

adhesive wear and plowing on the substrate. However, coating delamination/flaking remained the dominant wear mode at higher loads.

Together, these coating strategies illustrate how the intrinsic lubricity of PTFE can be integrated into rigid or conductive environments through appropriate binder selection and filler design. Composite PTFE-based films thus broaden the polymer's relevance for wear-resistant, corrosion-protective, and multifunctional surface-engineering applications.

6.3.8. Lubricated and superlubricated systems

Liquid lubrication and ionic-liquid-assisted interfaces provide an alternative pathway to reduce interfacial shear stresses in PTFE-based systems drastically. When combined with appropriate protic ionic liquids (PILs), PTFE composites can reach superlubricity—commonly defined as a friction coefficient below 0.01—by forming ordered, low-shear interfacial films that cannot be achieved under dry conditions. Zheng et al. [178] demonstrated robust macroscale superlubricity in a PTFE/steel tribopair lubricated with green protic ILs, achieving friction coefficients below 0.008 under specific laboratory conditions and strongly suppressed PTFE wear compared with conventional oils (e.g., polyalphaolefin PAO and polyethylene glycol PEG). Surface analyses supported the formation of a low-shear interfacial structure combining (i) an IL-derived interfacial layer (often rationalized as a dense Stern layer) and (ii) a tribochemical film on the steel counterface, consistent with a lubrication regime dominated by boundary film stability rather than solid transfer (Fig. 40).

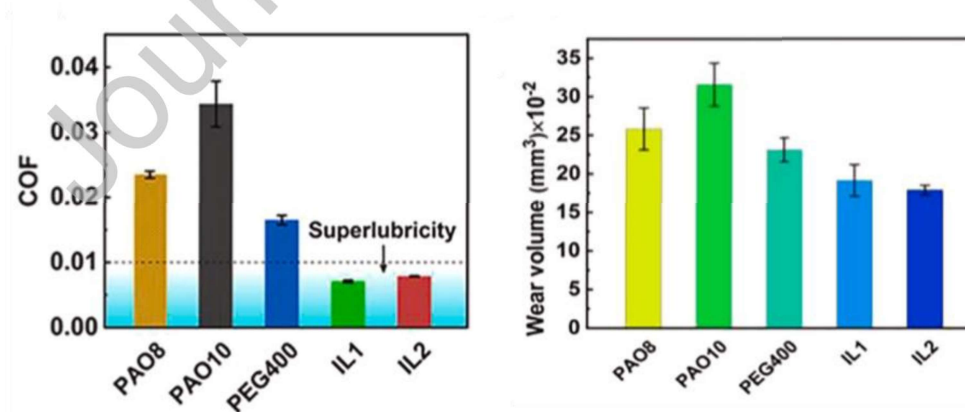


Fig. 40 : Left: Average friction coefficients of PTFE/stainless steel tribo-pair under lubrication of different lubricating oils (PAO8, PAO10, PEG4000) compared with ionic liquids (IL1 and IL2) under 5 N, 5 Hz. Right: Corresponding wear volumes vs these lubricating oils (reprinted with permission from ELSEVIER [178]).

Then, IL lubrication reveals that even trace amounts of reactive molecular species can reorganize the PTFE/metal interface, achieving friction levels several orders of magnitude

lower than those attainable with dry sliding. These findings open promising routes for engineering adaptive, low-shear, liquid-mediated interfaces in PTFE-based tribosystems.

6.3.9. *Summary of performance ranges*

Taken together, these strategies illustrate how mechanical reinforcement, chemical modification, and interfacial engineering can be combined to stabilize PTFE tribosystems. Their relative effectiveness and limitations are compared in the following section.

6.3.10. *Comparative analysis and design guidelines*

Across the wide range of PTFE-based systems described above, tribological performance can be rationalized in terms of three coupled mechanisms: (i) mechanical stabilization of the near-surface region, (ii) tribochemical anchoring and regeneration of the transfer film, and (iii) control of interfacial energy dissipation, either through viscoelastic damping or fluid-mediated lubrication. The best-performing materials are therefore not those with the lowest intrinsic friction, but those that maintain a cohesive, low-shear transfer layer over long sliding distances and under varying operating conditions. Because each stabilization mechanism becomes active at different length and time scales, PTFE systems tend to improve in a stepwise manner as additional reinforcement, chemical functionality, or lubrication pathways are introduced. Materials that resist transfer-film rupture, either by reinforcing the bulk, enhancing interfacial chemistry, or adding a fluid boundary layer, exhibit the most stable steady-state friction traces and the lowest wear rates [157,162,167,170].

