

viscoplastic material, with a yield-like stress and pronounced wall slip [105,106,123,128]. The constitutive relationship between shear stress (τ) and shear rate ($\dot{\gamma}$) follows a power law:

$$\tau = K \dot{\gamma}^n \quad (\text{eq 2})$$

with K a constant and n is about 0.5 (i.e., characteristic of a rheothinning behavior). The apparent viscosities often exceed 10^8 Pa·s. Such parameters place paste extrusion firmly in the solid-like flow regime rather than in fluid mechanics [128].

During extrusion, the PTFE particles align along the flow direction and coalesce into fibrillar aggregates under compressive stress [127] (Fig. 20). This fibrillation is the origin of PTFE's unique anisotropy: mechanical strength and modulus increase parallel to flow but decrease transversely. For instance, longitudinal tensile strength can exceed 30 MPa, whereas transverse tensile strength remains below 20 MPa [119]. After extrusion, controlled heating removes the lubricant (<200 °C), followed by sintering at 340–380 °C to fuse the fibrils into a coherent structure.

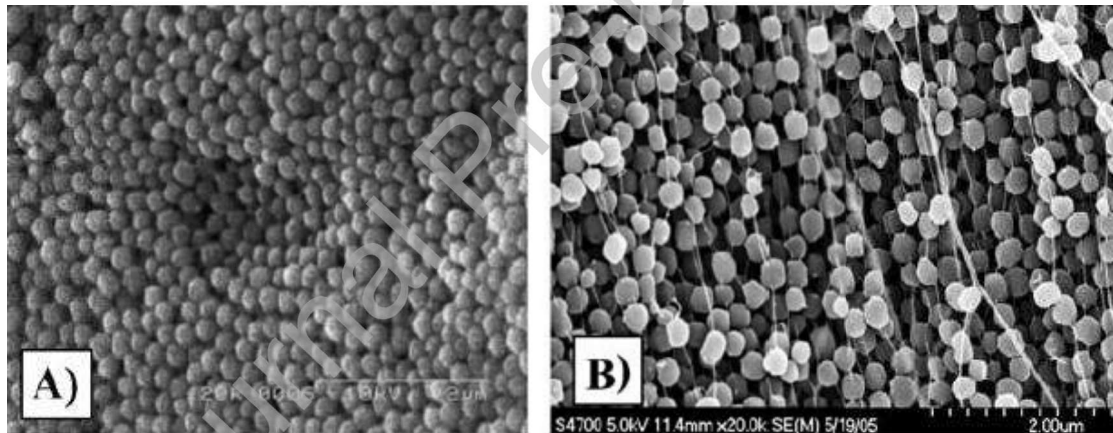


Fig. 20 : SEM micrographs of PTFE paste: (A) before extrusion and (B) after extrusion, illustrating shear alignment and fibril formation (the scale bar is 2 μm) (reprinted with permission from Walter de Gruyter GmbH [127]).

A long-standing question concerns the mechanism of fibril formation [105,127]. Briscoe et al. [120] attribute it to the mechanical interlocking of partially crystalline particles, while Ariawan et al. [106] suggested that oriented sintering of surface amorphous layers produces continuous fibrils. The reality likely involves both effects: local shear during extrusion induces orientation in the amorphous fraction, while subsequent sintering locks in this anisotropy through recrystallization.

Interestingly, paste extrusion transforms what is often viewed as a processing limitation (i.e., PTFE's inability to flow) into a structural advantage. Indeed, the resulting fibrillar texture

confers a combination of high toughness, low density, and directional stiffness unmatched by any other polymer. Expanded PTFE (ePTFE), obtained by post-stretching extruded billets, displays a near-zero Poisson's ratio, enabling use in biomedical implants and high-performance membranes [119,129].

However, the microstructural control of this process remains largely empirical. While shear-thinning and wall slip are well documented, the roles of lubricant migration, interfacial adhesion, and particle morphology remain underexplored [105,127,128]. Recent rheo-visualization studies [123] reveal that lubricant depletion near the die wall induces velocity gradients akin to plug flow, explaining both the uniform fibrillation and the tendency toward “sharkskin”-like instabilities. A comprehensive rheological model of PTFE paste extrusion must therefore integrate particle–lubricant interactions, pressure-dependent slip, and anisotropic densification, elements absent from conventional polymer melt theories [123,127].

4.10. Modeling viscoelastic and creep behaviors

The viscoelasticity of PTFE has inspired more than six decades of modeling efforts, ranging from classical spring–dashpot analogs to modern fractional-derivative frameworks. While these models reproduce experimental data with remarkable accuracy, they often obscure the underlying physics. A critical examination reveals both their utility and their limitations.

Early studies by McCrum [69] and Tobolsky et al. [72] modeled creep and stress relaxation using simple Maxwell or Voigt–Kelvin elements. These works captured the qualitative time dependence but failed to account for the extensive relaxation spectrum observed experimentally. The problem lies in PTFE's hierarchical structure: multiple relaxation modes (γ , β , α) span time constants from milliseconds to days, corresponding to motions ranging from local CF_2 rotations to collective lamellar slip. No finite number of discrete elements can capture such a continuum.

To address this, researchers introduced Burgers-type models that combine the Maxwell and Kelvin branches to account for both instantaneous and delayed deformation [114,115]. The strain response under constant stress is expressed as:

$$\varepsilon(t) = \sigma_0 \left(\frac{1}{E_1} + \frac{t}{\eta_1} + \frac{1}{E_2} (1 - e^{-t E_2 / \eta_2}) \right) \quad (\text{eq 3})$$

under an applied constant stress σ_0 within the linear viscoelastic regime [130,131].

Typical parameters at 25 °C: $E_1 \approx 0.9$ GPa, $E_2 \approx 0.4$ GPa, $\eta_1, \eta_2 \approx 10^{10}$ – 10^{12} Pa·s [114].

While such models fit short-term data well, they lack predictive power outside the experimental window because their parameters depend strongly on the temperature, crystallinity, and loading history. A significant advance came with fractional viscoelastic models, where non-integer derivatives relate stress and strain [115,116]. These models naturally reproduce power-law relaxation ($G(t) \propto t^{-\alpha}$, with $\alpha \approx 0.3$ – 0.6) without invoking discrete time constants. They also continuously bridge the gap between elasticity and viscosity, reflecting the “memory” behavior intrinsic to semicrystalline solids. However, fractional models remain phenomenological. In other words, they describe how PTFE relaxes but not why. Their parameters (α , E_0 , η_0) cannot be directly linked to physical microstructure without auxiliary assumptions.

More physically grounded approaches couple viscoelasticity with the evolution of microstructure. Wang et al. [116] combined fractional rheology with temperature-dependent crystallinity, reproducing both creep and recovery behavior up to 260 °C. Their model predicts an activation energy (ca. 140 kJ·mol⁻¹) corresponding to cooperative motion within the RAF. This aligns well with DMA evidence indicating that RAF-mediated slip predominates in long-term relaxation.

Despite these advances, several challenges remain unresolved. First, anisotropy arising from extrusion or stretching renders isotropic models inadequate: the relaxation modulus differs between orientations parallel and perpendicular to the orientation [119]. Second, the interplay between crystallization and relaxation complicates time–temperature superposition, often invalidating WLF-type scaling. Third, viscoelastic models rarely capture irreversible strain recovery or plastic flow, phenomena clearly observed in long-term creep experiments (Fig. 21) [114].

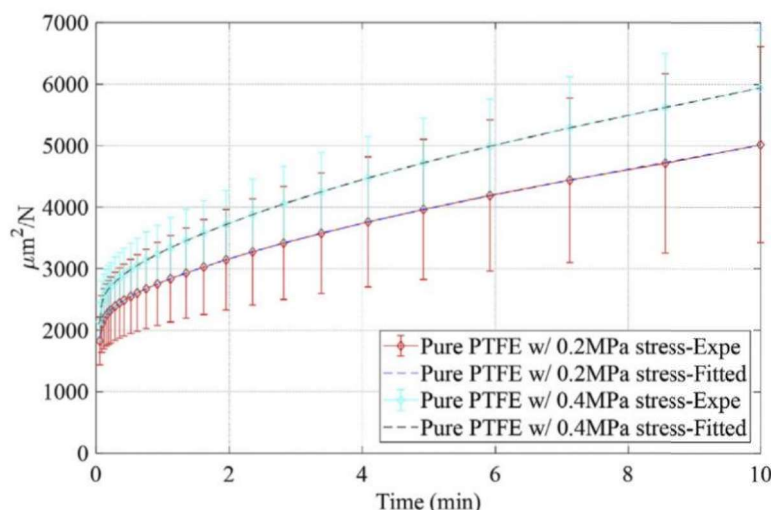


Fig. 21 : Creep compliances of PTFE-based materials under constant stress 0.2 MPa and 0.4 MPa *versus* time. The experimental data are fitted using a linear viscoelastic Prony-series model (reprinted with permission from ELSEVIER [114]).

In this context, the ongoing development of multiscale frameworks that couple fractional rheology, crystal plasticity, and diffusion-based sintering kinetics appears to be the most promising path forward [132]. Such integrative models can reconcile the disparate time and length scales governing PTFE deformation: molecular mobility, lamellar slip, and macroscopic creep. Ultimately, understanding PTFE's viscoelasticity is less about curve-fitting than about uncovering the subtle coupling between its hierarchical structure and its solid-state rheology.

4.11. Structure–rheology–processing correlations

Understanding PTFE's behavior requires a multi-scale view in which structure, rheology, and processing are inseparable. Each level of organization, from molecular conformation to particle morphology, imposes constraints that determine how the material deforms and consolidates. The processing routes developed for PTFE are, in fact, direct technological responses to its rheological singularity: the absence of actual melt flow.

At the molecular level, as mentioned above, the extraordinary regularity of the $-\text{CF}_2-\text{CF}_2-$ backbone and the 13/6 helical conformation create both high stiffness and limited chain mobility. The crystalline lamellae act as quasi-rigid plates, while amorphous tie chains form narrow interfacial zones that mediate deformation through shear and creep. Here, the RAF transmits stress between lamellae, and the MAF governs relaxation and damping. Both these sub-fractions behave cooperatively: when the RAF thickens upon annealing, mobility within the MAF decreases, shifting the α -relaxation to higher temperature. This interplay explains why

the rheological response of PTFE cannot be described by a single glass-transition-like event but rather by a continuum of coupled relaxations. At the mesoscopic level, the powder particle (an aggregate of lamellae and amorphous layers) constitutes the elementary rheological unit. Its surface amorphous layer dictates sintering kinetics, while its crystalline core determines dimensional stability.

