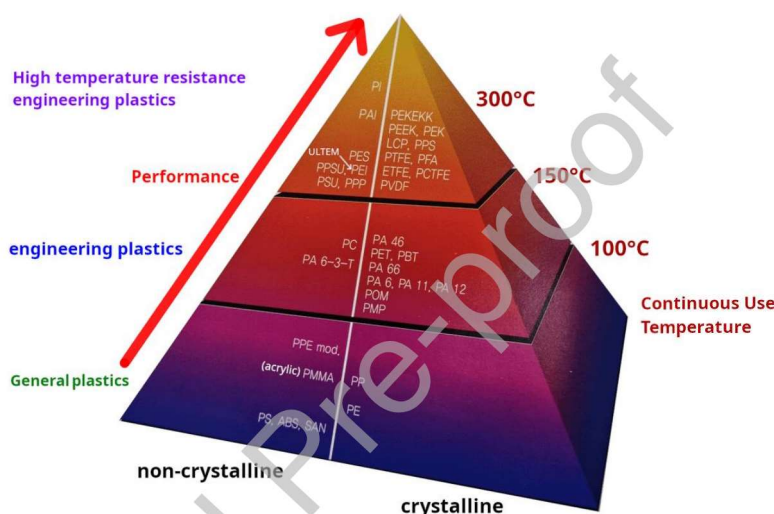
**VDF** vinylidene fluoride

**VCRP** Voluntary Cosmetic Registration Program

**μ** friction coefficient

## 1. Introduction

Fluoropolymers represent a class of specialty polymers (Fig. 1) known for their excellent properties, including remarkable chemical resistance, weather and aging stability, low surface energy, coefficient of friction, and dielectric constant. These exceptional properties arise from the strong and stable carbon-fluorine covalent bond, which is widely present in their chemical structures. Due to their unique chemical and physical properties, these technical polymers have found many applications in various fields such as electronics, construction, architecture, aerospace, automotive, and medical industries (Fig. 2) [1–5].

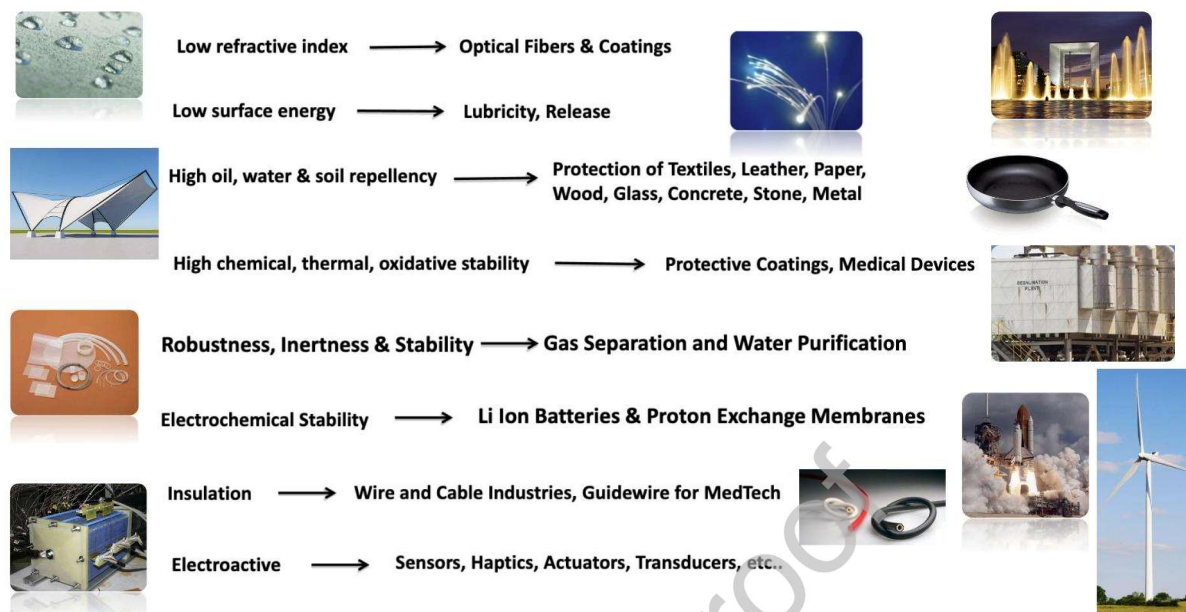


**Fig. 1 :** Pyramid of features, volume of production, and price of three kinds of polymers separating semi-crystalline and amorphous polymers).

Among fluoropolymers, polytetrafluoroethylene (PTFE) is one of the oldest produced after polychlorotrifluoroethylene (PCTFE) [6]. Discovered unexpectedly by Plunkett in 1938 [7–10] as a white powder insoluble in all solvents and thermostable, this specialty polymer has quickly been investigated and industrially implemented by the Dupont de Nemours Company. This was a real milestone in the development of fluoropolymers. Owing to its exceptional properties [11], it plays a significant role across a wide range of applications [12]. It is worth noting that PTFE was used during the Manhattan Project for handling uranium hexafluoride in the development of nuclear weapons.

Surprisingly, from the current terminology, PTFE is now classified as per- or polyfluoroalkyl substance (PFAS) and is expected to be restricted by the European Chemicals Agency (ECHA) [13] and Registration, Evaluation, Authorization and Restriction of Chemicals Regulation

(REACH), despite its high molar mass and the fact that it is insoluble, non-mobile, non-toxic, and non-bioaccumulative [14].



**Fig. 2 :** Application fields of fluoropolymers, including automotive and aerospace.

The objective of this study is to review recent articles and publications dealing with modern syntheses of PTFE, currently produced in aqueous medium without any surfactants, and to highlight recent characterizations of its molar masses as well as its thermal, dielectric, tribological, and mechanical properties, without neglecting its applications. Furthermore, since PTFE may be regarded as a PFAS, arguments will be presented demonstrating that, unlike low-molar-mass organic compounds, it displays a behavior consistent with materials considered to raise minimal environmental or health concerns dictated by regulation agencies. Indeed, PTFE satisfies the 13 criteria of the OECD as a “polymer of low concern”. Moreover, studies on recycling and degradation — including more recently by mechanochemistry in the presence of specific activators — will further illustrate this review. These recent developments have not been addressed or summarized in any previously published reviews or book chapters.

## 2. Synthesis

### 2.1. Synthetic routes and recent processes

As with many fluorochemicals, calcium fluoride ( $\text{CaF}_2$ ), commonly known as fluorite or flourspar, is a naturally occurring mineral found on Earth's surface, making fluorine the 13<sup>th</sup> most abundant element on Earth. Its reaction with sulfuric acid yields HF, which enables the fluorination of various compounds. The production of tetrafluoroethylene (TFE) starts with the

fluorination of chloroform, yielding  $\text{CHF}_2\text{Cl}$ , more commonly known as R-22 (Fig. 3). Such a derivative undergoes pyrolysis, producing difluorocarbene, which dimerizes to TFE via recombination (Fig. 3) [1,11,15,16]. The advantage of this process is the ability to obtain highly pure TFE. Other academic reactions leading to TFE have also been reported [17,18].

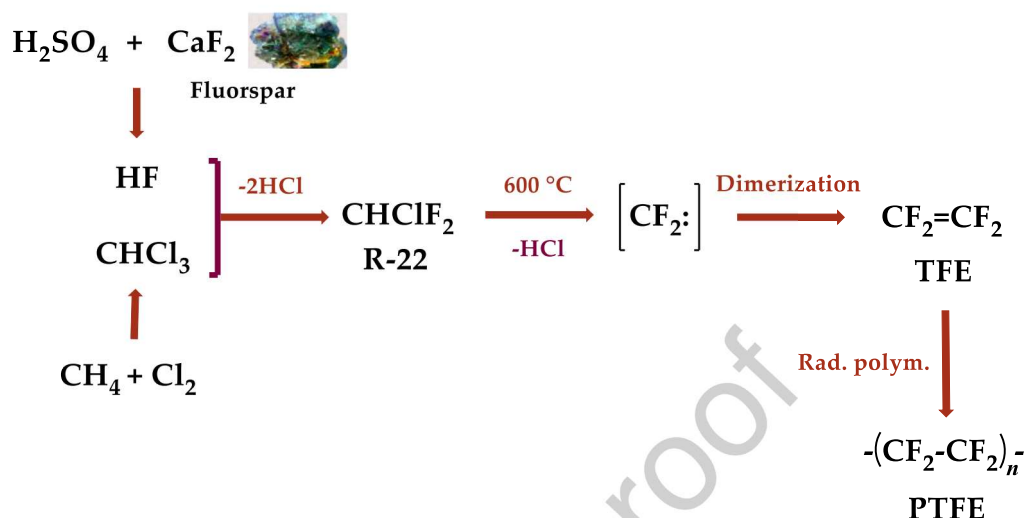


Fig. 3 : Synthetic route of tetrafluoroethylene (TFE) from  $\text{CaF}_2$  and PTFE.

TFE is a hazardous and explosive gas (b.p. =  $-75^\circ\text{C}$ ) [18], and can undergo a radical polymerization to give PTFE that usually occurs in three steps (Fig. 4). In the first one, free radicals are generated from the thermal degradation of the initiator (potassium persulfate in the case of Fig. 4). These radicals react onto TFE, forming a new free radical ( $^-\text{O}_3\text{SOCF}_2\text{CF}_2\cdot$ ). In the second step (propagation), macroradicals (polymer chains) grow by successive additions of TFE units from the active radical centers [16]. Lastly, termination of such macroradicals occurs exclusively *via* recombination [1]. Sometimes, transfer reactions may occur if the medium contains a chain-transfer agent or reactants with labile bonds.

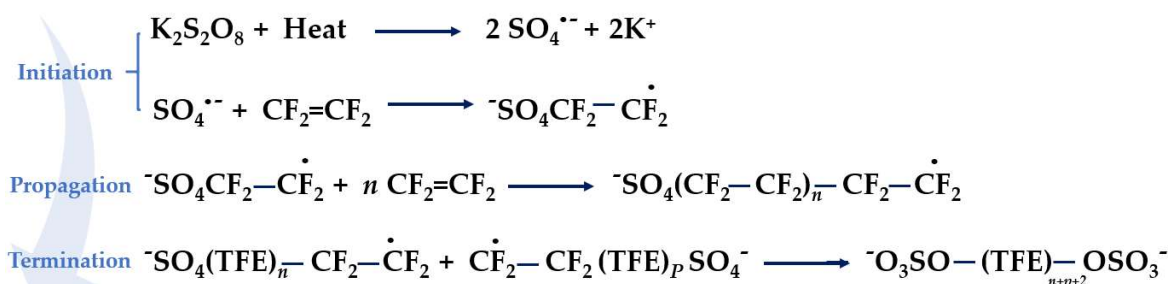


Fig. 4 : Mechanism of radical polymerization of tetrafluoroethylene (TFE).