6.3.11. *Performance hierarchy*

A comparison of the different approaches reveals a consistent performance hierarchy:

- *Virgin PTFE*: It exhibits excellent intrinsic lubricity ($\mu \approx 0.04\text{--}0.10$) but severe wear ($k \approx 10^{-4}\text{--}10^{-3} \text{ mm}^3\cdot\text{N}^{-1}\cdot\text{m}^{-1}$), reflecting the instability of its mechanically weak transfer film [152,159,179,180].
- *Fiber- and particulate-filled materials*: Adding glass or carbon fibers, bronze, or micro-sized ceramics reduces wear by one to two orders of magnitude, with a slightly higher friction coefficient (0.10–0.20) [156,157,167].

Table 6 : Representative friction and wear ranges and dominant stabilization mechanisms of PTFE-based systems

System type	Typical composition	Typical friction coefficient μ	Typical specific wear rate k ($\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$)	Dominant stabilizing mechanism	Key refs
Virgin PTFE	Neat polymer	0.04–0.10	10^{-4} – 10^{-3}	Low shear strength but weak cohesion; unstable transfer film	[150,151,156,157]
Fiber-filled PTFE	PTFE + GF or CF (≈ 15 – 25 wt%)	0.10–0.20	10^{-5} – 10^{-7}	Load sharing + subsurface stabilization; improved film compaction	[144,156,166,167]
Particulate / ceramic-filled PTFE	PTFE + Al_2O_3 / SiO_2 / TiO_2 (≈ 1 – 20 wt%)	0.10–0.18	10^{-7} – 10^{-9*}	Restricted plastic flow + tribochemical anchoring (metal fluorides)	[144,159,160,162,168]
Hybrid composites	GF + MoS_2 ; CF + Al_2O_3 / graphite	0.08–0.15	10^{-7} – 10^{-9}	Mechanical skeleton + boundary lubrication + film stabilization	[113,144,169,170]
Radiation-modified PTFE	γ /e-beam/proton irradiated PTFE	0.07–0.12	10^{-6} – 10^{-8}	Crosslinking/graphitization; improved cohesion of debris and film	[164,171,173]
Self-reinforced PTFE	PTFE + modified PTFE microphase (≈ 2 – 8 wt%)	≈ 0.08 – 0.11	10^{-6} – 10^{-7}	Cohesive “self” tribofilm via PTFE/PTFE interphase strengthening	[174]
Coating-based systems	Epoxy-PTFE, PTFE/ceramic coatings	0.12–0.18	10^{-7} – 10^{-9} (system-dependent)**	PTFE reservoirs + cohesive binder; added corrosion protection	[175–177]
Lubricated / IL-assisted contacts	PTFE composite + protic IL	0.006– 0.02	“below detection” / extremely low	Dual boundary layer + tribochemical fluid film	[178]

where GF, CF, PAI, and IL stand for glass fiber, carbon fiber, polyamide-imide, and ionic liquid, respectively.

* 10^{-7} – 10^{-9} is achievable in optimized nanofilled systems but remains strongly dependent on dispersion and operating conditions.

** For coatings, “specific wear rate” sometimes refers to wear depth per unit distance or per unit mass loss; comparisons must be made with caution.

- *Nanofilled and hybrid bulk composites:* Combining fibers, nanoparticles (SiO_2 , Al_2O_3), or lamellar solid lubricants (MoS_2 , graphite) yields low wear rates with μ comprised between 0.08 and 0.12 [144,168,169]. These systems derive their performance from synergistic mechanical and tribochemical stabilization of the transfer film.
- *Radiation-modified and self-reinforced PTFE:* γ -irradiation, electron-beam irradiation, or proton irradiation can emulate the performance of hybrid composites by creating crosslinked or graphitized surface layers. For optimized doses (i.e. tens to a few hundred kGy), wear can decrease by two to three orders of magnitude with minimal change in friction [164,171,173,174]. The advantages are the chemical homogeneity and the reduced filler/matrix mismatch.
- *Coating-based systems:* PTFE dispersed in epoxy or ceramic-rich matrices are characterized by μ values ranging from 0.12 to 0.18, while wear and corrosion resistance are improved.
- *Lubricated and ionic-liquid-mediated sliding:* With suitable protic ionic liquids, PTFE composites can enter the superlubricity regime with negligible wear, supported by the formation of a self-organized bilayer tribofilm [178]. But, system lifetime is then governed by lubricant stability rather than by the polymer.