During paste extrusion or compression, deformation is localized within these amorphous interfacial regions. This is why even “powder compaction” of PTFE displays viscoelastic hysteresis rather than purely plastic yield. As sintering proceeds, particle boundaries vanish through diffusion across the MAF, producing a continuous microstructure whose residual porosity reflects the efficiency of this interfacial coalescence.

At the macroscopic level, the cumulative effect of lamellar slip, interfacial diffusion, and anisotropic recrystallization produces the well-known directional mechanical behavior of sintered and extruded PTFE.

Creep and stress-relaxation data show a strong dependence on both processing route and orientation. For instance, extruded billets exhibit a storage modulus of up to 1.2 GPa parallel to the flow but only ca. 0.6 GPa transverse to the flow, confirming that processing history becomes an intrinsic structural variable. Expanded PTFE (ePTFE) membranes, created by cold stretching, represent an extreme case in which the lamellar network reorganizes into a fibrillar, node-and-fibril structure with near-zero Poisson’s ratio [119,133]. Such an architecture offers high toughness and tear resistance but also introduces permanent anisotropy, influencing dielectric and tribological behavior.

This hierarchy can be summarized in Table 5. While such a table is convenient, it can mask a more profound truth: the same structural parameters that ensure PTFE’s chemical inertness also induce its rheological rigidity. The dense C–F lattice, which enables resistances to solvents, oxidation, and aging, also prevents from chain interdiffusion. Thus, the processing challenge of PTFE is the direct corollary of its unrivaled stability.

A recurrent misconception in the literature is to treat the PTFE rheology as an anomaly to be circumvented, when in fact it represents a design principle: a material whose thermodynamic stability inherently dictates its deformation mechanisms. This viewpoint reframes PTFE not as a problematic material but as a benchmark for understanding how extreme crystallinity and molecular regularity dictate deformation mechanisms in semi-crystalline solids.

Table 5 : Various processing techniques of PTFE and related characteristics

Processing stage	Dominant structural feature	Rheological regime	Resulting morphology / property
Cold compaction	Semi-crystalline powder	Elastic–plastic	Green density formation
Paste extrusion	Oriented particle aggregate + lubricant	Pseudo-viscoplastic (yield + slip)	Fibrillation, alignment
Sintering (340–380 °C)	Lamellar coalescence via RAF diffusion	Diffusion / creep-controlled	Densification, recrystallization
Cooling / annealing	Crystallization shrinkage	Stress relaxation	Dimensional stability

5. Mechanical properties of PTFE

5.1. Temperature- and rate-dependent solid mechanics

The mechanical behavior of PTFE is dominated by temperature and strain-rate effects and cannot be reduced to a single set of “room-temperature properties”. This point is not related to experimental scatter but rather reflects the intrinsic deformation mechanisms of PTFE as a highly crystalline polymer. Reference datasets reported by Rae and Brown [134] in tension demonstrated that stress levels in the flow regime increase with strain rate [134]) (Fig. 22). In contrast, increasing temperature progressively reduces the resistance to deformation and enables large strains. Almost concomitantly, Rae and Dattelbaum [75] established a comprehensive compression dataset across cryogenic-to-high-temperature ranges and spanning quasi-static to dynamic loading, confirming that PTFE exhibits a similarly strong time–temperature sensitivity under compressive stress. Taken together, these studies provide a robust mechanical basis for evaluating PTFE properties, clearly placing it in the class of strongly rate-sensitive semicrystalline materials.

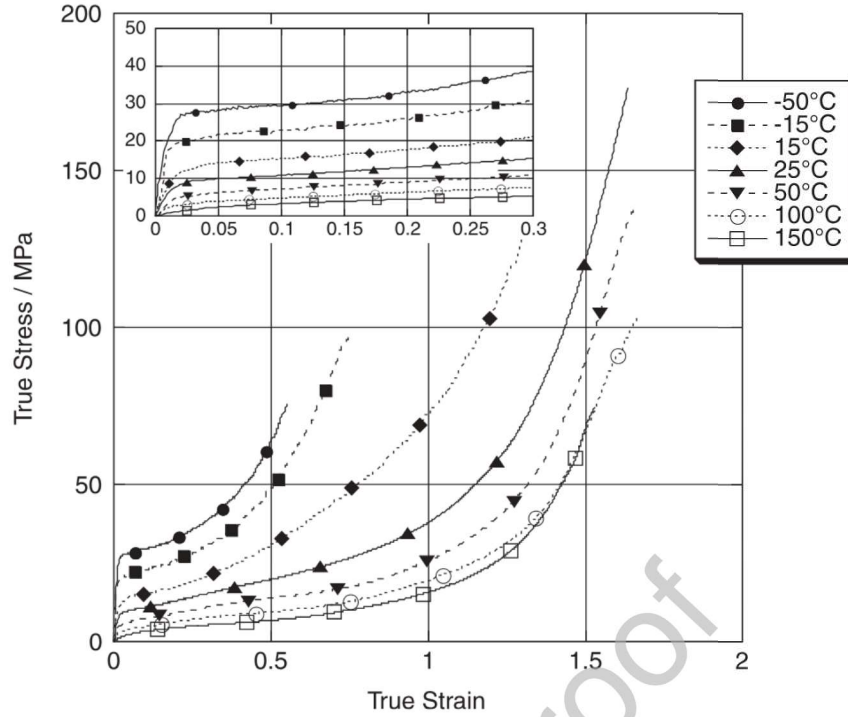


Fig. 22 : Influence of temperature on the tensile behavior of PTFE, referenced as 7C in the publication, under a strain rate of $5 \cdot 10^{-3} \text{ s}^{-1}$ (reprinted with permission from ELSEVIER [134]).

A practical implication is that PTFE is generally ductile at ambient temperature. In support of this view, Calleja et al. [58] reported a tensile experiment conducted at room temperature that evidenced a ductile response. This observation is consistent with the thermomechanical framework in which relaxation associated with the mobile amorphous fraction occurs well below ambient temperature (approximately -100°C). In other words, at room temperature, PTFE does not behave as a glassy polymer; it deforms as a viscoplastic, semicrystalline solid, whose microstructure governs the accessible deformation mechanisms.

5.2. Room-temperature transition and yielding

Early tensile investigations also indicated that PTFE exhibits mechanically detectable changes near room temperature due to solid-state transitions. Koo and Andrews [135] investigated tensile behavior near the room-temperature first-order transition and reported that the yield characteristics vary measurably in that temperature range [135]. Their analysis highlighted that the yield response is also sensitive to strain rate and thermal history, as evidenced by comparing quenched and slowly cooled materials, indicating that the transition cannot be treated merely as a thermal detail. It can directly translate into macroscopic changes in yield stress and yield strain near ambient temperature. Such results provide a clear reminder that PTFE yielding

around room temperature is not expected to vary smoothly with temperature, because phase-state rearrangements may locally modify the deformation mechanisms.

Subsequent studies extended this pattern by providing more comprehensive tensile maps. In particular, Rae and Brown [134] suggested a systematic dataset spanning both the temperature and strain-rate domains, in which the combined effects of these variables on the overall stress–strain response could be observed. Their work is particularly interesting because it reports full stress–strain curves across a wide range of temperatures and strain rates, thereby documenting not only yielding but also the subsequent flow regime and large-strain deformation of PTFE.

5.3. Strain-rate sensitivity and constitutive descriptions

Once PTFE is regarded as a strongly rate-dependent solid, it becomes natural to seek compact constitutive descriptions suitable for engineering use.

i) In tension, Nunes et al. [136] performed mechanical tests under different strain rates and confirmed that the flow stress increases with strain rate. They also emphasized the relevance of non-contact strain measurements and proposed a phenomenological modeling approach calibrated from a limited number of experiments. Although such models are not intended to represent molecular-scale mechanisms, their merit lies in providing a practical representation of PTFE rate sensitivity for design-level predictions.

ii) In compression, dynamic regimes have been investigated in detail. Rae and Dattelbaum [75] combined quasi-static and high-rate compression data to establish a temperature–rate map that explicitly displays the strong dependence of compressive modulus and flow behavior on both variables. Later, Jordan et al. [137] extended this approach to extruded PTFE by combining quasi-static and Hopkinson-type compression experiments (Fig. 23). Their study further demonstrated that processing history (extruded vs. annealed) can alter the response and should therefore be accounted for when comparing datasets. In addition, they discussed modeling strategies, including a Zerilli–Armstrong-type approach, and highlighted the importance of incorporating strain rate into constitutive frameworks for PTFE.

Rae and Dattelbaum [75] combined quasi-static and high-rate compression data over a broad temperature range and established a temperature–strain-rate map showing that both compressive modulus and flow behavior depend strongly on these variables. Their dataset remains a key reference because it documents PTFE response from cryogenic to elevated temperatures under both slow and dynamic loading conditions.

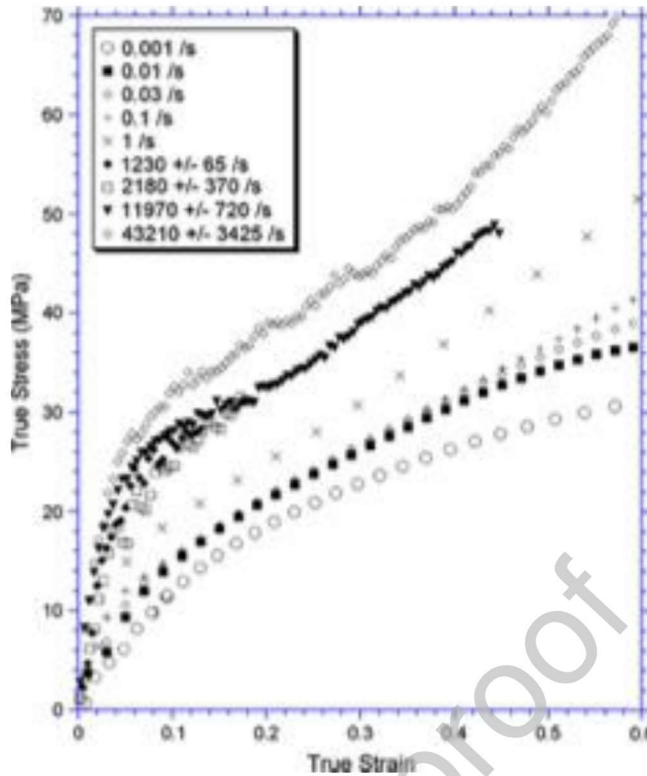


Fig. 23 : Polytetrafluoroethylene tested in compression across a range of strain rates at room temperature (reprinted with permission from ELSEVIER [137]).