Industrially, the polymerization happens in aqueous media (suspension, dispersion, or emulsion processes) [11]. In the final step, because TFE is highly hydrophobic, a surface-active reactant (or surfactant) is required to ensure the formation of micelles in which polymerization occurs [19]. After the discovery of Teflon® at DuPont (Fig. 3), the first generation of surfactants used was fluorinated [20], using perfluorooctanoic acid ( $C_7F_{15}CO_2H$ , PFOA) or perfluorooctane sulfonic acid ( $C_8F_{17}SO_3H$ , PFOS). Both of these compounds led to severe issues in the early 2000s (toxicity, bioaccumulation, persistence, and water solubility, thus spreading in creeks, rivers, and oceans) [21].

**Table 1 :** Non-exhaustive list of identified patents on PTFE produced in the presence of hydrocarbon surfactants

| Title of the patent                                                                                                                                                     | Company                    | Patent number                                       | Reference |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------|-----------------------------------------------------|-----------|
| Method for producing modified polytetrafluoroethylene, method for producing modified polytetrafluoroethylene powder, and method for producing stretched porous material | AGC                        | Higuchi et al.,<br>US 2020/0207880 A1               | [22]      |
| Aqueous polymerization of perfluoromonomer using hydrocarbon surfactant                                                                                                 | CHEMOURS                   | Brothers et al.,<br>US 2016/0122509 A1              | [23]      |
| Employing polyalkylene oxides for nucleation in aqueous polymerization of fluoromonomer                                                                                 | CHEMOURS                   | Brothers et Gangal al.,<br>EP 2019/<br>3 074 430 B1 | [24]      |
| Polytetrafluoroethylene production method                                                                                                                               | DAIKIN                     | Kato et al.,<br>US 2021/0340290 A1                  | [25]      |
| Process for preparing fluoropolymers and fluoroelastomers in presence of a non-fluorinated sulfonate type hydrocarbon containing surfactant thereof                     | GUJARAT<br>FLUOROCHEMICALS | Chauhan et al.,<br>US 2022/0372179 A1               | [26]      |
| PTFE-based formulation for the insulation of integrated circuits                                                                                                        | SYENSQO                    | Kapeliouchko et al.,<br>US 2006/ 6,982,308 B2       | [27]      |

So, many countries and companies no longer use them [28]. Under the EU Regulation on Persistent Organic Pollutants (REACH and ECHA), PFOS has been restricted since 2019, while PFOA has been banned since 2006 [21]. These surfactants were replaced by fluorinated ones with shorter fluorinated group ( $C_5F_{11}CO_2H$ ,  $C_4F_9SO_3H$  or  $C_3F_7CO_2H$ ) [29] or bearing ether group (e.g.,  $C_3F_7OCF(CF_3)CO_2NH_4$  Gen®X or  $CF_3OC_3F_6OCHF_2CO_2NH_4$  Adona®) [30]. However, reversed effects of both last ones were noted, showing even more toxicity [21,30–33]. After many years of efforts, the PTFE manufacturers used hydrocarbon surfactants for the production of PTFEs which are claimed to have the same properties as those produced with fluorinated surfactants [21–27,34].



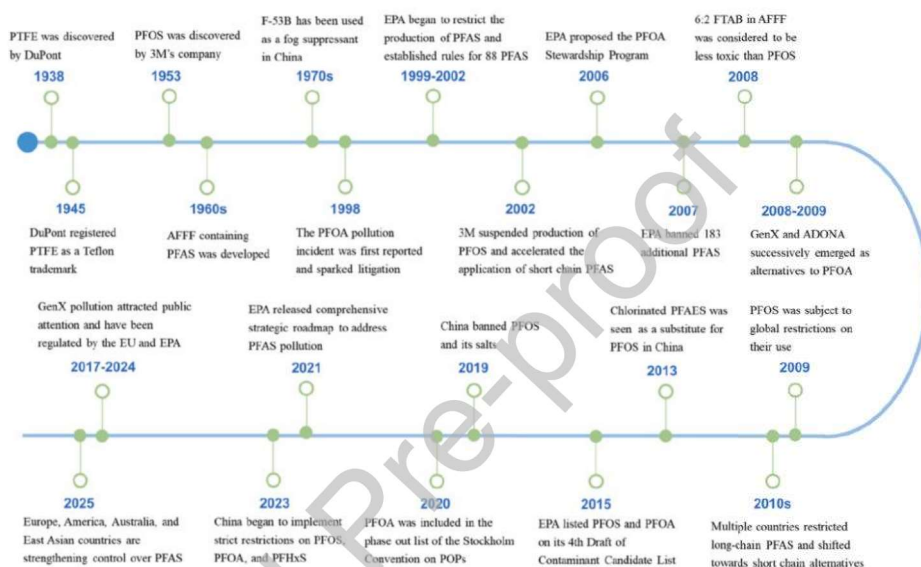
**Table 2 :** Main PTFE suppliers and their trademarks

| Trademarks                                                                    | Suppliers                                         |
|-------------------------------------------------------------------------------|---------------------------------------------------|
| Teflon®                                                                       | Chemours (formerly DuPont)                        |
| Hostaflon®                                                                    | Manufactured by Dyneon and later part of Celanese |
| Fluon®                                                                        | AGC Chemicals                                     |
| Polyflon®                                                                     | Daikin                                            |
| Dyneon™                                                                       | Dyneon                                            |
| Various series as DF®-201, DF®-16                                             | Dongyue Group                                     |
| Polymist® and Algoflon®                                                       | Syensqo (ex-Solvay Solexis)                       |
| Soreflon®                                                                     | Arkema                                            |
| Inoflon®                                                                      | Gujarat Fluorochemicals Limited (INOX Group(GFL)) |
| Heroflon®                                                                     | Heroflon USA (Daikin)                             |
| FluoroPlast™                                                                  | Halopolymer                                       |
| Various series as CGF®218, CGF®238, CGF®2021, CGF®219                         | Haohua Chemical Science                           |
| Flontech®                                                                     | Flontech USA LLC                                  |
| Various series as MF®-4DW, MF®-4DA, MF®-4DM                                   | Fujian Sannong                                    |
| Various series as LM®-PSR102, LM®-PSR104                                      | Lee and Man Chemical                              |
| PTFE ROD ML01                                                                 | Luxi Chemical                                     |
| Various series as SFN®-1, SFN®-2, SFN®-1002, SFN®-2301, etc.                  | Sinochem                                          |
| Various series as CGM®031, CGM®021, CGM®-16 (F), CGM®3101, CGM®3102, CGM®1101 | Sinochem                                          |
| 3F® FR002A                                                                    | Shanghai Huayi 3F New Materials Technology        |
| Various series as 4S01-B, 4S02-A                                              | Shandong Huafu Chem                               |
| Various series as 3M™ PTFE Film Tape 5490, 3M™ PTFE Film Electrical Tape 60   | 3M                                                |
| Various series as Gr® - C525                                                  | Zhejiang Juhua                                    |
| Niflon®                                                                       | Jinhua Yonghe Fluorochemical                      |

A non-exhaustive list of patents deposited by various companies is given in Table 1. Finally, and more recently, several companies manufacturing FPs announced that they would not use any surfactants in their TFE polymerization processes, *e.g.*, AGC, Syensqo and Arkema. The main PTFE suppliers and their trademarks are listed in Table 2.

Indeed, it appears reasonable to claim that fluoropolymers, which are manufactured without the use of PFAS polymerization aids, should be exempted from any regulatory initiative and that their uses should be allowed without any unjustified restriction [14,35].

In addition, fluoropolymer manufacturers have made stringent efforts to control PFAS emissions from their production processes. Such progress is based on improvements in abatement techniques, but, more importantly, on the removal of PFAS polymerization aids and the introduction of alternative technologies that do not require these chemicals [21]. Nowadays, most fluoropolymer productions are developed completely free from PFAS polymerization aids [21]. A brief historical overview illustrating the evolution of PFAS, from the discovery of PTFE to REACH regulations, is presented in Fig. 5 [36].



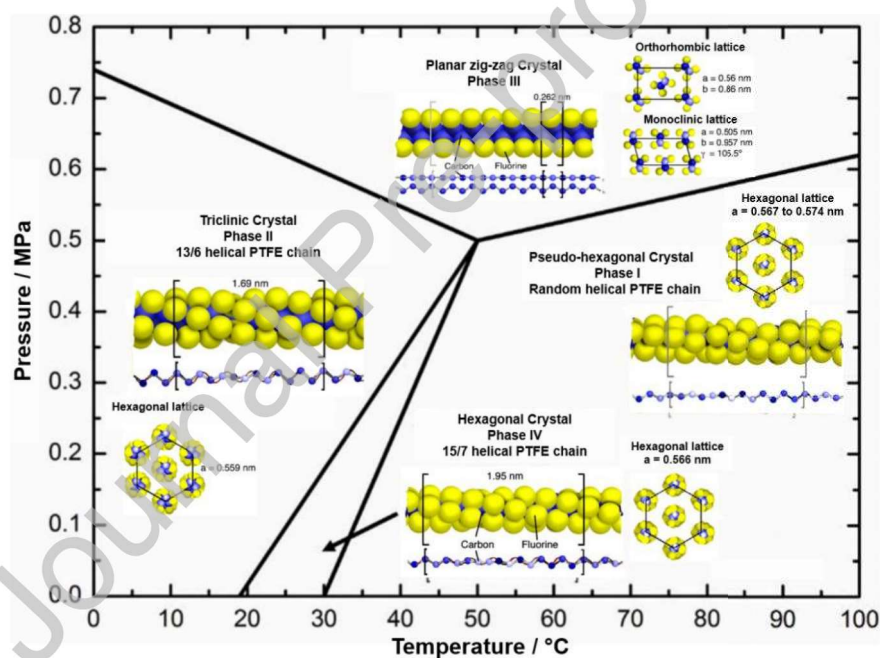
**Fig. 5 :** Historical timeline of the emergence and prohibition of PFAS and the rise of their alternatives (reprinted with permission from Elsevier [36]).