Putting these classes together, a practical performance ranking for bulk materials can be constructed as follows: virgin PTFE < conventional fiber/microfilled composites < nanofilled and hybrid composites < radiation-modified or self-reinforced materials.

Coating-based and lubricated systems can surpass bulk materials in specific environments, but only when adhesion and lubricant chemistry are strictly controlled. The hierarchy thus reflects not only intrinsic material properties but also the robustness of the complete tribosystem.

Table 6 summarizes representative ranges of friction and wear, along with the dominant stabilization mechanisms for each class of PTFE-based system.

6.3.12. Dominant mechanistic factors

Across all PTFE-based systems (filled, hybrid, irradiated, coated, or lubricated), three mechanistic pillars consistently govern tribological performance. These principles repeatedly emerge from the literature and represent the common foundation underlying durable, low-friction, low-wear behavior.

- *Stabilization of subsurface deformation:* Durable PTFE systems consistently suppress subsurface shear localization, which otherwise triggers fibrillation, crack initiation, and transfer-film rupture. Mechanical stabilization can arise from fiber skeletons [156,157,167], ceramic inclusions that restrict plastic flow [162,168], or irradiation-induced crosslinking that reinforces lamellar cohesion [164,171,173]. Despite their different origins, these mechanisms converge toward the same outcome: creation of a coherent near-surface zone that limits cold-flow wear and maintains transfer-film attachment.
- *Control of interfacial thermal fields:* Transfer-film stability requires that flash temperatures remain within a limited operational window. High-conductivity fillers, such as CFs, graphite, or bronze [144,166,170], help to distribute frictional heat, preventing localized melting and thermal softening of the PTFE matrix. In contrast, systems dominated by insulating phases (glass fibers, SiO₂) exhibit greater sensitivity to thermal instabilities unless hybridized with conductive phases [169]. The most stable composites are those that homogenize the interfacial temperature field, thereby avoiding the oscillatory friction and episodic film rupture commonly observed in unfilled PTFE [157].
- *Regulation of tribochemical reactions:* Long-term wear resistance correlates strongly with the ability to balance interfacial reactivity. Beneficial tribochemical processes, such as the formation of metal fluorides (AlF₃, FeF₂) or oxide-enriched boundary layers, anchor the film and promote its renewal [151,162]. However, excessive reactivity can lead to embrittlement or oxidative depletion of the film. This balance can be tuned through the catalytic surfaces (e.g., alumina, titania), irradiation [171,173], or fluid-mediated boundary layers such as protic ILs [178], all of which improve transfer-film adhesion and continuity. The best-performing systems tend to exhibit self-regulated tribochemistry, neither too inert nor overly degradative.

Together, these comparative trends highlight that durable PTFE tribosystems are not defined by a single material parameter but by the coordinated tuning of mechanical stability, thermal

management, and interfacial chemistry. These insights provide the basis for the unified discussion presented in the following section.

6.4. General discussion and concluding remarks

The tribological response of PTFE emerges from a delicate interplay between molecular mobility, tribochemical activation, and mechanically driven film renewal. Across all PTFE-based systems, virgin, reinforced, irradiated, or hybrid, the persistence of a cohesive, low-shear transfer film is the central determinant of long-term friction and wear performance.

6.4.1. Unified mechanism

PTFE tribology can be rationalized as a self-regulating cycle in which mechanical shear generates debris. Then, tribochemical reactions anchor this debris to the counterface, and the resulting film protects the underlying polymer from further degradation.

6.4.2. Dominant parameters

Three main groups of parameters consistently govern the performance:

- Microstructure and mechanics.
- Thermal and tribochemical factors.
- Environmental.

Ultimately, long-term tribological stability in PTFE systems is achieved when interfacial renewal, mechanical integrity, and thermal dissipation evolve in a mutually compatible manner under sliding.

7. Surface, wettability, and adhesion

Objects manufactured from pure PTFE exhibit inherent hydrophobicity and low surface adhesiveness [181]. Hydrophobic polymers are generally identified by static water contact angles exceeding 90°. For PTFE, static contact angles measured on smooth, clean, sintered surfaces are typically in the 108-114° range [182], and values approaching ca. 118-120° have also been reported for unmodified PTFE [183]. Interestingly, according to Zhang et al. [183], stretching PTFE can drive the material surface into the superhydrophobic regime, with apparent contact angles up to ca. 165°, consistent with roughness-amplified wetting (Cassie–Baxter-type behavior). Hydrophobicity can also be enhanced through ion-plating treatments applied to PTFE coatings [184]. The origin of PTFE's hydrophobic behavior lies in the minimal