5.4. Microstructure-controlled plasticity: band morphology and deformation modes

Early investigators recognized that the mechanics of PTFE cannot be understood without considering its characteristic semicrystalline morphology. Speerschneider and Li [138] proposed one of the most influential mechanistic correlations by linking macroscopic flow behavior to microstructure and temperature. Using tensile experiments performed from cryogenic conditions (i.e., about -196°C) to 100°C , together with electron microscopy, these authors reported that PTFE transitions from a high-strength, low-ductility regime at low temperatures to a low-strength, highly ductile regime at higher temperatures. Importantly, their analysis did not treat this transition as a purely thermal softening effect. Instead, it was interpreted as a change in deformation mechanisms. At low temperatures, crystalline deformation modes (including bowing and kinking) were reported to dominate, whereas at higher temperatures, non-crystalline modes such as sliding and rotation were predominant [138] (Fig. 24).

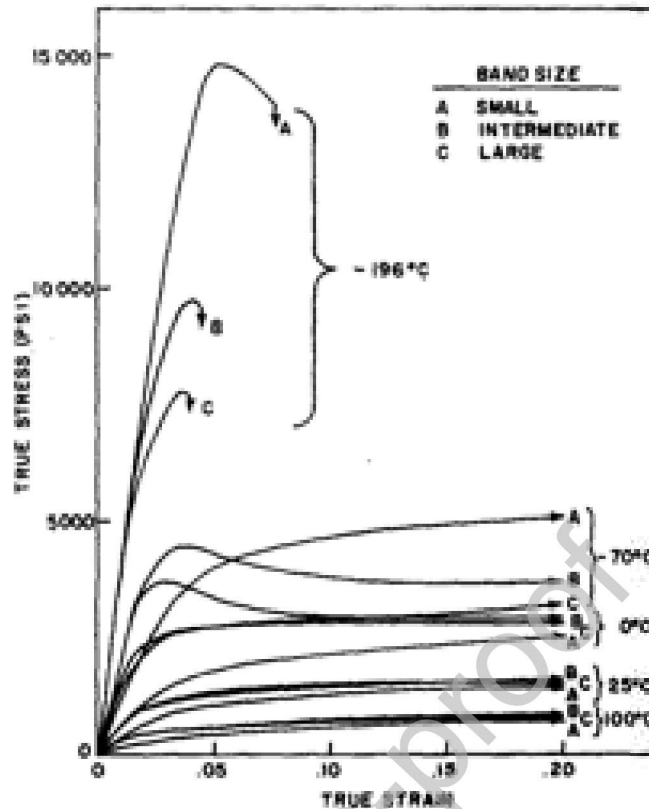


Fig. 24 : Effect of temperature and band size on flow stress of PTFE measured with traction experiments (reprinted with permission from AIP Publishing [138]).

In addition, Speerschnider and Li [138] introduced a microstructural variable, named “band size”, controlled by cooling rate from the sintering temperature. They revealed that band size affects flow stress at low temperatures and reported a stress-drop phenomenon in the flow-stress relations under cryogenic conditions. These results indicate that PTFE plasticity is controlled not only by the amount of crystalline phase but also by which deformation mechanisms are active, crystalline modes dominating at low temperature and non-crystalline modes at higher temperature. Subsequent works on room-temperature behavior further supported that PTFE’s response may change abruptly when transitions are crossed. As discussed above, Koo and Andrews [135] observed measurable changes in yielding characteristics around the room-temperature first-order transition, together with sensitivity to strain rate and cooling history. When combined with microstructure-driven interpretations, these observations reinforce the trend that seemingly moderate temperature changes around ambient conditions may translate into detectable changes in yield and flow response in PTFE.

5.5. Crystallinity and fracture: limitations of ductile mechanisms

Whereas stress–strain maps characterize PTFE plasticity in terms of flow stress and deformability, fracture studies highlight more directly how microstructure governs damage evolution. Brown and colleagues [139] investigated the effect of crystallinity on PTFE fracture behavior and demonstrated that ductile mechanisms, such as plastic deformation and fibrillation, contribute significantly to fracture resistance. Their analysis also indicated that increased crystallinity may restrict these ductile mechanisms, thereby reducing the fracture resistance. From a structure–property perspective, this provides a key complement to flow-stress descriptions: crystallinity not only alters stiffness and yield but also constrains the mechanisms that enable energy dissipation at the crack tip.

A further interest of the study by Brown et al. lies in the explicit consideration of solid-state transitions around room temperature. Their discussion supports the idea that transitions may influence deformation and fracture behavior, consistent with earlier studies on yielding. The overall message is that PTFE mechanical integrity should not be assessed solely by tensile strength or ductility but must also account for microstructure-controlled fracture mechanisms, particularly in applications involving notch sensitivity, crack propagation, or repeated loading.

5.6. Molar mass as a mechanical lever

Chain architecture provides another way to understand and tailor PTFE mechanics. Włochowicz and Śacigala [140] examined the influence of molar mass on mechanical properties. They reported correlations between number-average molar mass and tensile behavior, including strength and elongation at break, as well as density trends; as expected, after high molar mass, these features no longer change. Their work is valuable because it explicitly treats PTFE as a family of materials rather than as a single reference polymer. Indeed, variations in molar mass translate into measurable shifts in the strength–ductility balance. In the context of a review, this provides a valuable framework to rationalize differences reported across datasets and grades, even when processing routes appear similar [140] (Fig. 25).

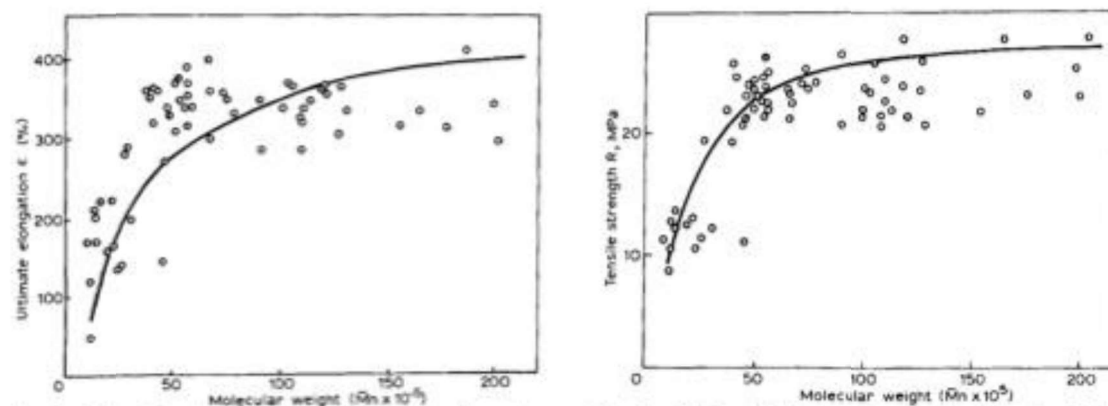


Fig. 25 : Effect of molar mass on the ultimate elongation for PTFE (left) and on the tensile strength (right) (reprinted with permission from WILEY [140]).

5.7. Post-treatments and microstructure tailoring: irradiation effects

In addition to molar mass and cooling history, mechanical response can be modified by post-treatments. In graphite-filled PTFE composites, Barylski et al. [141] investigated the combined effects of graphite content and electron-beam irradiation. These authors reported improvements in mechanical properties, as measured by compression and hardness tests, and discussed an optimal irradiation dose window. Such results indicate that irradiation can be used as a microstructure-modifying tool to enhance deformation resistance under appropriate conditions. However, this effect should not be interpreted as monotonic: as in many polymers, excessive irradiation doses may trigger degradation processes, such as chain scission, which can ultimately reduce mechanical integrity. The mechanical performance of PTFE must therefore be considered as resulting from a balance between beneficial microstructural modifications at moderate doses and degradation at higher doses.

5.8. Large-strain deformation, fibrillation, and non-classical kinematics

While tensile strength and modulus are commonly used to rank polymer performance, PTFE often operates in regimes in which large-strain deformation and microstructural reorganization dominate the response. In this context, paste-extruded PTFE provides a particularly instructive example. Vavlekas and co-workers [119] investigated paste-extruded PTFE under uniaxial extension using a Sentmanat extensional rheometer configuration and reported several distinctive features. First, the ultimate tensile strength increased with extrusion temperature and reduction ratio, while decreasing with testing temperature. Second, the tensile strength followed a power-law dependence on Hencky strain rate. Beyond these strength trends, the same work

revealed an unusual deformation kinematics: the specimen diameter remained approximately constant during extension, implying a near-zero Poisson's ratio ($\nu \approx 0$) under the studied conditions.

A key contribution of these authors [119] is their linking of these macroscopic features to microstructural evolution during stretching. Density measurements indicated a decrease in relative density with increasing extension, suggesting that stretching is accompanied by porosification (Fig. 26). SEM observations were discussed in relation to fibrillation processes, providing a physically consistent picture in which PTFE elongational deformation produces a reorganized, fibrillar architecture rather than a classical incompressible rubber-like response. This study is quite helpful because it emphasizes that PTFE mechanics at large strains can involve volume changes and the development of microstructural damage, which must be accounted for when PTFE is used in membrane-like components or subjected to elongational flow paths (Fig. 26).

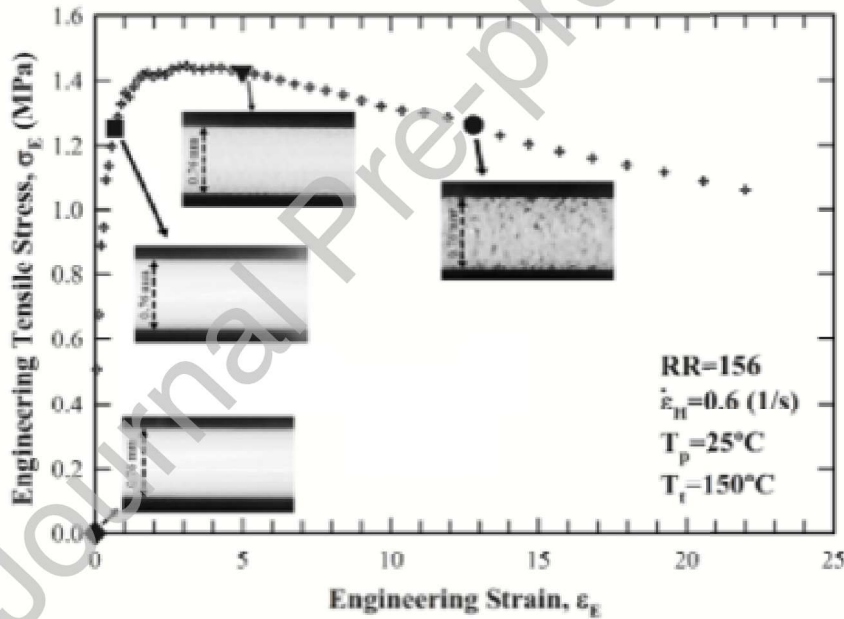


Fig. 26 : Experiments on PTFE (0.6 s^{-1} , 150°C): evidence for porosification at large strain values (reprinted with permission from ELSEVIER [119]).