## 2.2. Chemical structure, molecular organization, and morphology

PTFE has a chemical structure composed of carbon and fluorine atoms, represented by the  $\text{CF}_2$ - $\text{CF}_2$  repeating unit. Commercially available PTFE is generally described as predominantly linear and unbranched. However, branching and network formation can be introduced intentionally (e.g., via irradiation-assisted routes) or in specific solid-state polymerization pathways [37,38]. As a result, the linear PTFE is semi-crystalline, exhibiting a high degree of crystallinity, typically reported in the 93–98% range depending on grade and thermal history [1,37]. The structure of PTFE is like that of polyethylene (PE), except that fluorine atoms have replaced all hydrogen atoms. Since the size of the fluorine atom is larger than that of the hydrogen atom (0.064 nm *versus* 0.028 nm, respectively), steric hindrance increases along the carbon backbone. Consequently, the fully extended planar zigzag conformation characteristic of PE (the pitch of which is 1.68 nm) is replaced by a helical chain conformation in PTFE

(pitch of 1.95 nm), shielded by a fluorine-rich sheath surrounding the carbon backbone. This fluorinated sheath reduces polarizability and interfacial cohesive interactions, which underlie PTFE's exceptionally low surface energy, weak adhesion, and outstanding chemical resistance [39].

Additionally, the C-F bond is among the strongest single bonds in polymers (460.2 kJ/mol against 410 kJ/mol and 372 kJ/mol for C-H and C-C, respectively), contributing to the high thermal stability and chemical inertness of PTFE relative to hydrocarbon polymers [1,7,11,15,40]. The high chain symmetry and stiffness also favor high crystallinity, but at the expense of melt processability [39]. Commercial PTFE is marketed with a reported number average molar mass range of  $10^6$ - $10^7$  g.mol<sup>-1</sup> [11]. Based on Suwa's equation [41], the molar mass of PTFE can be estimated from the heat of crystallization measured by DSC, which establishes an empirical relationship between the enthalpy of crystallization and the polymer's molar mass [41,42].



**Fig. 6 :** Molecular structures and phase transition diagram of PTFE crystallization zone at different temperatures and pressures. Adapted from Brown et al. [43–47].

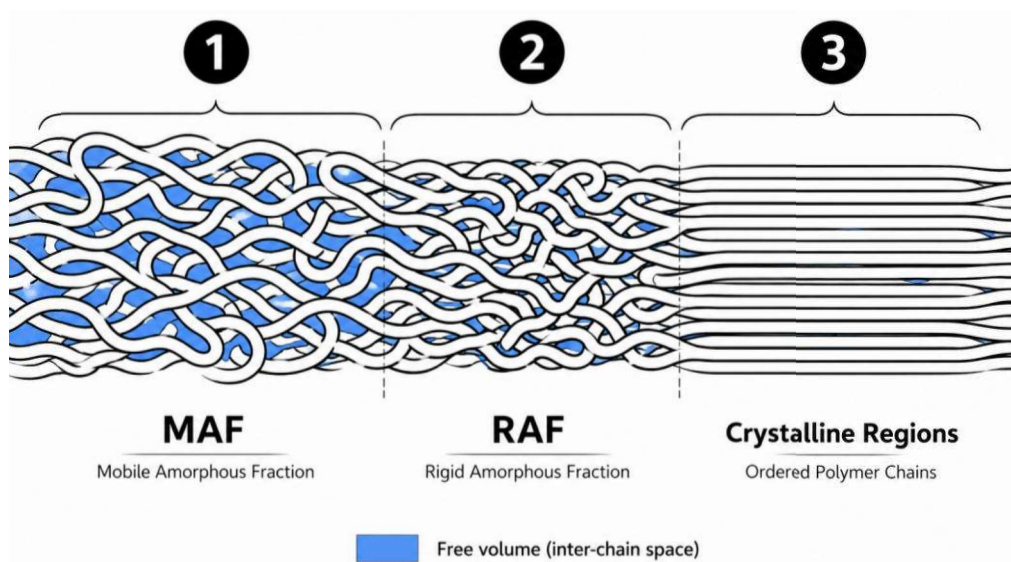
PTFE is a semi-crystalline polymer composed of crystalline and amorphous regions. Its crystalline fraction undergoes two solid-solid phase transitions near 19 °C and 30 °C [11,37,48–51] (Fig. 6). At atmospheric pressure, upon heating, PTFE transforms from a well-ordered triclinic crystal (phase II,  $T < 19$  °C) with a 13/6 helical chain conformation (i.e., 13 CF<sub>2</sub> units complete six turns to recover the initial fluorine registry) [48], to a partially ordered hexagonal phase (phase IV, 19 °C–30 °C). In this intermediate phase, the chains adopt a 15/7 helical



conformation, with a repeating distance (pitch) of ca. 1.95 nm along the molecular axis and an interchain spacing of ca. 0.566 nm [52]. Above ca. 30 °C, PTFE evolves toward a pseudo-hexagonal phase (phase I), often described as rotationally disordered, in which the chain conformation is commonly reported as 13/6 [11,50] (Fig. 6). Under high pressure, PTFE can undergo a distinct conformation/packing change towards a planar zig-zag arrangement (phase III) [43,53]. The four crystalline phases of PTFE are summarized in Fig. 6, with phase I predominating at ambient conditions above ca. 30 °C [11,49] (Fig. 6). In addition, in 1975 Young [54] discovered that PTFE nascent crystals deform mostly by crystallographic slips along macromolecular chains under a very low shear of 2.5 MPa.

The helical arrangement imparts a relatively stiff, rod-like character to PTFE chains, favoring crystallites composed of extended-chain segments (stems) and highly ordered packing. Diffraction analyses confirm that PTFE crystallites consistently exhibit this packing, which contributes to the high crystallinity observed in both virgin and sintered materials [55]. However, alternative routes, such as radiation-induced solid-state polymerization, can introduce branching or network points, yielding microstructures reminiscent of electron-beam-modified PTFE [38,56,57] with direct implications for relaxation dynamics, sintering behavior, and radiation response.

The amorphous phase of PTFE is composed of two types of disordered macromolecular populations. Chains located near regions of high crystallinity exhibit lower molecular mobility than that characteristic of more distant chains. The former defines a so-called rigid amorphous fraction, often abbreviated as RAF. The latter, which possesses increased molecular mobility, defines the mobile amorphous fraction, denoted MAF (Fig. 7). Due to their significant differences in molecular mobility, all regions (crystalline and amorphous) exhibit markedly different critical temperatures, as discussed in the following section.



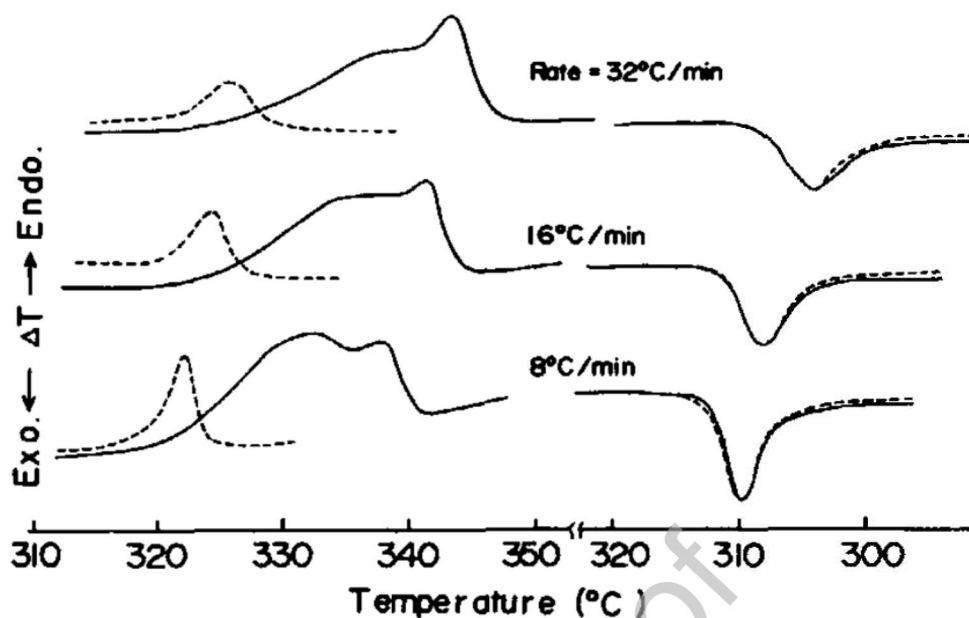
**Fig. 7 :** Schematic illustration of PTFE structure. (1): mobile amorphous phase; (2): rigid amorphous phase; (3): crystalline phase (inspired by ELSEVIER from Calleja et al., 2013 [58]).

### 3. Thermal properties of PTFE

#### 3.1. Melting behavior: a history-dependent thermal hallmark of semi-crystalline PTFE

As discussed in the preceding morphology section, PTFE is a semi-crystalline fluoropolymer with high crystallinity. Then, its thermal response is logically dominated by melting. Although a melting temperature near 327 °C is frequently reported [1], a critical examination of calorimetric studies indicates that PTFE does not exhibit a single universal melting point. Instead, reported melting temperatures and peak shapes depend strongly on thermal history, crystal perfection, and kinetic superheating [41,59,60].

DSC measurements on virgin (i.e., “never melted”) PTFE powders typically exhibit two melting endotherms in the 320-350 °C temperature range (Fig. 8). In contrast, PTFE that has been melted and recrystallized generally displays a single melting peak at a lower temperature (Fig. 8), [41]. This behavior has been interpreted as reflecting distinct crystalline populations, with highly perfect chain-extended crystals present in virgin powders being progressively replaced by less perfect lamellar morphologies after melting and recrystallization [41,60].



**Fig. 8 :** DSC thermograms of PTFE at various heating and cooling rates, where the solid line corresponds to the melting of virgin polymer and its first crystallization from the melt. The dotted line is specific to the sample after melting and crystallization, consecutive to the first run (reprinted with permission from WILEY [41]).

The strong dependence of the melting signature on the calorimetric protocol was convincingly established by Starkweather [59], who highlighted that the relative intensity of the high-temperature melting event increases with heating rate, consistent with pronounced superheating effects in PTFE and non-equilibrium melting behavior [59]. Quantitatively, Huang et al. [60] reported an apparent melting temperature of approximately 342 °C for “never-melted” PTFE *versus* 327 °C for melt-processed material, confirming that the widely cited 327 °C value corresponds primarily to melt-crystallized states rather than to the most perfect native crystals [60].

Previous thermodynamic analyses can support this distinction. Indeed, using perfluoro-*n*-alkane analogs, Starkweather [61] estimated an equilibrium melting temperature for virgin PTFE close to 340 °C and discussed an extended-chain upper bound of ca. 347 °C for highly perfect crystals [61]. In agreement, dissolution and gelation studies in perfluorinated media also distinguished “virgin” PTFE melting around 345 °C from pre-melted PTFE melting near 327 °C, reinforcing that PTFE melting must be interpreted as a history-dependent response rather than as a single intrinsic material constant [62].