polarizability of its chains and the resulting low surface energy, which prevents strong specific interactions (e.g., hydrogen bonds) with water. This is consistent with the critical surface tension of PTFE, experimentally determined to be among the lowest reported for any solid polymer, in the range of ca. 18-20 mN/m [185]. However, PTFE wettability can be markedly altered in the presence of surfactants, which reduce the liquid–vapor surface tension and can adsorb at the solid–liquid interface, thereby lowering the effective interfacial tension. Various classes of surfactants –nonionic (e.g., Triton X100, Triton X165), cationic (cetyltrimethylammonium bromide, pinacyanol bromide), anionic (sodium dodecyl sulfate), and zwitterionic– have been studied, encompassing both hydrocarbon- and fluorocarbon-based molecules. The extent to which surfactant-containing aqueous solutions wet PTFE depends strongly on surfactant chemistry [186].

Because PTFE engages only weakly in van der Waals interactions, organisms such as ants and geckos, whose climbing abilities rely on these forces, exhibit limited adhesion on PTFE surfaces [187,188]. This same lack of intermolecular attraction also explains why conventional adhesives fail to bond to PTFE. Surface modification is possible, however, either by incorporating small quantities of comonomers or by applying various post-treatments to the material, including electron-beam irradiation [117,189], UV photon-exposure [190], glow-discharge processes [191,192], jet-plasma treatments [193], wet-chemical methods [194], and grafting techniques [195]. PTFE's surface properties are often reported to depend more strongly on surface conditions (cleanliness, roughness, oxidation/defluorination, and processing defects) than on molar mass or as-polymerized microstructure. In practice, surface-property measurements are almost always performed on sintered sheets or films, where defects introduced during shaping can dominate the results. Nevertheless, potential links between powder morphology (e.g., rod-like vs. spherical particles), dispersity, and the resulting surface/topography remain insufficiently studied, constituting a clear gap in the literature.

Although PTFE is often taken as the benchmark, its contact angle should be interpreted in the broader context of fluorinated polymers (FPs) to identify underlying structure–surface property relationships. Fig. 41 illustrates the wetting behavior of polar protic liquids on FP surfaces [196]. For fully FPs, the measured contact angles lie within experimental uncertainty ($\pm 2^\circ$), rendering them essentially indistinguishable. This convergence reflects the dominance of a CF_2 -rich surface layer with extremely low polarizability and negligible specific interaction capability.

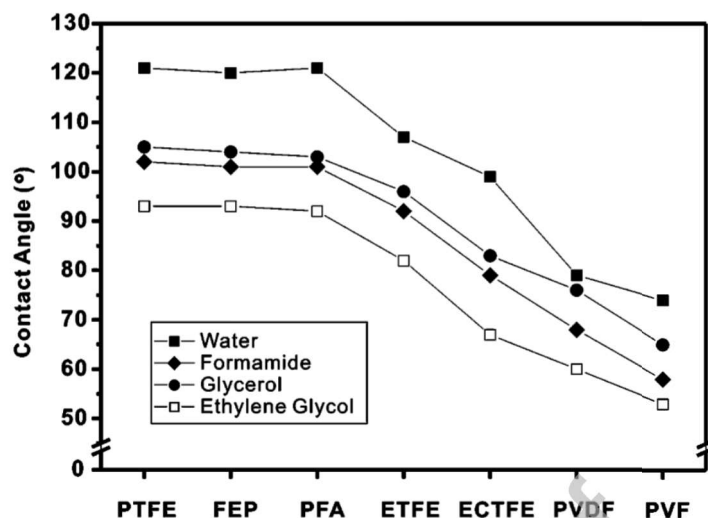


Fig. 41 : Advancing contact angles of various liquids on the surfaces of fluoropolymers. Polar protic liquids: water (filled squares), formamide (filled diamonds), glycerol (filled circles), and ethylene glycol (open squares) (reprinted with permission from ACS [196]).

In contrast, partially FPs exhibit progressively higher wettability as the surface chemistry departs from a fully fluorinated environment. Poly(vinylidene fluoride) (PVDF) and poly(vinyl fluoride) (PVF) exhibit the highest wettability within this class due to the presence of surface dipoles associated with C–H and C–F bond asymmetry, as well as acidic hydrogen atoms. These features enable multiple modes of interaction with contacting liquids, including dipole-dipole, dipole-induced dipole, and acid-base interactions (notably hydrogen bonding). Poly(ethylene-*co*-chlorotrifluoroethylene copolymer (ECTFE), which contains a substantial density of weak dipoles, displays intermediate wettability: higher than that of ETFE, whose dipoles are fewer and weaker, yet lower than those of PVDF and PVF [196].