5.9. Processing routes as primary features of mechanical performance

Processing plays a central role in PTFE mechanics because it governs porosity, interparticle adhesion, crystalline morphology, and molecular orientation. This feature is not limited to composites: in pure PTFE, processing may induce mechanical properties that rival those of reinforced systems. An obvious demonstration was provided by Uehara and co-workers [142], who applied biaxial melt-drawing to prepare void-free PTFE membranes with high

transparency and enhanced mechanical properties. Their strategy combined a two-step molding process designed to improve adhesion between PTFE powder particles and minimize residual voids, followed by simultaneous biaxial drawing from the molten state. Under these conditions, the resulting membranes achieved a tensile strength of up to 120 MPa, i.e., approximately five times higher than that of a commercially available PTFE film. The interest of the study by Uehara et al. lies in its direct, processing-based pathway to “structural PTFE” that relies on the absence of fillers. The authors explicitly attributed the combination of strength and transparency to defect-free structures produced by controlled preform consolidation and low-stress melt drawing. In contrast, films containing residual voids (e.g., those associated with lubricant-assisted processing routes) were shown to retain or amplify scattering defects during drawing, limiting both transparency and mechanical integrity. Such comparisons reinforce a broader observation across several PTFE systems: porosity and interfacial defects are critical structural flaws that govern mechanical performance, and their control is therefore a primary requirement rather than a secondary processing detail [142,143].

5.10. Processing history and high-rate response: extrusion and annealing effects

Processing sensitivity is also apparent in the mechanical response under compressive stress states and dynamic loading. As discussed previously, Jordan and co-workers [137] examined extruded PTFE and compared the “as-received” and annealed states. Their study combined quasi-static and high-rate compression experiments and discussed constitutive descriptions, including a Zerilli–Armstrong-type approach that captures rate sensitivity. Notably, the authors emphasized that the processing route (i.e., extruded condition and post-annealing) can alter the measured response. This reinforces the idea that PTFE datasets should not be compared without at least minimal information on processing history, since microstructural differences induced during extrusion and annealing may influence compressive stiffness and flow behavior, particularly when the strain-rate domain is extended to dynamic conditions [138].

5.11. Filled PTFE: stiffening mechanisms and modulus–ductility trade-offs

The most widely used strategy to improve the mechanical performance of PTFE is to incorporate fillers and reinforcements [144]. Although specific goals may vary (e.g., wear, dielectric stability, thermal conductivity), the mechanical trends are often systematic. In a comprehensive comparative study, Tóth et al. [83] prepared neat and mono-filled PTFE with several nanoparticle types (graphene, alumina, boehmite, hydrotalcite) and varying filler

contents [83]. Their mechanical characterization included tensile, compressive, and shear testing, as well as DMA and hardness measurements. A central result is that all fillers increased the storage modulus and the tensile/shear moduli, whereas ductility decreased relative to neat PTFE. Such results support a general view of nanoparticle reinforcement in PTFE: increased stiffness is typically achieved at the expense of extensibility, likely due to restricted chain mobility and earlier activation of damage mechanisms such as micro-voids at the interfaces. At higher filler fractions, porosity and interfacial quality often become decisive. Sasikala and Sebastian [143] investigated Mg_2SiO_4 -filled PTFE composites, including micro- and nanosized fillers (Fig. 27) [143]. They evaluated mechanical properties using microhardness and strength measurements obtained from flexural and diametrical compressive tests. Their work evidenced that hardness increases with increasing filler content. Notably, the authors highlighted that silane treatment reduces porosity and increases microhardness, demonstrating that interfacial engineering can mitigate void-driven mechanical degradation under high loading (Fig. 27).

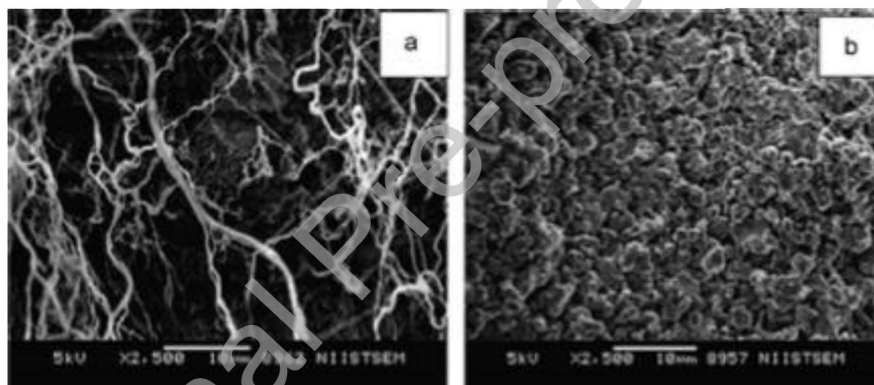


Fig. 27 : SEM images of fractured surfaces of PTFE loaded with (a) 40 vol% untreated Mg_2SiO_4 (b) 40 vol% silane-treated Mg_2SiO_4 (the scale bar is 10 μm) (reprinted with permission from ELSEVIER [143]).

A similar “functionality–mechanics compromise” is observed in composites filled with plate-like ceramic fillers intended for thermal or dielectric applications. Zimmermann-Ptacek et al. [145] studied h-BN-filled PTFE composites across a broad range of volume fractions and reported tensile properties such as modulus, tensile strength, and elongation [145]. They observed that mechanical properties are negatively affected by ceramic loading. However, they also noted that ca. 40% of the tensile strength can be preserved at filler fractions up to 30 vol%. This type of quantitative boundary is particularly valuable for engineering design, as it explicitly specifies the mechanical cost associated with incorporating functional fillers. In practical terms, such a limit is relevant for PTFE-based substrates or insulating components that require enhanced thermal conductivity or dielectric performance without sacrificing mechanical integrity. For example, in electronic packaging or high-frequency circuit substrates, filler

loadings must remain compatible with handling, machining, and assembly stresses. The identification of a filler fraction window in which functional gains are obtained while retaining a defined fraction of tensile strength, therefore, provides a direct guideline for balancing mechanical reliability against thermal or dielectric performance [146].

5.12. Structural PTFE composites: continuous fiber laminates and interlaminar integrity

In addition to particulate fillers, continuous fiber reinforcement enables PTFE-based structural composites with significantly enhanced stiffness and strength. In an interesting study, Riul et al. [147] reported the processing and mechanical evaluation of glass fiber-reinforced PTFE laminates [147]. They measured tensile and flexural properties using full-field strain analysis (named DIC). The reported tensile modulus and strength ($E = 14.2$ GPa and $\sigma = 165$ MPa, respectively) confirm that PTFE can serve as a matrix for load-bearing laminates when architecture and processing are suitably controlled. In addition, they highlighted that sintering time influences fiber–matrix adhesion, highlighting that interface development during sintering is a key parameter controlling laminate integrity.

Interlaminar properties, such as interlaminar shear strength, represent a key aspect of mechanical performance in PTFE laminates, particularly when PTFE is used as a coating or matrix in textile-based composite structures. Bandaru and co-workers [148] investigated PTFE-coated glass fabric composites and evaluated interlaminar shear strength (ILSS) as a function of textile architecture and surface hybridization. They reported that adding metallic mesh in surface layers improves ILSS, with gains depending on the fabric structure. These results illustrate that architectural design and interlayer engineering can enhance load transfer and delamination resistance in PTFE-based laminates.

5.13. Durability under cyclic loading

For many PTFE applications (e.g., bearings, seals, sliding parts, structural composites in service), the relevant mechanical performance is not only a *quasi*-static strength but also durability under repeated loading. Mazur et al. [149] produced PTFE composites filled with bronze, glass fibers, coke, and graphite under static compression and compression–compression fatigue up to 100,000 cycles. Their analysis revealed that filler type and morphology influence both modulus, dispersion energy, and cyclic mechanical response, supported by morphological observations. Such studies support the general conclusion that reinforcement strategies must be

evaluated under service-like loading modes, since fillers which improve stiffness or wear resistance do not necessarily optimize fatigue behavior (Fig. 28).

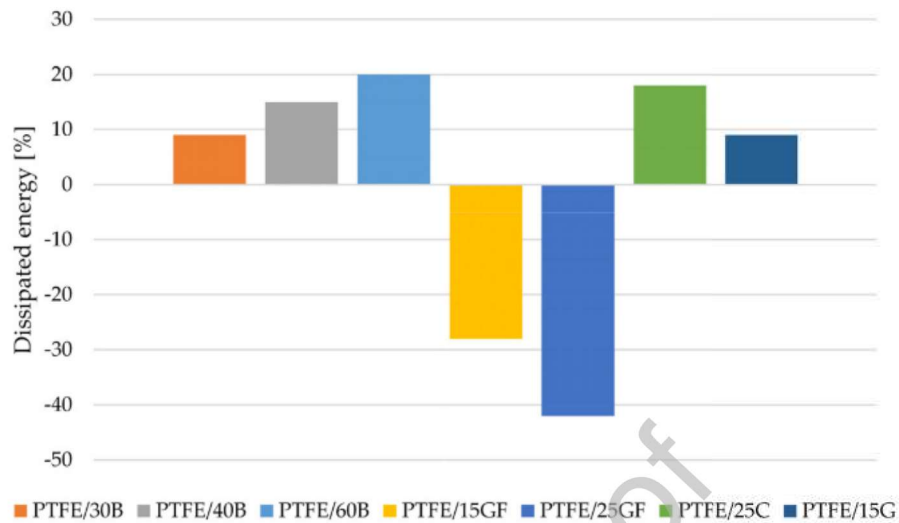


Fig. 28 : Change of the dispersion energy of composites based on PTFE filled with different weight percentages of particles: B=bronze; GF=glass fiber; C=coke and G=graphite (reprinted with permission from MDPI [149]).