Using temperature-modulated DSC, Pucciariello and Villani [63] provided additional evidence that the melting behavior of PTFE can involve partially reversible contributions, particularly in

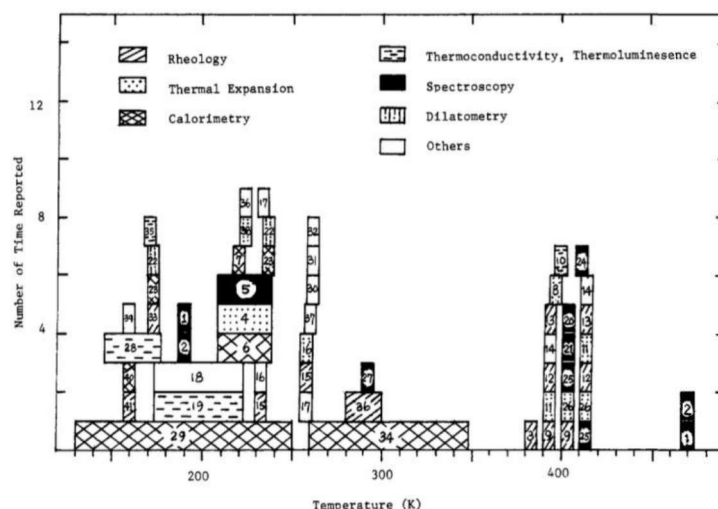
native specimens. By separating the reversing and non-reversing heat-flow components, they highlighted a broad reversible signal in the melting/crystallization region, which they interpreted as surface melting/crystallization processes. Further, they reinforced the strong dependence of calorimetric signatures on thermal history [63].

Because DSC traces of PTFE may be strongly influenced by morphology, thermal lag, and kinetic superheating, reliable thermodynamic comparisons benefit from robust calorimetric baselines. Recommended thermodynamic datasets and transition reconstructions have been discussed based on adiabatic calorimetry and calorimetric rationalizations [64,65].

Although PTFE exhibits a first-order endothermic transition near ca. 327–335 °C, it remains essentially non-melt-processable under conventional flow conditions because the melt viscosity is extremely high [11,63]. PTFE components fabricated by powder-processing are therefore sintered at or slightly above this temperature to promote particle coalescence. The apparent melting point depends strongly on molar mass and crystallinity [66,67], typically falling between ca. 300 and ca. 335 °C, with values near 327 °C often cited for common grades, and approaching ca. 335 °C in highly crystalline materials [66,67]. PTFE produced by solid-state polymerization exhibits a decrease in this transition temperature with increasing radiation dose, consistent with the corresponding loss of crystallinity [38].

### **3.2. Glass transition: brief note on DSC limitations and literature scatter**

The glass-transition behavior of PTFE is considerably more complex [11,58] than that of conventional semi-crystalline polymers. On one hand, its calorimetric detectability is limited by its very high crystallinity. Consequently, DSC signatures corresponding to  $T_g$  may be weak and broadened, and reported values have historically exhibited large scatter [65,68]. On the other hand, the coexistence of different amorphous fractions (RAF and MAF, respectively), as well as the use of various experimental techniques, has led to a wide range of  $T_g$  values reported in the literature. For instance, some reports indicate a low  $T_g$  (ca. -100 °C) while others claim a high temperature transition (ca. +100 °C) [58] (Table 3). More recent analyses using rheometry and dynamic mechanical methods indicate that PTFE exhibits two distinct amorphous-phase relaxation signatures [58]. The lower-temperature transition is attributed to the mobile amorphous fraction (MAF) (Fig. 7), in which chain segments retain substantial mobility and display a relaxation analogous to the conventional  $T_g$  of many polymers.



**Fig. 9 :** Reported glass transition temperatures in the literature and registered with different experimental techniques (reprinted with permission from ACS [65]).

The higher-temperature signature is associated with the rigid amorphous fraction (RAF) located in the crystal–amorphous interphase (Fig. 7). The nearby lamellae constrain chain segments and therefore relax at higher temperatures. Within this framework, the  $T_g$  most consistently associated with the MAF is near  $-103\text{ }^{\circ}\text{C}$  [58]. A glass transition has long been discussed in PTFE (Table 3). However, its calorimetric detectability is limited by its very high crystallinity and a constrained amorphous fraction. Consequently, DSC signatures corresponding to  $T_g$  may be weak and broadened, and reported values have historically exhibited large scatter [65,68].

In the present review,  $T_g$  is therefore mentioned only to prevent confusion between thermodynamic transitions and relaxational phenomena: PTFE does not exhibit a single sharp  $T_g$  readily detected by DSC, and the interpretation in terms of mobile/rigid amorphous fractions (MAF/RAF) and multiple glass-like transitions is more convincingly addressed *via* thermomechanical and dielectric methods. These aspects are therefore treated in detail in the dedicated sections on viscoelasticity (sections 4.2 and 4.7) and electrical properties (section 8) (Fig. 9).

### 3.3. Crystalline solid–solid transitions near ambient temperature

Besides fusion, PTFE exhibits reproducible crystalline transitions at temperatures close to ambient conditions. Adiabatic calorimetry provided early rigorous evidence for the two first-order transitions at approximately 293 K and 303 K (i.e., around  $20\text{ }^{\circ}\text{C}$  and  $30\text{ }^{\circ}\text{C}$ ), associated with rearrangements in crystalline packing [64]. Calorimetric studies subsequently confirmed these transitions and remain a thermodynamic hallmark of PTFE [59,65].

**Table 3.** Reported apparent glass-transition/ $\alpha$ -relaxation temperatures for PTFE across techniques. The dispersion reflects (i) different probed length/time scales and (ii) the coexistence of a mobile amorphous fraction (MAF) and a rigid amorphous fraction (RAF), which can yield distinct relaxation signatures rather than a single, universal  $T_g$ .

| Technique                            | $T_g$ value ( $^{\circ}\text{C}$ ) | Author and reference         |
|--------------------------------------|------------------------------------|------------------------------|
| Dynamic mechanical analysis (DMAs)   | -110                               | McCrum [69]                  |
|                                      | -103                               | Calleja [58]                 |
|                                      | +116                               | Calleja [58]                 |
|                                      | +130                               | Starkweather [70]            |
|                                      | +130                               | Wortmann [71]                |
| Steady or transient rheometry        | +110                               | Tobolsky [72]                |
|                                      | +110                               | Araki [73]                   |
| Mechanical measurements              | -110                               | Woodward and Sauer [74]      |
|                                      | -110                               | Rae and Dattelbaum [75]      |
| Dilatometry (CTE)                    | +123                               | Araki [76]                   |
| Thermally stimulated currents (TSCs) | +130                               | Sauer [77]                   |
| Calorimetry and thermodynamics       | -50                                | Durrell [68]                 |
|                                      | -110                               | Lau [78]                     |
| Calculational methods                | -75                                | Marchionni [79]              |
| Acoustic                             | -110                               | Kvacheva and Perepechko [80] |
| Permeability measurement             | <20                                | Fossati [81]                 |

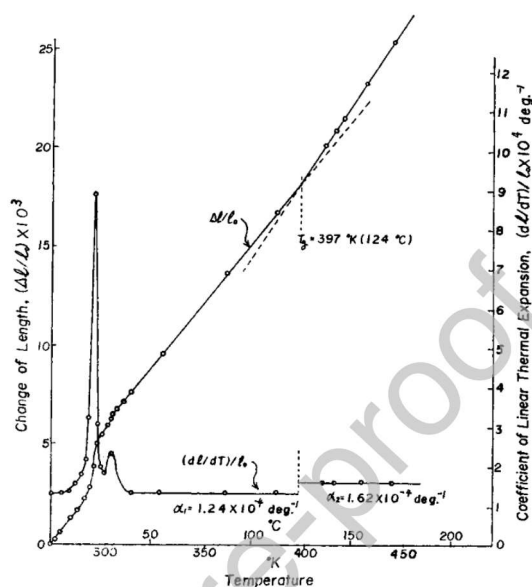
Although their enthalpic magnitude is modest relative to melting, these transitions are technologically important because they occur within typical service temperature ranges and can affect dimensional stability and thermal expansion. Their detailed manifestations in the thermo-mechanical response and their coupling with viscoelastic phenomena are discussed in the dedicated PTFE rheology section to avoid redundancy.

### 3.4. Thermal expansion and dimensional stability

PTFE is characterized by a high coefficient of thermal expansion (CTE) and a strong sensitivity of its dimensional response to morphology and thermal transitions. Typical engineering values



are on the order of  $(10\text{--}15)\times 10^{-5} \text{ K}^{-1}$ , although significant variability exists depending on temperature, crystallinity, and prior thermal history. Araki [76] provided early quantitative evidence that PTFE expansion behavior depends strongly on the amorphous fraction and exhibits marked changes around 388–402 K (averaging 396 K), emphasizing the need to interpret CTE values as morphology-dependent rather than universal constants [76] (Fig. 10).



**Fig. 10 :** Experimental variations of PTFE linear expansion coefficient (reprinted with permission from WILEY [76]).

Reducing thermal expansion and improving dimensional stability under thermal cycling are central motivations for PTFE compounding. Chen et al. [82] investigated PTFE/silica composites and showed that filler incorporation can reduce the CTE. However, effectiveness depends on filler dispersion and interfacial quality, as weak adhesion may limit the expected constraining effect of microfillers. These results highlight that dimensional stability in PTFE composites cannot be predicted solely from filler fraction. It must also account for constraints imposed on the amorphous regions, stress transfer, and microstructural continuity.

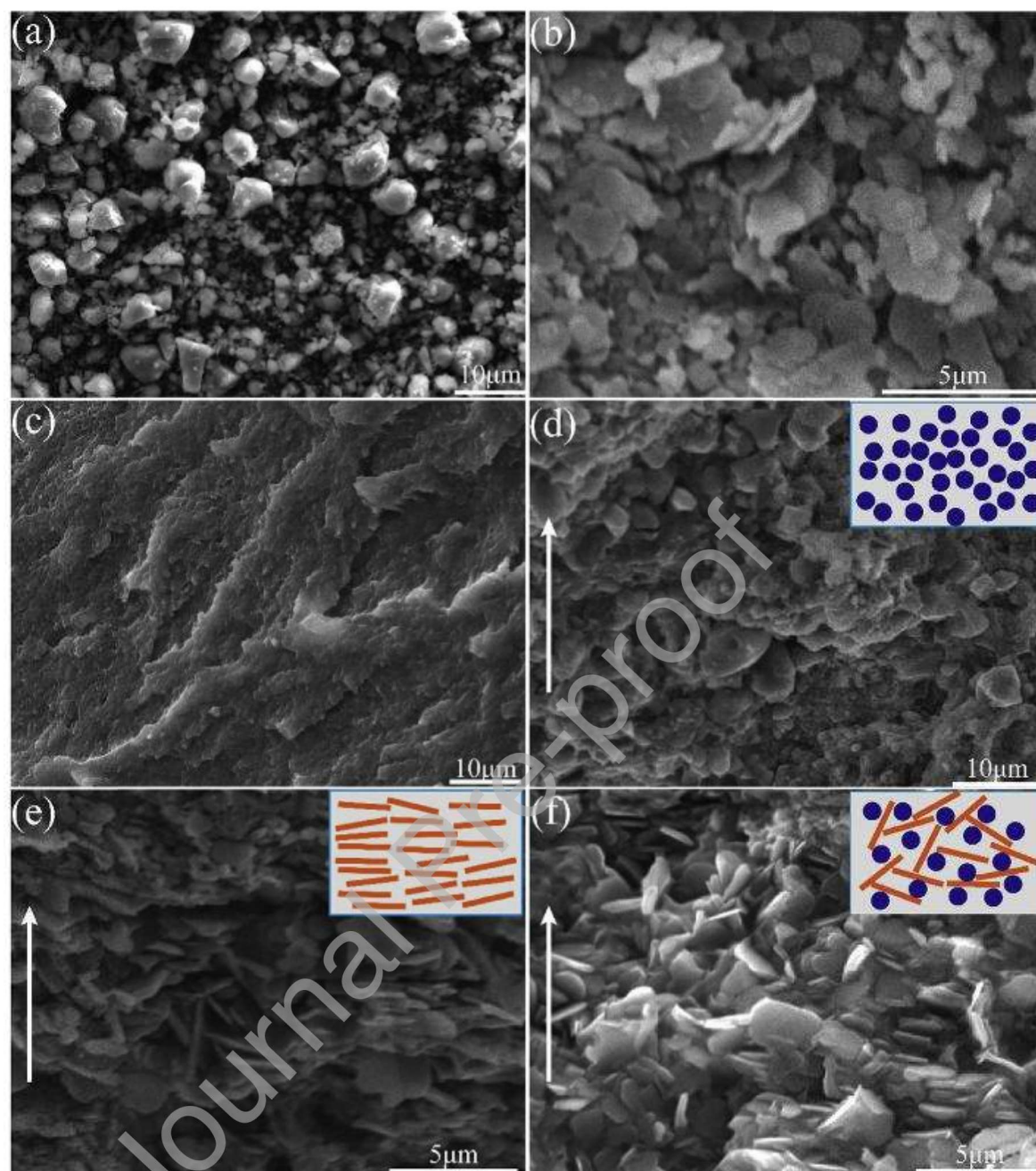
### 3.5. Thermal transport properties and strategies to enhance conductivity

Neat PTFE exhibits a low thermal conductivity (ca.  $0.2\text{--}0.3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ), which may limit heat dissipation in applications involving frictional heating or thermal management under electrical insulation requirements [83]. Notably, heat transport is influenced by microstructure. For instance, Price and Jarratt reported that the thermal conductivity of PTFE increases approximately linearly with crystallinity, underscoring that processing history affects not only fusion signatures but also transport properties [84].

Several studies have therefore explored PTFE-based thermally conductive composites. Hexagonal boron nitride (hBN) is a particularly attractive filler due to its high intrinsic thermal conductivity and dielectric character [85]. However, in hBN/PTFE systems, effective conductivity is frequently limited by platelet alignment and interfacial thermal resistance. Pan et al. [86] demonstrated that hybrid filler architectures can mitigate anisotropy. Indeed, combining hBN platelets with aluminum nitride (AlN) particles reduced preferential in-plane alignment and promoted through-plane pathways, yielding a through-plane thermal conductivity of ca.  $1.04 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 30 vol % total filler (Fig. 11) [86]. In the same study, the authors reported that, at 30 vol % filler loading, the through-plane thermal conductivity reached  $0.723 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  for the hBN-only composite, compared with  $0.680 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  for AlN-only and  $1.04 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  for the hybrid hBN/AlN formulation, highlighting the central role of orientation and filler–filler connectivity in determining thermal transport.

Beyond BN-based approaches, alternative thermally conductive fillers have also been evaluated in PTFE. Ferenc Tóth et al. [83] investigated graphene-, alumina-, boehmite-, and hydrotalcite-filled PTFE composites prepared by pressing and free sintering. They reported that graphene provided the most significant enhancement. Indeed, at 16 wt.% graphene, the thermal conductivity increased from 0.24 to  $0.62 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  [83]. Complementary approaches have been reported using other fillers and architectures, including halloysite nanotubes and related strategies to control dispersion and interfacial heat transfer in PTFE matrices [87,88].

At higher filler contents, thermal conduction may further increase, but typically at the expense of processability. Yuan et al. [89] reported high-volume-fraction  $\text{Si}_3\text{N}_4$ /PTFE composites (ca. 62 vol %) yielding thermal conductivities ca.  $1.3 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ , illustrating the need for high filler connectivity and percolation to reach the  $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  regime [89]. Overall, improving thermal transport in PTFE requires simultaneous control of filler network formation, orientation anisotropy, and interfacial thermal resistance, rather than relying solely on filler fraction.

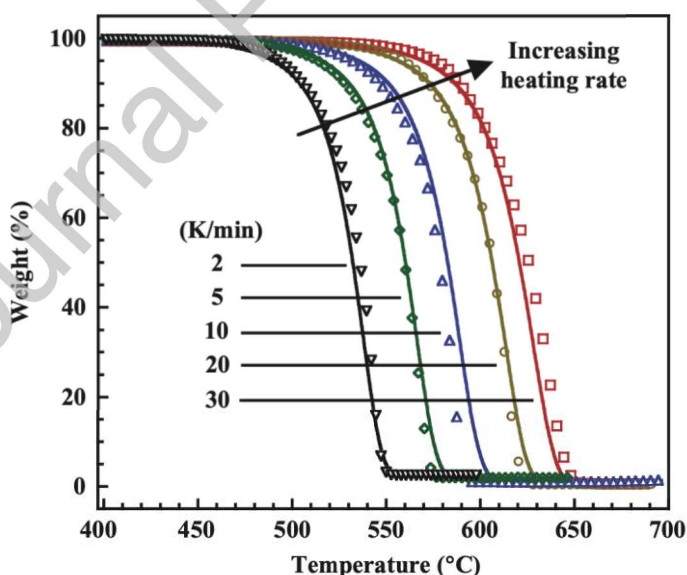


**Fig. 11 :** Illustration of the interest in combining spherical aluminum nitride (AlN) fillers with hexagonal boron nitride (hBN) tablets for improving thermal conductivity of PTFE (reprinted with permission from ELSEVIER [86]).

### 3.6. Thermal stability and degradation

PTFE is often regarded as thermally stable. Actually, its degradation behavior depends strongly on the atmosphere, heating rate, specimen geometry, and chemical history. Conesa and Font [90] provided a detailed thermoanalytical assessment of PTFE decomposition under different atmospheres using coupled thermogravimetric–mass spectrometric (TG–MS) analysis. They identified multiple fluorinated products and emphasized the formation of hazardous species such as perfluoroisobutylene (PFIB) under severe overheating or combustion conditions [90].

A key methodological conclusion emerging from the literature is that kinetic insights cannot be derived from single-rate TGA alone. Hondred et al. [91] compared PTFE and ETFE at multiple heating rates and applied isoconversional analysis, providing evidence that PTFE degradation can be described by a global autocatalytic framework across broad conversion windows, whereas copolymers often require multistep descriptions (Fig. 12) [91]. Such multi-ramp experiments are particularly informative because they enable the determination of conversion-dependent activation energies ( $E_a$ ) and the verification of the extent to which PTFE degradation can be approximated by a global single-step representation *versus* an evolving multistep pathway. Such an observation was confirmed in 2025 [92].

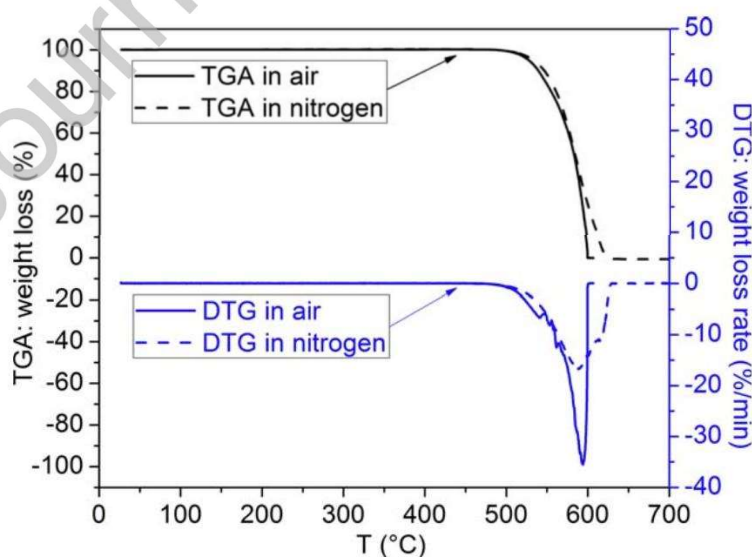


**Fig. 12 :** Influence of the heating rate on the TGA data of PTFE degradation in air. Symbols: experiments; lines:  $n^{\text{th}}$ -order, single-step autocatalytic reaction model (reprinted with permission from SAGE [91]).