5.14. Time-dependent response: creep and hysteresis in PTFE composites

Time-dependent mechanical response is another recurrent feature of PTFE systems, particularly when both reinforcement and processing induce anisotropy. Martins et al. [132] provided a focused mechanical characterization of silica-reinforced PTFE matrix composites, explicitly addressing the influence of strain rate, creep loading, and cyclic loading–unloading sequences [132]. Their results underscore that the mechanical response depends on the loading history (i.e., rate effects and creep). Significant hysteresis is observed upon cycling, reflecting the viscoelastic/viscoplastic nature of the PTFE matrix and the role of composite architecture, including directional effects in processed plates.

6. Tribological and surface behavior of PTFE

6.1. Intrinsic Tribological Behavior of Virgin PTFE

6.1.1. Frictional response, microstructure, and chain orientation

The intrinsic tribological behavior of virgin PTFE results from the interplay between its low surface energy and the weak intermolecular cohesion associated with its *quasi*-cylindrical CF₂ helices. These molecular features yield a very low friction coefficient, μ , (typically ranging

from 0.04 to 0.10) but also a high wear rate, typically on the order of $10^{-4} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ under dry sliding [150,151]).

The microstructure of PTFE is a central parameter governing its frictional response, in particular its degree of crystallinity, fibrillation, and chain orientation. Drawing-induced fibrillation, as reported by Liu et al. [152], increases crystallinity and promotes the formation of more cohesive transfer films as described later. Orientation effects have been demonstrated at multiple scales. Jang et al. [153], using AFM and microtribometry, observed a strong anisotropy, with friction coefficients of 0.05 along the orientation direction and 0.15 perpendicular to it. Molecular-dynamics simulations further support the role of the chain alignment: Barry et al. [154] showed that the interfacial shear is accommodated by rotational motions of CF_2 units and local chain rearrangements, consistent with experimentally measured low shear strengths. More recently, Cai et al. [155] reported that PTFE drawn by factors of 2–5 exhibits μ values in the 0.03–0.06 range and a much more stable sliding trace, attributed to homogenized molecular alignment.

A defining feature of PTFE tribology is the formation of a transfer film, which enables low friction but remains mechanically fragile. The mechanisms governing its formation, chemical stabilization, and long-term durability are detailed in Section 6.2.2.

The frictional response of PTFE depends on normal load and sliding speed. Ünal et al. [156,157] found that increasing the load from 0.2 to 7.0 MPa reduces μ from 0.16 to 0.08 while simultaneously increasing wear.

These observations highlight that the outstanding lubricity of PTFE originates from its molecular mobility and orientation, while its poor wear resistance reflects the mechanical fragility of the interfacial layer formed during sliding. The thermomechanical and tribochemical processes governing this behavior are examined in the following sections.

6.1.2. Thermomechanical and viscoelastic coupling

The tribological behavior of PTFE cannot be fully described without accounting for its pronounced viscoelasticity. Internal mechanical losses, arising from molecular relaxations in both amorphous and crystalline fractions, play a central role in frictional heating and energy dissipation during sliding. Wieleba et al. [158] demonstrated that PTFE exhibits significant internal friction ($\tan \delta$ of about 0.16 at 3 MPa), which leads to local flash-temperature rises well above the bulk temperature.

Temperature acts as a dual factor, lubricating and degrading the interface simultaneously. Burris et al. [159,160] identified a thermally activated friction mechanism with activation energies of 3-5 kJ mol⁻¹, consistent with shear accommodated by local chain mobility. At moderate temperatures (<100 °C), enhanced segmental motion reduces friction, whereas excessive heating increases wear exponentially as the polymer approaches the onset of crystalline melting near 327 °C (Fig. 29).

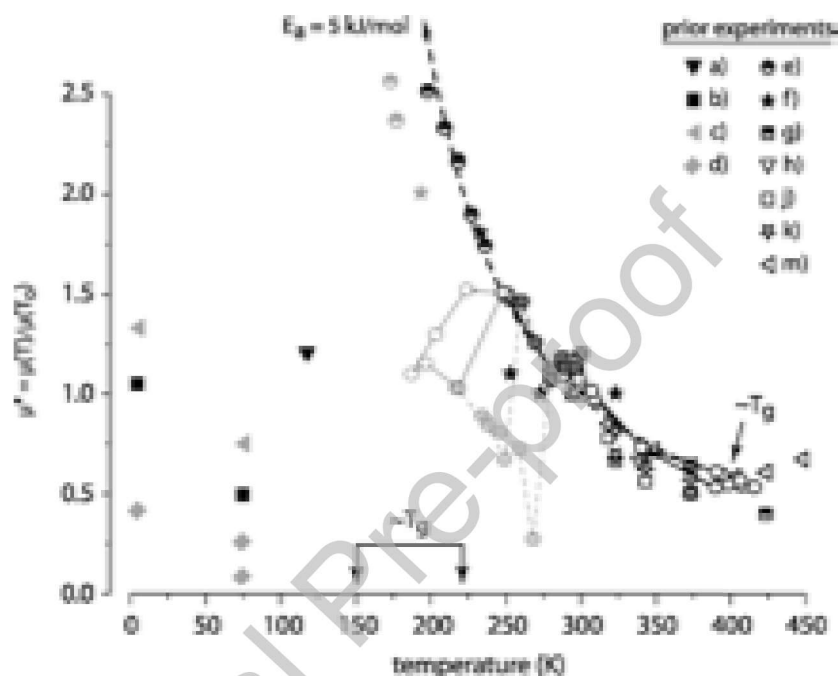


Fig. 29 : Normalized friction coefficient plotted *versus* interface temperature for variable temperature studies of PTFE in the literature from various sources (reprinted with permission from Taylor & Francis [160]).

Thermal effects also interact with molecular relaxations. Babuska et al. [161] mentioned that changes in friction and damping across a wide temperature range (from -150 °C to +175 °C) coincide with the activation of distinct modes of molecular motion (Fig. 30). These transitions reflect the various mobilities of the MAF and the RAF [58]. This interplay defines an operational window in which PTFE maintains a self-replenishing transfer layer without catastrophic softening or brittle failure.

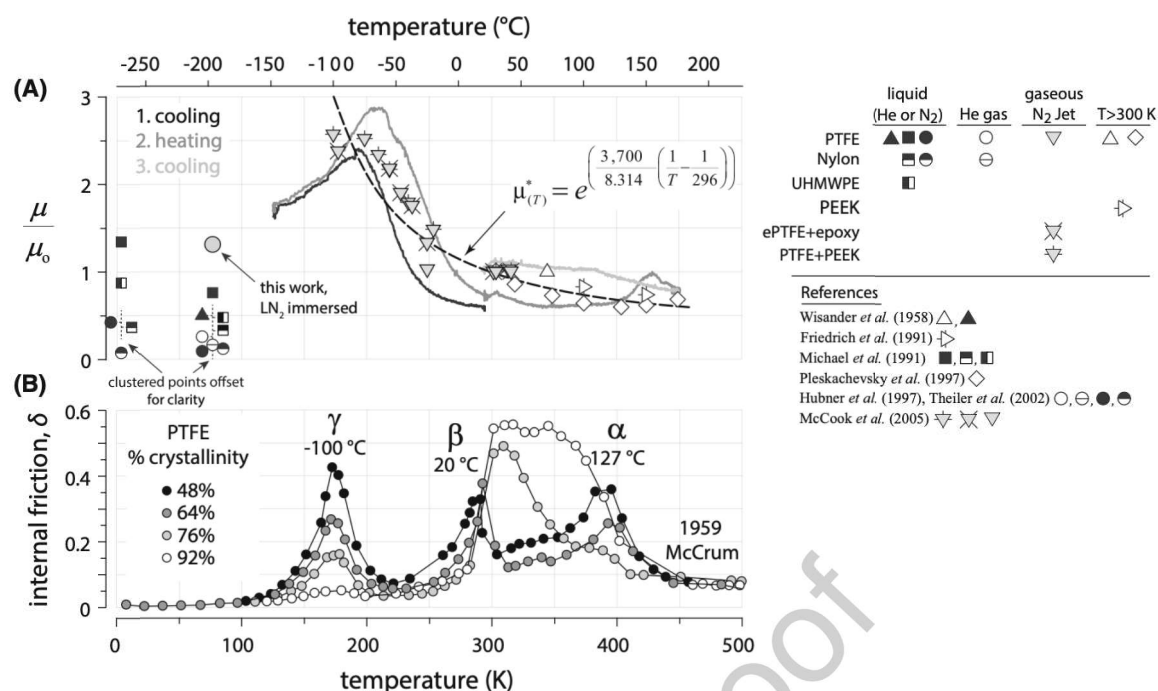


Fig. 30 : A) Normalized temperature-dependent friction of self-mated PTFE (including literature data of other polymers); B) Internal friction from torsional energy dissipation (reprinted with permission from Springer Nature [161]).

Dynamic mechanical analyses by Tan and Stephens [114] confirmed that the storage modulus (E') and loss factor ($\tan \delta$) vary systematically with both temperature and frequency. These rheological trends correlate directly with friction hysteresis, supporting the view that PTFE friction is a bulk-mediated phenomenon. In this framework, the apparent friction coefficient, μ , reflects the superposition of interfacial shear and viscoelastic damping.

Thermomechanical coupling also influences the steady-state friction. Indeed, when the frictional heat exceeds the dissipation capacity, limited by low thermal conductivity of PTFE ($0.25 \text{ W m}^{-1} \text{ K}^{-1}$), melting can propagate into the subsurface, leading to microcracking and sudden friction spikes.

Generally, viscoelastic dissipation and frictional heating strongly condition the formation and durability of the interfacial layer generated during the sliding. The chemical and mechanochemical processes governing this layer are discussed in the following section.

6.2. Tribochemistry and transfer film dynamics

6.2.1. Film formation and evolution

The tribological response of PTFE is fundamentally governed by the formation and evolution of its transfer film. The initial stages of transfer-film development are dominated by subsurface cracking and the release of fibrillar or platelet-like debris. Several studies indicate that such debris progressively compact and evolve under shear and frictional heating, yielding a transfer film whose interfacial region becomes enriched in degraded (partially defluorinated and carbon-enriched) fragments that adhere strongly to metals bearing native or tribo-oxidized surface layers (e.g., $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ on steel, Al_2O_3 on aluminum alloys, and TiO_2 on titanium alloys) [151,160,162].