Abiodun et al. [92] extended this kinetic framework to PTFE composites and provided a robust example of modern methodology. They investigated PTFE and modified



polytetrafluoroethylene (mPTFE, containing less than 1 wt.% perfluoropropyl-vinyl ether, PPVE, comonomer), as well as their nanocomposites containing 20 wt.% glycine-functionalized boron nitride nanobarbs (BNNB-G). The materials were examined under nitrogen using multi-heating-rate TGA at heating rates of 2, 5, 10, and 20 °C min<sup>-1</sup>, coupled with evolved-gas analysis (TGA–MS). A suite of isoconversional methods (Friedman, OFW, and KAS) was also employed, complemented by numerical optimization using Vyazovkin's method and its advanced variant. The latter enables the extraction of  $E_a(\alpha)$  without imposing an *a priori* reaction model and is especially useful when kinetics are multistep. At 5 °C·min<sup>-1</sup>, the BN nanofiller produced a modest increase in the onset temperature, defined as the temperature at which the relative mass loss reaches 5%. At the same time, it induced a more pronounced upward shift in  $T_{\max}$  from 579.0 °C (PTFE) to 591.4 °C (PTFE/BNNB-G). Here,  $T_{\max}$  corresponds to the temperature of the maximum weight-loss rate, i.e., the peak temperature of the derivative thermogravimetric curve (DTG). At low conversion, the apparent activation energy related to thermal degradation increased substantially from 256 kJ·mol<sup>-1</sup> (PTFE) to 316 kJ·mol<sup>-1</sup> (PTFE/BNNB-G) at 5 % weight loss, resulting in lifetime predictions increased by ca. one order of magnitude depending on the selected temperature window. Importantly, conversion-dependent  $E_a(\alpha)$  profiles highlighted three conversion regimes, supporting a multistep degradation scenario. This kinetic interpretation was consistent with the evolved-gas analysis, which was dominated by CF<sub>x</sub> and C<sub>n</sub>F<sub>m</sub> fragments (e.g., CF, CF<sub>2</sub>, CF<sub>3</sub>, C<sub>2</sub>F<sub>3</sub>, C<sub>2</sub>F<sub>4</sub>), whose relative intensities were altered by the nanofiller.



**Fig. 13 :** TGA and DTG curves of virgin PTFE under different atmospheres (reprinted with permission from WILEY [93]).

Degradation profiles are also affected by oxidative conditions. Huang et al. [93] studied the thermal aging and degradation of PTFE in the 340-450 °C range. They reported that, while PTFE remains essentially stable up to very high temperatures in air or an inert atmosphere, the degradation profiles diverge once weight loss begins, with oxidative environments leading to more pronounced weight loss than nitrogen (Fig. 13). This should not be interpreted as a drastically lower onset temperature in air, but rather as a modification of degradation pathways and apparent kinetics once decomposition is triggered [60].

This atmosphere dependence is consistent with conclusions from evolved-gas studies: under inert conditions, PTFE degradation is dominated by fluorocarbon depolymerization/fragmentation, whereas oxidative environments enable secondary oxidation of fluorocarbon fragments, producing lighter oxygenated species such as CO, CO<sub>2</sub>, or COF<sub>2</sub>, thereby altering apparent weight-loss kinetics [90,94]. Chemical history and defect chemistry may also affect apparent stability. Electron-beam irradiation studies have revealed that oxidative irradiation can generate peroxide species and oxygen-containing functionalities, which evolve upon annealing, thereby modifying the early thermal response and the onset of degradation [95,96].

A further key parameter for filled grades is the influence of inorganic phases. Puts and Crouse [97,98] systematically demonstrated that contact with metal sulfates, fluorides, or oxides may lower degradation onset temperatures and shift product distributions, indicating that degradation can be catalytically accelerated or chemically redirected depending on mineral surface chemistry [97,98]. Using TG-FTIR, Odochian et al. [94] observed that bronze or carbon additives affected the initiation range and CO/CO<sub>2</sub> ratio resulting from PTFE thermal degradation. In contrast, these authors reported that the prevailing monomer release remained essentially unchanged [94].

Finally, macroscopic transport may influence apparent kinetics. Van der Walt et al. [99] investigated the pyrolysis of PTFE granules (800-1000 µm). They proposed a shrinking-particle model, showing that the degradation behavior may be controlled by surface availability and heat transfer, thereby depending on particle geometry and characteristic length scales [99]. This framework implies that surface-to-volume ratio can affect apparent degradation rates, which is especially relevant for extrapolating laboratory-scale TGA to practical overheating scenarios.



### 3.7. Concluding remarks and transition to viscoelastic properties

From a thermal standpoint, PTFE combines (i) a high-temperature melting behavior strongly controlled by crystal perfection and processing history, (ii) crystalline solid–solid transitions near ambient temperature that can influence dimensional response, (iii) a low intrinsic thermal conductivity that can nevertheless be improved through rational composite compositions, and (iv) a high apparent thermal stability whose assessment requires careful kinetic methodology, atmosphere control and consideration of inorganic surfaces.

Because thermal transitions and thermal history strongly condition chain mobility and constrained amorphous fractions, they also govern the viscoelastic response. The following section, therefore, focuses on the viscoelastic properties of PTFE and discusses relaxation phenomena and flow-related behavior in relation to morphology and processing conditions.

## 4. Rheology and Processing of PTFE: Governing Mechanisms

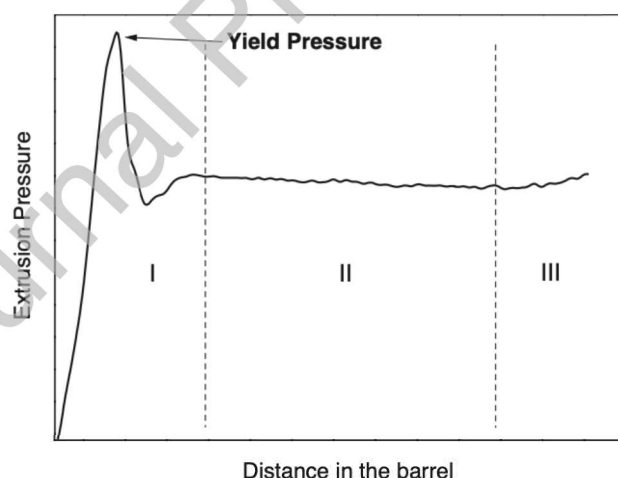
### 4.1. Absence of actual melt flow

Unlike most thermoplastics, PTFE cannot be shaped by conventional melt-processing techniques because of its exceptionally high melt viscosity above its crystalline melting temperature. Consequently, industrial PTFE components are generally manufactured using powder-processing routes. Depending on the geometry of the final component, the most widely used industrial processes include compression molding followed by free sintering, ram extrusion, paste extrusion, and, for selected complex geometries, isostatic pressing. Although the specific processing parameters vary considerably with component dimensions, PTFE grade, fillers and industrial practice, these manufacturing routes all rely on the same fundamental mechanisms involving powder compaction, particle coalescence during sintering, and crystallization during cooling. Understanding these mechanisms is essential because they ultimately govern the microstructure and therefore the final physical and mechanical properties of PTFE components.

Among all synthetic polymers, PTFE occupies a unique rheological domain. Above its crystalline melting point ( $T_m$  about 327 °C), it does not exhibit actual viscous flow [1]. Apparent melt viscosities range from  $10^{11}$  to  $10^{15}$  Pa·s, depending on the measurement technique [72,100,101], which is far beyond the measurable range of conventional rheometers. This non-flow behavior is not a consequence of degradation or experimental limitations—it is an intrinsic property of PTFE's molecular architecture.

The chain structure, composed exclusively of  $-\text{CF}_2-\text{CF}_2-$  units, forms an extraordinarily regular backbone stabilized by strong intrachain F–F repulsion and dense interchain packing [101,102]. The resulting crystallinity often exceeds 90 %, forming lamellar stacks that resist disentanglement even above  $T_m$ . Early investigators interpreted this “solid-like melt” as the persistence of metastable crystallites embedded in a highly viscous matrix [100]. However, later studies demonstrated that the phenomenon is not due to incomplete melting but to restricted chain mobility arising from extreme molar mass ( $10^7$ – $10^8$  g·mol<sup>-1</sup>) and strong interchain cohesion [103].

Above  $T_m$ , PTFE enters a metastable short-range ordered state. This regime appears like a melt but differs in molecular mobility [104]. From a thermodynamic standpoint, the enthalpic stabilization of the  $\text{CF}_2$  crystal lattice ( $\Delta H_m$  about 31–42 J·g<sup>-1</sup>) outweighs the entropy gain associated with amorphous disordering. The exact enthalpy value varies with processing history, crystalline perfection, and purity [92]. As a result, the free-energy barrier for long-range reptation remains prohibitive, even at 30–50 °C above  $T_m$ . PTFE thus behaves as a viscoelastic solid, deforming by creep, surface diffusion, or localized slip rather than by continuous viscous flow (Fig. 14) [105].

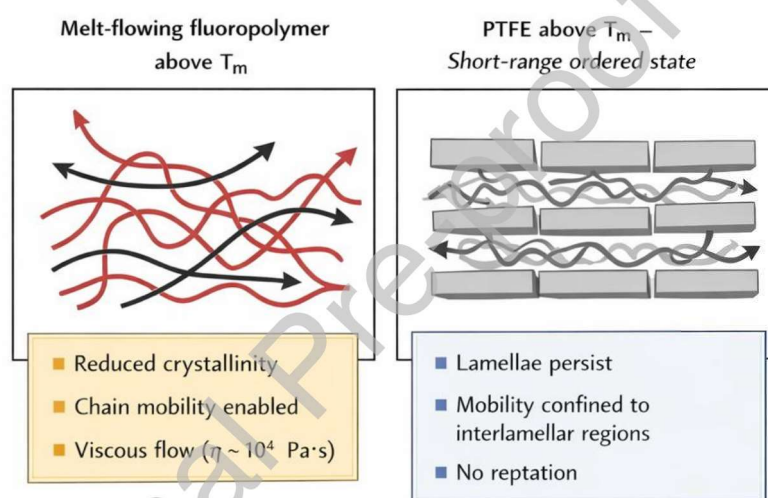


**Fig. 14 :** Typical behavior of a pressure transient during PTFE paste extrusion (reprinted with permission from ELSEVIER [105]).

Comparisons with melt-processable copolymers such as PFA or FEP highlight this exceptional behavior (Fig. 15). In those systems, incorporation of small comonomer units disrupts the chain regularity, reduces crystallinity to 40–60 %, and decreases molar mass, thereby allowing measurable viscosities ( $10^3$ – $10^4$  Pa·s) near 300 °C [106]. These structural “defects” introduce chain-mobility pathways that are absent in PTFE. Yet, such modifications invariably sacrifice some of the chemical inertness and dielectric purity that define PTFE’s technological value.

The classical interpretation that PTFE lacks an actual liquid phase is now widely accepted, but it has occasionally been challenged. Some DSC and rheo-optical studies report transient softening or shear-thinning near 345–355 °C, interpreted as partial chain slippage or mesophase formation. However, these phenomena represent localized viscoelastic relaxation rather than bulk flow: no steady-state shear is sustained once stress is removed. The distinction is subtle but crucial: PTFE deforms but does not flow [92,103].

This unique rheological identity underpins all industrial shaping processes: cold compaction, paste extrusion, and sintering. Each relies on manipulating PTFE in its viscoelastic-solid regime, exploiting plastic deformation, particle rearrangement, or solid-state diffusion rather than liquid-phase viscosity.



**Fig. 15 :** Schematic comparison between melt-flowing fluoropolymers and PTFE behavior above  $T_m$ .

#### 4.2. Solid-state viscoelasticity and relaxation spectrum

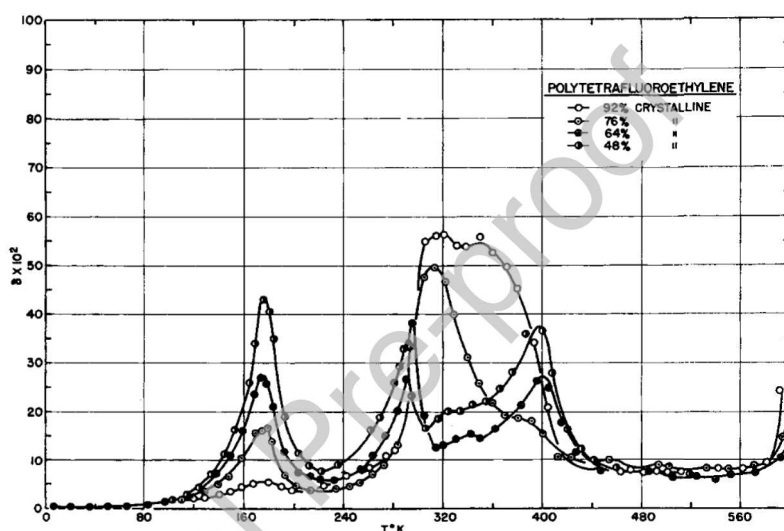
The viscoelastic spectrum of PTFE extends over a wide temperature range, spanning more than 500 K, i.e., from cryogenic to pre-decomposition conditions. This vast range reflects the complex interplay between crystalline lamellae and amorphous domains, as well as between local  $\text{CF}_2$  rotations and collective chain slip (Fig. 16).

Early dynamic mechanical and internal friction studies [69,103,107] identified at least three reproducible relaxation processes:

- $\gamma$  relaxation (about -100 °C): local reorientation of  $\text{CF}_2$  groups within the amorphous fraction but linked to restricted segmental motion;

- $\beta$  relaxation (about 25 °C): disordering of crystalline phase II and transition to phase IV, involving limited cooperative motion of chains;
- $\alpha$  relaxation (about 120 °C): large-scale interlamellar slip and interface softening within the crystalline stacks.

Subsequent studies added nuance to this picture. Sasuga & Takehisa [108,109] reported that unsintered PTFE, containing a higher fraction of amorphous material, exhibits much stronger  $\gamma$  and  $\beta$  peaks. In contrast, sintered samples with increased crystallinity display reduced low-temperature mobility. Such a behavior was attributed to restricted segmental motion as crystallites coalesce during annealing.



**Fig. 16 :** Influence of temperature on the logarithmic decrement (internal friction) of several PTFE samples with specific crystallinities (reprinted with permission from WILEY [69]).

The interpretation of these relaxations, however, remains a subject of debate. Some authors (Table 4) [69,107–111] proposed that  $\beta$  and  $\alpha$  relaxations correspond to crystalline transitions, while others [103,112,113] argued for a dominant interlamellar mechanism, whereby amorphous tie chains slip between ordered lamellae. More recent positron-annihilation and dielectric studies [112] introduced the concept of dual amorphous fractions: MAF and RAF (as seen in section 2.2.). The MAF exhibits glass-transition-like mobility (with a mean free-volume hole volume  $V_h$  about 120 Å<sup>3</sup>), while the RAF, constrained by adjacent crystallites, highlights limited segmental freedom ( $V_h$  close to 80 Å<sup>3</sup>).

This dual-phase view provides a unifying framework for PTFE's distributed relaxation spectrum. The  $\gamma$ -process originates from local motion within the MAF, the  $\beta$ -process from coupling between RAF and imperfect crystallites, and the  $\alpha$ -process from collective slip at the crystal–amorphous interface [58].

However, this interpretation is not universally accepted. For instance, Lau et al. [65] previously reported a broad calorimetric transition around 200 K, suggesting that PTFE exhibits a continuous rather than a discrete glass transition. Similarly, Hu [111] questioned whether distinct RAF/MAF phases can exist in such a highly crystalline polymer, arguing instead for a continuous gradient of chain constraint. This controversy is partly methodological, since crystallinity quantified by DSC does not capture the lamellar connectivity that governs relaxation.

**Table 4 :** Summary of  $\gamma$ ,  $\beta$ , and  $\alpha$  relaxations in PTFE with associated phase origins and activation energies.

| Relaxation          | Typical temperature (°C) | Phase origin                                   | Molecular mechanism                                                                                        | Activation energy (kJ·mol <sup>-1</sup> ) | Sensitivity to crystallinity                                                                      | Key references  |
|---------------------|--------------------------|------------------------------------------------|------------------------------------------------------------------------------------------------------------|-------------------------------------------|---------------------------------------------------------------------------------------------------|-----------------|
| $\gamma$            | -120 to -80              | Mobile amorphous fraction (MAF)                | Local CF <sub>2</sub> segmental motions; glass-transition-like mobility in unconstrained amorphous domains | 40–70                                     | Increases with amorphous content; attenuated after sintering or annealing                         | [58,69,107,112] |
| $\beta$             | 15–30                    | Crystalline phase transitions (phase II → IV)  | Rotational disordering within crystalline lamellae; lattice rearrangement                                  | 80–120                                    | More pronounced in paracrystalline or defect-rich PTFE; reduced in highly annealed samples        | [107–110]       |
| $\alpha$            | 100–130                  | Interlamellar / rigid amorphous fraction (RAF) | Cooperative slip of constrained amorphous chains between lamellae; interlamellar shear                     | 150–250                                   | Shifts to higher temperature with increasing crystalline perfection; linked to lamellar thickness | [58,65,103]     |
| Pre-melting process | 120–150                  | Lamellar interface                             | Lamellar coalescence and defect annealing prior to melting                                                 | >250                                      | Strongly dependent on thermal history; associated with recrystallization phenomena                | [101,111]       |

Despite these divergences, consensus has emerged on several points:

- PTFE lacks a sharp glass transition and exhibits distributed segmental mobility;
- The relaxation hierarchy ( $\gamma \rightarrow \beta \rightarrow \alpha$ ) reflects increasing cooperativity of motion;
- Crystallinity and thermal history dictate the relative amplitude of these processes.

At room temperature, the storage modulus ( $E'$ ) lies near 1 GPa, decreasing gradually to ca. 0.6 GPa at 100 °C before a marked drop near 150 °C [101]. Loss tangent values ( $\tan \delta < 0.05$ ) confirm predominantly elastic behavior. This limited energy dissipation directly stems from the scarcity of interlamellar tie chains, which restricts large-scale viscoelastic flow while enabling limited micro-slip under load. Creep tests [113,114] reveal substantial strain accumulation over long times even below  $T_m$ , consistent with solid-state viscoelasticity rather than plastic yielding. Fractional Maxwell and Burgers models [115,116] successfully capture this broad spectrum, with characteristic time constants ranging from  $10^2$  to  $10^5$  s.

Importantly, low-frequency experiments indicate non-linear compliance: strain increases *quasi*-linearly with applied stress once a micro-slip threshold is exceeded. This transition marks the onset of lamellar shear, a phenomenon more reminiscent of crystalline plasticity than of amorphous flow. PTFE, therefore, combines the time dependence of viscoelastic materials with the structural anisotropy of semicrystalline solids. This underscores that PTFE's time-dependent deformation is governed not by viscous flow but by discrete structural events—slip, rotation, and constraint release—within a rigid lamellar network.

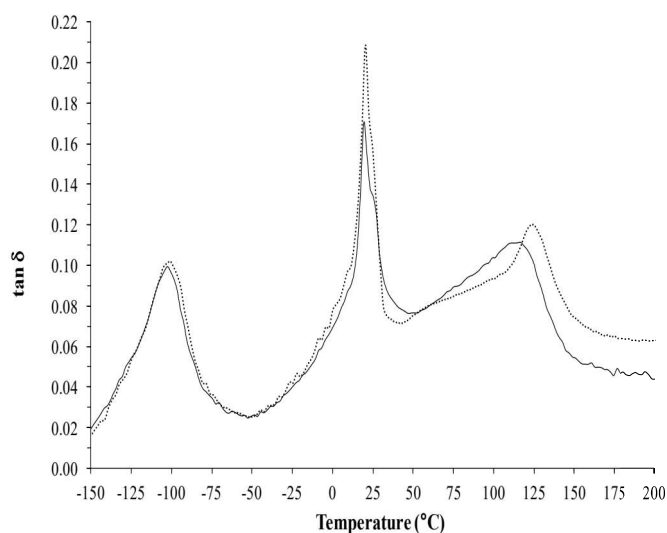
#### **4.3. Influence of microstructure and thermal history**

The rheological and relaxation behaviors of PTFE depend sensitively on its microstructure, particularly crystallinity, lamellar thickness, and defect density. Thermal annealing, irradiation, and mechanical deformation can each alter the balance between crystalline, rigid amorphous, and mobile amorphous regions.

#### **4.4. Annealing and recrystallization.**

Takenaga et al. [110], using dynamic mechanical relaxation measurements (internal-friction/damping spectra), reported that annealing at 300 °C converts paracrystalline zones into well-ordered lamellae, thereby sharpening the  $\beta$ -transition and eliminating low-temperature anomalies near 208 K.





**Fig. 17 :** Non-isothermal  $\tan \delta$  curves of the initial PTFE (solid line) and after annealing at 105 °C for 3 days (dotted line) (reprinted with permission from ELSEVIER [58]).

This process increases stiffness but suppresses mobility within amorphous domains. Similarly, Calleja et al. [58] observed that annealing at 105 °C increases the melting enthalpy (from 31 to 37 J·g<sup>-1</sup>) based on DSC measurement, while the thermomechanical  $\alpha$ -relaxation is shifted from 116 °C to 124 °C, consistent with stronger crystalline–amorphous coupling (Fig. 17).