Tribochemical interactions between defluorinated polymer fragments and the native oxides of the counterface further stabilize the film. Lu et al. [151] identified inorganic–organic complexes formed by such reactions that lower interfacial energy and promote film attachment. The morphology and cohesion of the resulting film depend sensitively on the interfacial chemistry and on the continuity of debris supply.

Environmental conditions also influence film stability. Johansson et al. [163] observed that humid and oxygen-rich atmospheres destabilize the transfer layer and increase the wear. In contrast, dry nitrogen favors thinner yet more cohesive films, underscoring the importance of tribo-oxidation in governing film integrity (Fig. 31).

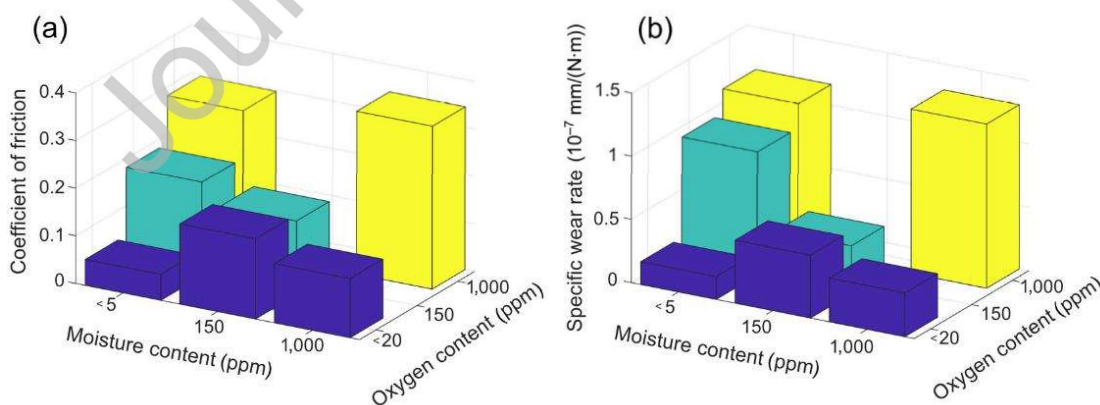


Fig. 31 : (a) Coefficient of friction and (b) specific wear rate of PTFE filled with carbon fibers in different environmental conditions (reprinted with permission from Springer Nature [163]).

Thermal effects further shape film evolution. Local heating at asperity contacts softens or partially melts the near-surface region of PTFE, promoting flow into the tribolayer and

facilitating compaction. However, excessive thermal accumulation accelerates chemical degradation. Liu et al. [164] reported that irradiated or heavily degraded PTFE forms dense carbonaceous residues that limit film mobility and may ultimately compromise lubrication.

6.2.2. Tribochemical and mechanochemical interactions

At the molecular scale, the tribochemical activity of PTFE is commonly attributed to shear-driven C–F bond scission. Although the exact stress required for bond cleavage is difficult to quantify experimentally, numerous studies support the homolytic formation of carbon-centered radicals during sliding [150,164]. These reactive species undergo secondary reactions with counterfacial oxides, atmospheric oxygen, and adjacent PTFE chains, yielding partially defluorinated and oxidized fragments.

Defluorination represents the key tribochemical pathway. Lu et al. [151] and other IR spectroscopic studies [162,163], reported the emergence of C–CF_x, C=O, and C–O–C functions after prolonged sliding under nominal ambient conditions (Fig. 32). However, the interfacial temperature cannot be assumed to remain at room temperature, and the observed chemistry is consistent with chain scission and mild oxidation enabled by frictional heating. Loss of fluorine increases the polarity and reactivity of degraded PTFE fragments, thereby enhancing adhesion to metallic substrates while also reducing the polymer's intrinsic chemical inertness. The balance between these competing effects is central to long-term interfacial stability.

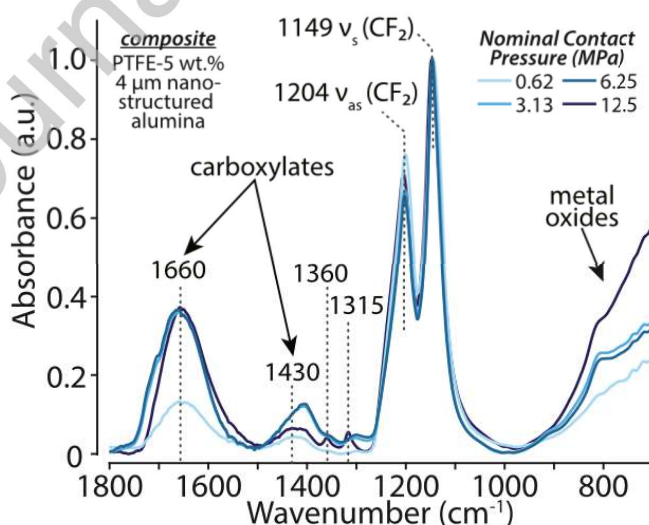


Fig. 32 : IR spectra of the wear surfaces of PTFE filled with 5 wt% 4 μm nanostructured alumina tested at nominal contact pressures of 0.62, 3.13, 6.25, and 12.5 MPa. (reprinted with permission from ELSEVIER [162]).

As previously mentioned, the surrounding atmosphere and its moisture content also modulate tribochemical pathways [163]. This environmental sensitivity explains part of the variability among published wear rates for unfilled PTFE.

These tribochemical processes govern the adhesion, renewal, and durability of the transfer film and therefore provide the mechanistic basis for the use of fillers, irradiation, and surface engineering strategies discussed in the following sections.

6.3. Reinforced and modified PTFE systems

6.3.1. Fiber and particulate reinforcements

Reinforcement with fibers and ceramic particulates has long been the most effective strategy to overcome the inherently high wear rate of virgin PTFE. Since the early development of PTFE composites in the 1960s, systems incorporating glass fibers (GF), carbon fibers (CF), bronze, graphite, and a variety of ceramic fillers (such as alumina, silica, and titanium oxides, *vide-infra*) have been engineered to stabilize the soft polymer matrix, restrict cold flow, enhance load support, and promote the formation of more cohesive transfer films [165].

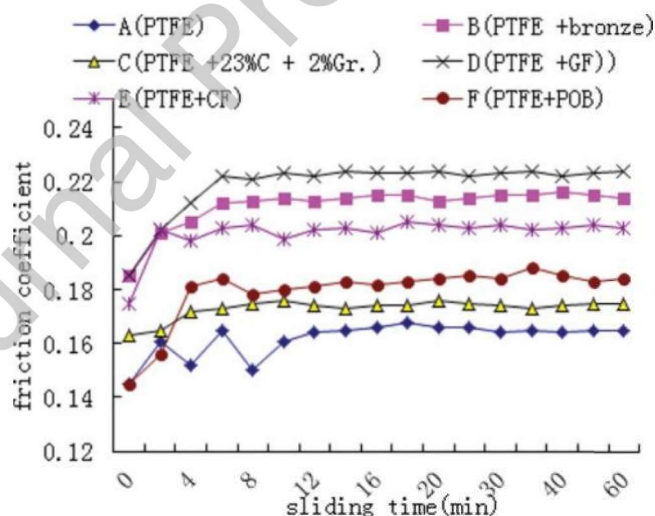


Fig. 33 : Frictional behavior of PTFE and PTFE composites under ambient conditions where C: carbon, Gr: graphite, CF: carbon fiber, GF: glass fiber, and POB: poly-p-oxybenzoyl (reprinted with permission from Taylor & Francis [166]).

Different studies describe how these fillers act through several complementary mechanisms [144,157,166]. Fibers increase stiffness and constrain plastic deformation, particulates enhance counterface conformity and abrasion resistance, and metallic or ceramic additives can anchor

degradation products within the tribofilm. Collectively, these mechanisms disrupt the continuous removal–reformation cycle characteristic of virgin PTFE and greatly extend wear life (Fig. 33).

Previous studies clearly show that the performance of reinforced PTFE depends strongly on filler type, morphology, and interfacial chemistry. Fibrous reinforcements generally provide the most significant improvement in load-bearing capacity, while lamellar or platelet-shaped fillers help to stabilize transfer films. Hybrid formulations that combine fibers with oxides or solid lubricants often induce synergistic effects, producing composites whose friction stability and wear resistance far exceed those of single-filler systems. Across all reinforced systems, improvements arise from a combination of subsurface mechanical stabilization, enhanced heat dissipation, and more cohesive anchoring of the transfer film. These trends and their quantitative outcomes are discussed in detail in the following subsections.

6.3.2. *Glass and carbon fiber reinforcements*

Glass fibers (GF) are among the earliest and the most widely implemented reinforcements for PTFE, valued for their ability to enhance dimensional stability and abrasion resistance while maintaining electrical insulation. Khedkar et al. [167] demonstrated that incorporating 20–25 wt.% GF reduces the specific wear rate of PTFE from 3×10^{-4} to $5 \times 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$, with only a modest increase in the friction coefficient value from $\mu = 0.08$ to 0.12. The performance improvement is due to increased load capacity and to the transfer film being more mechanically anchored, enabling it to resist delamination under shear. Mnif et al. [113] confirmed these effects for GF–MoS₂ hybrids.

Despite these advantages, the brittleness and relatively low thermal conductivity of GF (ca. $1 \text{ W m}^{-1} \text{ K}^{-1}$) can lead to localized heating and microcracking under heavy loads. Carbon fibers (CF) provide a more balanced reinforcement by combining higher stiffness with significantly better thermal conductivity (typically $10\text{--}20 \text{ W m}^{-1} \text{ K}^{-1}$). Their incorporation at 15–25 wt.% generally decreases both friction and wear by enhancing heat dissipation and stabilizing the interfacial layer. Sujuan et al. [166] reported that CF-filled PTFE composites exhibit the lowest and most stable friction traces (μ ranging from 0.09 to 0.12) across a wide temperature range (from 23 to 180 °C) among fiber-reinforced systems. In contrast, GF- and bronze-filled systems display higher and more temperature-sensitive friction coefficients (μ ranging between 0.15–0.30).

Overall, GF- and CF-reinforced PTFE composites typically exhibit friction coefficients in the 0.08–0.15 range and specific wear rates of 10^{-7} to 10^{-9} $\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$, representing several orders of magnitude improvement over virgin PTFE [144]. Achieving optimal performance requires balancing the reinforcement fraction, interfacial bonding, and matrix ductility to maintain PTFE's self-lubricating behavior while maximizing wear resistance.

6.3.3. Particulate and ceramic fillers

Particulate fillers provide an alternative pathway to enhance the mechanical stability and tribochemical robustness of PTFE. Aderikha et al. [168] observed that adding as little as 1 wt.% SiO_2 nanoparticles, decreases the specific wear rate of PTFE by approximately two orders of magnitude, while preserving a low friction coefficient (μ about 0.10) (Fig. 34). At higher loadings (5 wt.%), wear increases again because particle agglomeration disrupts film continuity and promotes local stress concentrations. These observations highlight the importance of achieving a well-dispersed particulate phase. In other words, such improvements critically depend on particle dispersion and interfacial compatibility.

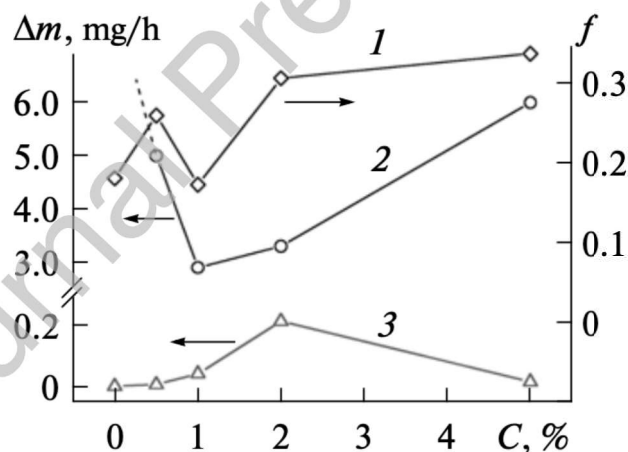


Fig. 34 : Dependences of friction coefficient (1) and wear rates of PTFE–silica composites (2) and steel counterbody (3) on filling degree. The wear rate of the original PTFE is ≈ 630 mg/h (reprinted with permission from Springer Nature [168]).

MoS_2 and graphite fillers function primarily through solid-lubricant mechanisms. Mnif et al. [113] reported that PTFE/ MoS_2 composites maintain friction coefficient values in the range 0.10–0.15 over prolonged cycling, with wear reduced by a factor of 3–5 relative to that of virgin PTFE. Graphite provides comparable friction levels but may exhibit less stable behavior under humid or high-temperature conditions, consistent with its known susceptibility to oxidative degradation.

Ceramic-filled systems also influence transfer-film morphology. Lu et al. [151] demonstrated that oxide surfaces promote the formation of adherent tribofilms enriched in degraded PTFE fragments and iron–oxygen–fluorine species when sliding against steel. These chemically modified films improve interfacial adhesion and help prevent subsurface delamination, a failure mode typically observed in unfilled PTFE.

Hybrid formulations that combine fibers with ceramic or lamellar fillers often display enhanced performance through complementary mechanisms: fibers provide load support and thermal stabilization, whereas particulates improve abrasion resistance and help maintain tribofilm continuity. Although the exact synergy depends on the composite architecture, such systems typically lead to lower friction and more stable wear behavior than their single-filler counterparts.

Quantitatively, particulate-reinforced PTFE composites generally exhibit friction coefficients in the 0.10–0.18 range and specific wear rates between 10^{-7} to 10^{-9} mm³ N⁻¹ m⁻¹. Wear reductions are most pronounced when ceramic particles are well-dispersed and chemically compatible with the matrix, confirming the critical role of microstructural control in achieving durable tribological performance [113,151,168].

6.3.4. *Hybrid, irradiated, and lubricated systems*

The inherent duality of PTFE, characterized by low friction and high wear, has motivated numerous attempts to design materials that combine the polymer's outstanding self-lubrication with enhanced cohesion and thermal stability. Beyond simple fiber or ceramic fillers, recent developments have focused on hybrid composites, radiation-modified PTFE, and lubricated or coating-based systems. Each strategy aims to i) stabilize the tribofilm, ii) improve interfacial bonding, or iii) regulate the energy-dissipation pathways that govern friction and wear.

6.3.5. *Hybrid and multiscale composites*

Beyond single-filler systems, hybrid PTFE materials exploit synergistic effects between fibrous, particulate, and lamellar fillers to combine mechanical reinforcement, enhanced thermal transport, and boundary lubrication within a single multiphase architecture. The goal is to integrate complementary functionalities that individually improve only one aspect of PTFE performance but, together, stabilize friction and suppress wear.

Mnif et al. [113] found that combining GF (15 wt.%) with MoS₂ (5 wt.%) results in significantly lower wear and more stable friction than either constituent alone. The fibers provide structural reinforcement and restrict cold flow, while MoS₂ contributes to additional shear planes that facilitate sliding at asperity contacts. Under dry sliding at 0.1 m s⁻¹ and 20 °C, the friction coefficient remained within the 0.18-0.22 range, while wear decreased by approximately a factor of 3 relative to that of virgin PTFE (Fig. 35).

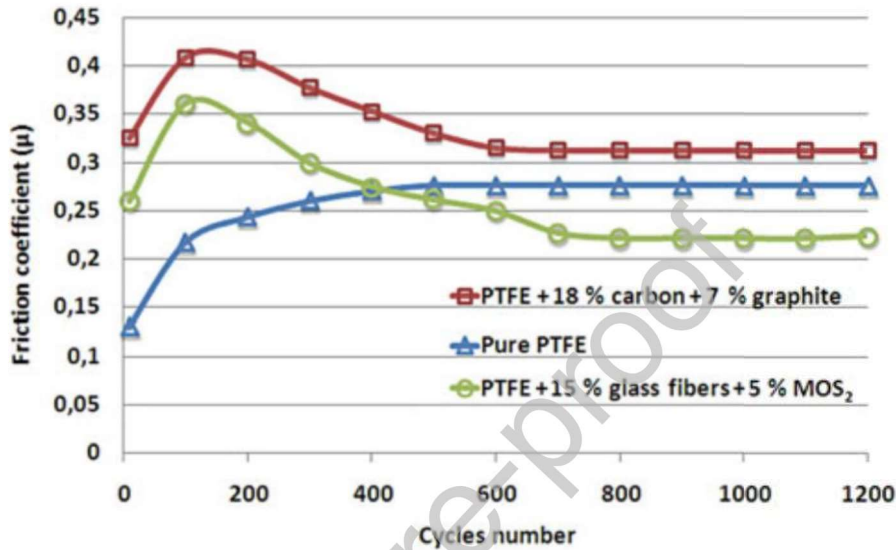


Fig. 35 : Variation of friction coefficient with cycle number for pure PTFE and PTFE composites (reprinted with permission from Taylor & Francis [113]).

Vasilev et al. [169] extended this concept to multiscale systems incorporating carbon fibers, basalt microfibers, and ultrafine PTFE powders. These composites achieved friction coefficients of 0.08-0.10 and exhibited wear rates up to one order of magnitude lower than those of conventional PTFE-CF materials. The improved performance was attributed to the formation of a hierarchical tribofilm in which the large fibers act as a mechanical scaffold. At the same time, the ultrafine PTFE phase fills interstitial gaps, promoting more uniform load transfer. Similar synergistic effects have been reported for other fiber/lamellar combinations [144,166,170].

Hybridization further enables tailoring of thermal behavior. The combination of conductive fillers such as CF, graphite, or bronze with harder ceramic particles (e.g., SiO₂, Al₂O₃) can help to distribute frictional heat more uniformly and reduce localized softening or melting in the near-surface region. Such thermal stabilization has been associated with smoother friction traces and extended steady state sliding regimes in several composite systems [170] (Fig. 36).

In summary, hybrid and multiscale composites illustrate the versatility of PTFE-based systems: by integrating reinforcement, lubrication, and thermal management within a single microstructure, these formulations achieve tribological stability levels unattainable with single-filler materials.

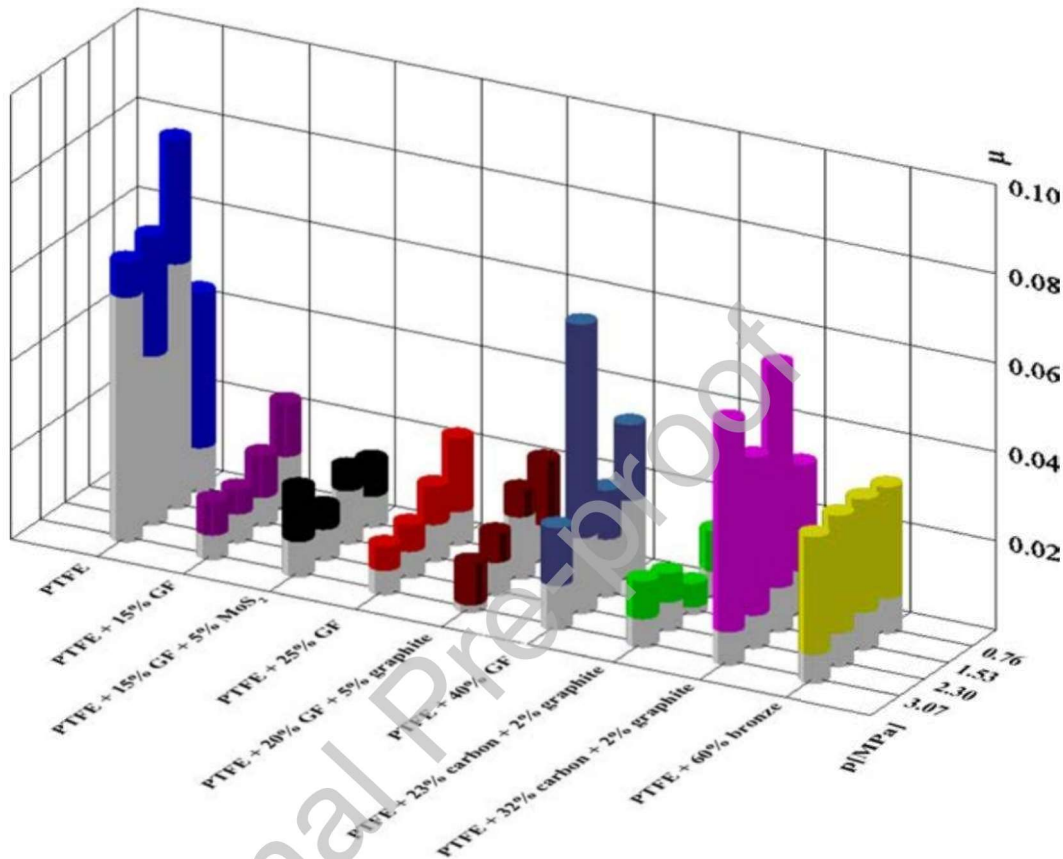


Fig. 36 : Friction coefficient under water lubrication for pure PTFE and various PTFE composites (reprinted with permission from Emerald Publishing [170]).