#### 4.5. Irradiation and defect formation.

In contrast,  $\gamma$ -irradiation experiments, typically performed using a <sup>60</sup>Co source, promote chain scission and, depending on dose and irradiation atmosphere, competing crosslinking reactions. These radiation-induced defects reduce crystalline perfection and may enhance low-temperature relaxations in dynamic mechanical spectra [108,109]. In parallel, crosslinked PTFE has been reported to exhibit the disappearance of  $\beta/\beta'$  relaxations, with shifts in the  $\gamma$  and  $\alpha$  peaks [56], supporting the view that each process originates from molecular or structural mechanisms. More generally, defect-rich materials tend to exhibit higher damping but lower modulus, illustrating the classic stiffness–mobility trade-off in semicrystalline polymers. Reported irradiation effects on PTFE relaxation behavior nevertheless remain scattered, as they depend strongly on irradiation conditions (dose, temperature, oxygen availability, and post-irradiation thermal history [117]), making direct comparison across studies inherently difficult [118].

#### 4.6. Interpretative challenges.

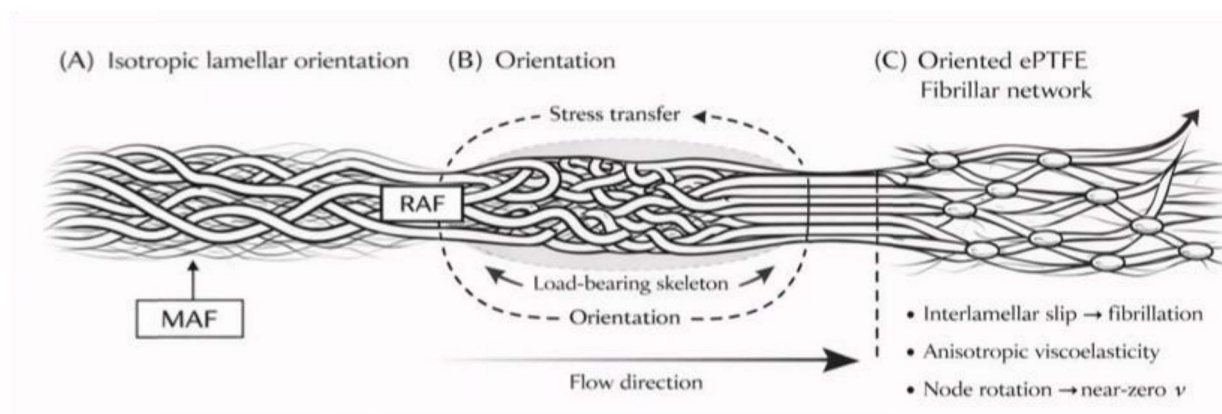
Despite decades of study, the relationship between crystallinity and viscoelastic response remains controversial. Some authors [103,107] considered relaxation shifts purely thermodynamic, controlled by the amorphous/crystalline fractions ratio, while others [58,112] argued that the degree of interfacial coupling between lamellae and amorphous tie chains is the genuine governing factor. Indeed, even two samples with identical crystallinity may exhibit different mechanical damping if their interfacial morphology and molar mass differ. This may explain why reports of glass-transition-like steps [65] vary widely among laboratories.

#### 4.7. Anisotropy and processing effects.

Mechanical orientation during extrusion or stretching introduces lamellar alignment and fibrillation [119]. Aligned structures exhibit enhanced modulus and creep resistance along the flow direction but increased transverse compliance, consistent with interlamellar slip dominating deformation.

In extreme cases (e.g., expanded PTFE membranes), the fibrillar network allows significant extensibility and a near-zero Poisson's ratio, a unique mechanical response attributed to rotation and reorientation of elongated nodes.

Taken together, these findings portray PTFE not as a “frozen” polymer from a rheological standpoint but as a dynamically heterogeneous solid whose viscoelasticity can be tuned by its structural history. The RAF counterpart acts as a load-bearing skeleton, transferring stress between lamellae, while the MAF provides limited relaxation and energy dissipation. Understanding this coupling is key to explaining why PTFE can deform plastically without melting and why its long-term dimensional stability is simultaneously exceptional and history-dependent (Fig. 18).



**Fig. 18 :** Schematic representation of the structural origin of PTFE viscoelasticity heterogeneity and anisotropy.

#### 4.8. Sintering mechanisms

Because PTFE cannot be processed through melt flow, solid-state sintering remains the principal route for obtaining dense, defect-free parts [1,3,9,51]. Yet, despite decades of industrial practice, the mechanism of PTFE sintering remains the subject of persistent debate.

The classical description proposed by Airolidi et al. [100] and refined by Briscoe et al. [120] portrays sintering as a four-stage process:

- (1) particle rearrangement;
- (2) neck growth by surface diffusion;
- (3) plastic deformation under pressure.
- (4) pore elimination through chain interdiffusion.

This framework, inspired by ceramic sintering, has been widely adopted. However, it oversimplifies the molecular-scale complexity of PTFE densification, in which crystalline–amorphous interplay governs diffusion kinetics far more than particle geometry.

Experimental studies using dilatometry, DSC, and SEM reveal that densification begins around 340 °C and is complete near 380 °C, slightly above the nominal melting temperature [58,101].

Instead, sintering relies on localized viscous deformation and segmental diffusion within constrained amorphous regions. This has been modeled as an Arrhenius-type process with an activation energy of ca. 480 kJ·mol<sup>-1</sup>, comparable to the C–C bond energy, indicating that large-

scale reptation is thermally inaccessible. This latter value reflects cooperative segmental motion rather than bond dissociation.

Nevertheless, alternative interpretations have been proposed. Some authors, such as Hu [111], observed small but reproducible endothermic shoulders in DSC thermograms near 350 °C and argued for the existence of a transient “mesomorphic” phase enabling limited slippage of lamellae. Others [103] proposed that these anomalies reflect partial recrystallization rather than actual melting. Recent *in situ* X-ray diffraction [92] supports the latter interpretation, showing that the (100) and (110) reflections sharpen continuously during sintering rather than disappearing, as they would do in a liquid.

A further controversy concerns the role of pressure. Under uniaxial compression, sintering proceeds much faster, and densification kinetics often fit a Coble-type model where the rate scales as:

$$(\sigma/\eta) \times (1/r^2) \quad (\text{eq 1})$$

suggesting that stress-assisted diffusion accelerates neck formation. In this latter expression,  $\sigma$ ,  $\eta$  and  $r$  denotes the applied uniaxial stress, the effective viscosity reflecting the resistance to viscoelastic deformation and interfacial diffusion, and the characteristic pore radius, respectively. The  $1/r^2$  dependence highlights the strong acceleration of densification for finer PTFE powders. However, pressureless sintering, which is relevant to many industrial processes, relies almost entirely on interfacial diffusion and is significantly slower. Some reports claim that moderate pressure (ca. 10 MPa) reduces porosity from 3% to <0.5% within a few minutes, whereas pressureless sintering requires hours for similar densification [120].

The above studies raised an ongoing question: is PTFE sintering predominantly diffusion-controlled or creep-controlled? Most modern interpretations acknowledge that both contribute, with diffusion dominating in the early stages and viscoelastic creep in the later stages, when the interfacial area becomes continuous [100,120]. Morphologically, sintering induces lamellar thickening and increased crystalline perfection, as evidenced by narrowing of XRD peaks and sharpening of DSC endotherms [101,103,111]. This recrystallization explains why sintered PTFE often exhibits a higher modulus and lower damping than its pre-sintered counterpart [101,108–110].

However, excessive annealing can generate internal stresses and warpage due to non-uniform contraction upon cooling, an effect often misinterpreted as “dimensional instability.” This is a

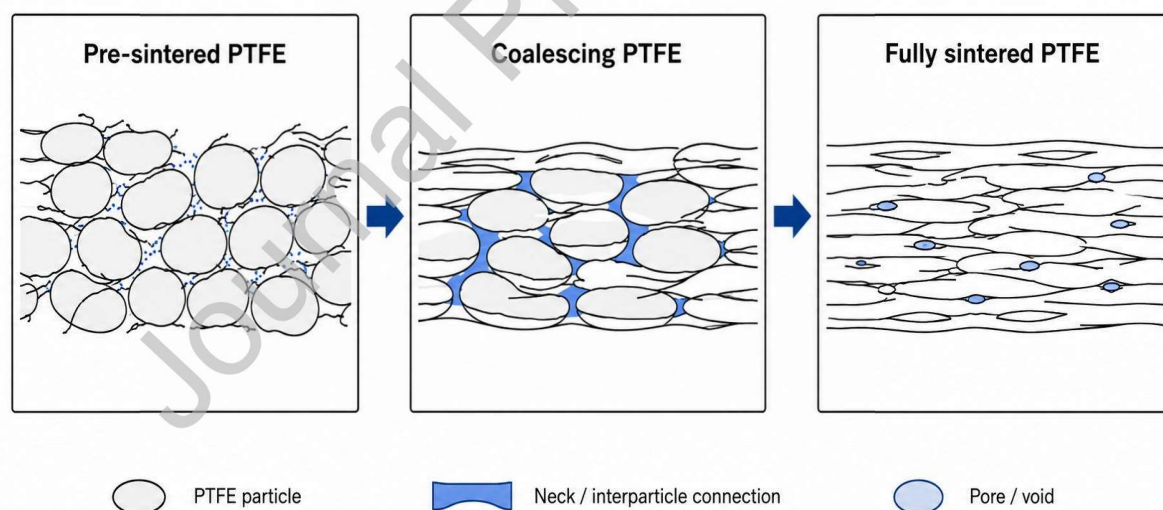
manifestation of viscoelastic stress relaxation within the RAF during post-crystallization shrinkage [112,113].

Thus, sintering of PTFE remains a striking example of a non-classical rheological transformation: the material densifies and coalesces without melting, driven by the diffusion of chain segments through narrow amorphous channels [100,103,120–122].

The process sits at the intersection of solid mechanics and rheology: a slow, diffusion-limited viscoelastic flow occurring in the absence of a liquid phase [100,121–123] (Fig. 19).

#### 4.9. Paste extrusion and fibrillation.

Among the peculiarities of PTFE, its ability to be paste-extruded is perhaps the most technologically remarkable feature. Paste extrusion converts fine PTFE powders, nominally non-flowing, into continuous, fibrillated structures with controlled anisotropy. The process, though superficially mechanical, is profoundly rheological.



**Fig. 19 :** Schematic illustration of the successive stages involved in PTFE particle coalescence during sintering. This figure (created with assistance of AI tools) is a conceptual representation rather than a quantitative description of molecular orientation or stress distribution.

PTFE fine powders consist of submicron particles (0.2–0.5  $\mu\text{m}$ ) with extremely high surface area and strong interparticle friction [124–126]. To enable deformation, a hydrocarbon lubricant (15–25 wt. %, typically C11–12 isoparaffin, also known under the trademark Isopar H®) is incorporated, forming a deformable “wet paste” [105,106,127]. This paste behaves as a *pseudo*-