6.3.6. Radiation-modified and self-reinforced PTFE

An alternative strategy, independent of fillers, is based on radiation processing, including γ -rays, electron beams, and proton irradiation. Irradiation offers a molecular-level strategy to enhance PTFE's tribological behavior without altering its intrinsic low-shear surface chemistry. Controlled irradiation generates radicals, induces local crosslinking, and modifies lamellar organization, thereby improving the cohesion of the transfer film and the resistance of near-surface regions to shear-induced damage [117,171,172].

Tang et al. [173] demonstrated that γ -irradiation leads to partial crosslinking and densification of the PTFE microstructure. Under dry sliding, moderately irradiated samples exhibited a substantial reduction in wear, accompanied by a small increase in friction. However, at high doses, excessive crosslinking and chain scission led to embrittlement and microcracking, underscoring the need to fine-tune irradiation levels to avoid over-modification (Fig. 37).

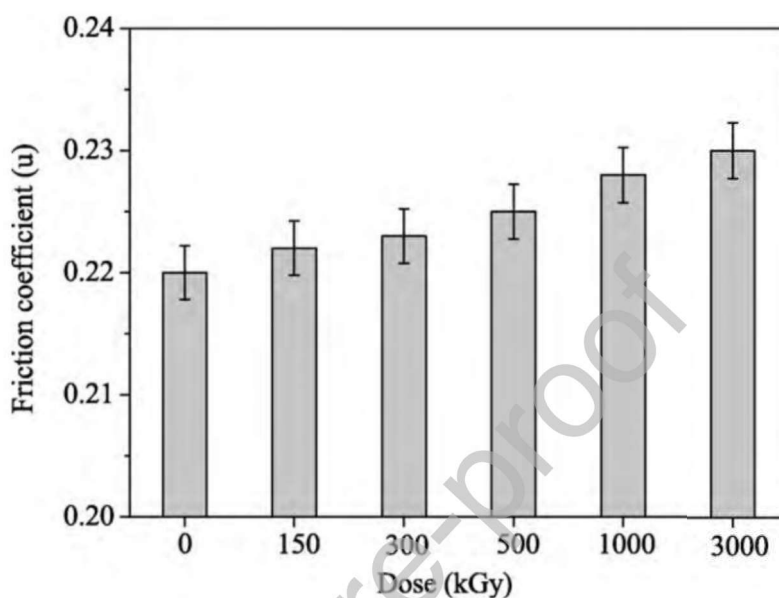


Fig. 37 : Effect of electron beam irradiation dose on average friction coefficient of PTFE samples (reprinted with permission from ELSEVIER [173]).

Chai et al. [171] refined this understanding by identifying an optimal γ -dose near 20 kGy. At this intermediate level, the friction coefficient remained low (about 0.08), while the specific wear rate decreased by approximately a factor of five relative to the pristine polymer. XPS and Raman analyses revealed the formation of CF_2 and CF-CF_x fragments, indicating mild defluorination but no extensive degradation of the helical backbone. These authors attributed the improved tribological stability to the development of a nano-crosslinked lamellar network that resists delamination during cyclic shear.

Proton irradiation induces a different modification pathway. Liu et al. [164] reported that proton-treated PTFE develops a carbon-enriched, partially graphitized surface layer, which increases hardness and reduces susceptibility to subsurface plastic flow. This densified interfacial zone improves wear resistance while maintaining friction below 0.1. Spectroscopic evidence confirmed both a decrease in fluorine content and the formation of carbon-rich domains, consistent with the enhanced compaction and mechanical robustness (Fig. 38).

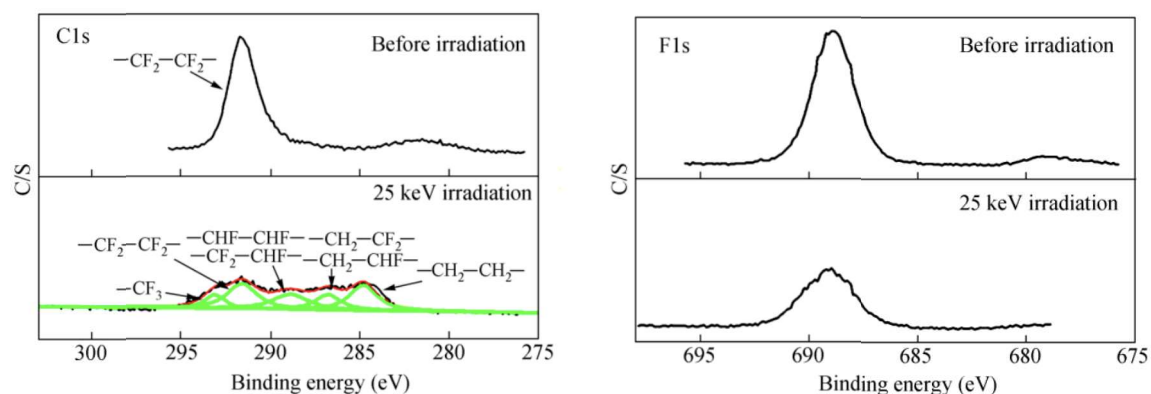


Fig. 38 : C1s and F1s XPS spectra of PTFE before and after proton irradiation (reprinted with permission from Springer Nature [164]).

A complementary approach to molecular modification was proposed by Wang et al. [174], who developed self-reinforced PTFE (SR-PTFE) by incorporating a small fraction (<8 wt.%) of pre-irradiated γ -ray-treated PTFE powders into the blend. The irradiated particles possessed residual radicals and partially crosslinked lamellae, enabling interdiffusion and chemical bonding with the virgin matrix during sliding. At an optimal loading of 4 wt.%, the composite exhibited a 43% reduction in wear and a 9% decrease in the friction coefficient compared with unmodified PTFE. SEM and XPS analyses revealed a dense and cohesive tribofilm enriched in compacted PTFE nanofragments and mixed Fe–O–F species when sliding on steel. At higher loadings (>8 wt.%), particle agglomeration led to embrittlement and reduced performance. This self-reinforcing strategy offers a unique route to enhance PTFE durability while maintaining chemical homogeneity, effectively bridging the gap between classical filler reinforcement and intrinsic molecular modification.

Together, these studies demonstrate that radiation-modified PTFE—whether *via* direct irradiation or self-reinforcing architectures—enhances tribological performance by improving the cohesion, chemical stability, and load-bearing capacity of the transfer film. By tuning the radical density, lamellar crosslinking, and interfacial chemistry, radiation-based approaches broaden the design space for PTFE tribomaterials beyond what is achievable with traditional fillers alone [117,164,171,172].

6.3.7. Coating-based and hybrid film systems

A fundamentally different approach uses coating-based designs to extend the benefits of PTFE lubrication to metallic or ceramic substrates. Such a method involves embedding the fluoropolymer in polymeric binders or hybrid organic–inorganic matrices. Unlike bulk

composites, where load support arises from the filler–matrix architecture, coating systems rely on controlled interfacial bonding, film integrity, and the progressive release of PTFE-rich debris to sustain a low-shear interface during sliding.

McCook et al. [175] demonstrated that incorporating expanded PTFE (ePTFE) into epoxy films produces a self-lubricating coating in which fibrillated PTFE acts as a reservoir of low-shear material. The improved performance results from enhanced crack resistance, improved film compaction, and PTFE debris' ability to maintain a continuous tribofilm on the counterface.

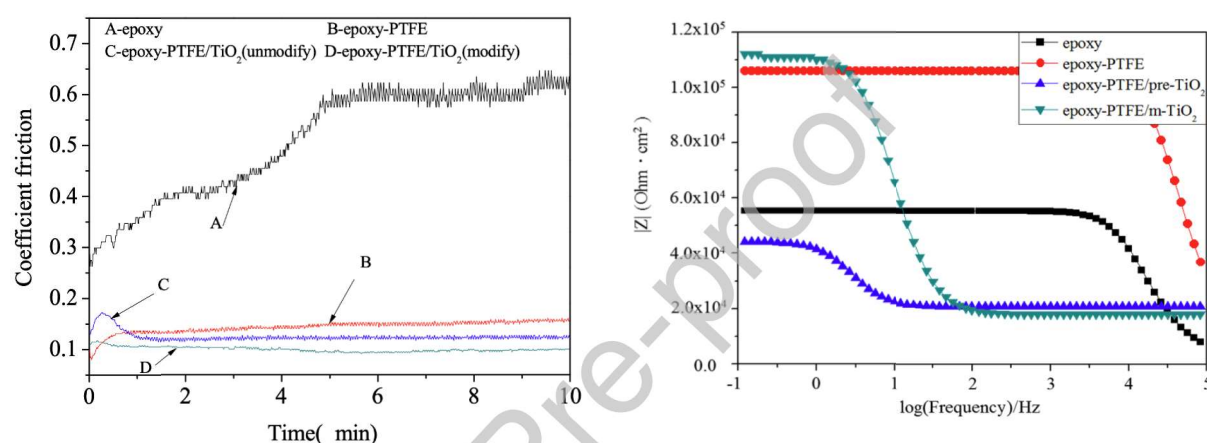


Fig. 39 : Friction coefficients and electrochemical impedance of the coatings in a Bode diagram (reprinted with permission from MDPI [176]).

Ying et al. (2020) [176] reported similar improvements in epoxy–PTFE composite coatings reinforced with silane-modified TiO₂ nanoparticles. The combined presence of PTFE and well-dispersed TiO₂ reduced the friction coefficient from $\mu \approx 0.22$ to 0.10 and significantly enhanced wear resistance, while also improving corrosion protection through coating densification and enhanced interfacial compatibility (Fig. 39).

For harder substrates such as cemented carbides, PTFE-based coatings provide an effective route to suppress direct hard–hard contact. Wang et al. [177] deposited PTFE coatings on YT15 cemented carbide using a PAI binder and spray processing, followed by thermal curing, and reported a marked reduction and stabilization of the friction coefficient under dry sliding against WC/Co balls: the uncoated carbide typically exhibited COF values around 0.35–0.45, whereas the PTFE-coated specimens remained around ca. 0.09–0.15 depending on load and speed. The improvement was attributed to the presence of a low-shear PTFE-rich surface layer and reduced