Calleja et al. [197] further examined the evolution of ETFE surface properties upon fluorination. Hydrophobicity and lipophobicity were characterized using dynamic contact angle measurements with water and diiodomethane via advancing–receding protocols (Table 7). Fluorinated ETFE samples, particularly ETFE-f150 (fluorinated at 150 °C), and to a lesser extent ETFE-f95 (fluorinated at 95 °C), exhibited higher advancing and receding angles. This trend indicates a reduction in surface free energy due to enrichment of fluorinated groups at the outermost surface. The simultaneous increase in apparent contact angle hysteresis is consistent with nanoscale roughness amplification effects, where fluorination modifies both chemistry and topography.

Table 7 : Water and Diiodomethane Dynamic Contact Angle Values for ETFE (virgin), ETFE-f95 (fluorinated), ETFE-f150 (fluorinated), and PTFE (reprinted with permission from WILEY [197]).

	Water			ICH2I		
	θ_a	θ_r	H	θ_a	θ_r	H
ETFE-f95	99.2 $\pm$ 4.0	68.3 $\pm$ 4.2	31.0	73.3 $\pm$ 10.7	54.5 $\pm$ 6.9	18.8
ETFE-f150	111.5 $\pm$ 8.9	90.8 $\pm$ 3.2	20.7	92.8 $\pm$ 5.0	79.0 $\pm$ 6.1	13.7
ETFE	96.8 $\pm$ 8.0	60.3 $\pm$ 8.3	36.5	66.7 $\pm$ 2.5	52.2 $\pm$ 11.2	14.6
PTFE	81.4 $\pm$ 3.3	50.5 $\pm$ 3.3	30.9	69.4 $\pm$ 7.0	53.7 $\pm$ 6.4	15.7

A more comprehensive understanding of PTFE surface-liquid interactions can be obtained by complementing contact angle data with an analysis based on Hansen Solubility Parameters (HSP) [198]. HSP describes intermolecular interactions through three contributions: dispersive (δ_D), polar (δ_P), and hydrogen-bonding (δ_H), which together define a three-dimensional Hansen space. While initially developed to rationalize bulk solubility behavior, HSP can also provide a practical semi-quantitative framework for interpreting trends in interfacial affinity. HSP values are typically obtained experimentally from solubility or swelling tests, or estimated using group-contribution methods [199]. Fig. 42 positions PTFE within Hansen space alongside reference liquids, where higher contact angles indicate lower affinity. This Figure combines a pseudo-3D representation with a projected color map, in which contact angles are color-coded as low (gray to purple: 0-30°), intermediate (blue to green: 30-90°), and high (yellow to red: 90-120°). Because PTFE is not soluble in conventional solvents (section 2), its Hansen parameters are commonly inferred from swelling-based approaches rather than accurate dissolution tests. For PTFE (with $\delta_D=16.20$, $\delta_P=1.80$, and $\delta_H=3.40$ (J/cm³)^{1/2}, grade L80 CR) [199], the location in Hansen space is clearly separated from polar and hydrogen-bonding liquids such as water, formamide, and ethylene glycol, consistent with its chemical inertness and weak specific interactions.

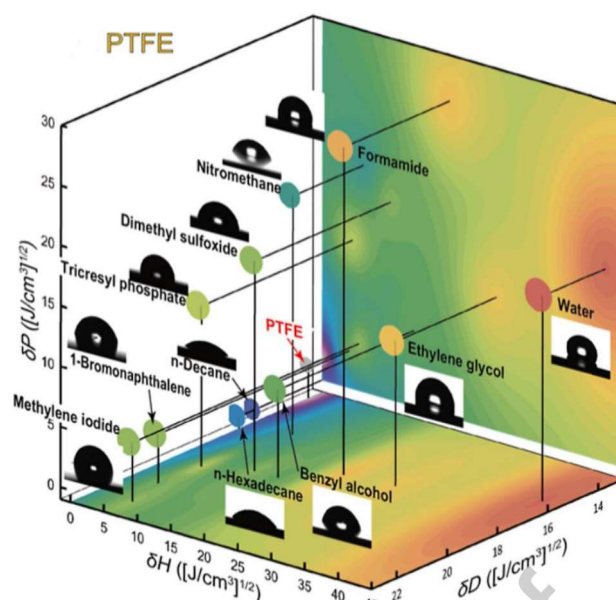


Fig. 42 : Pseudo 3D plot of probe liquids in HSP space with Cartesian coordinates (δ_D , δ_P , and δ_H axes), where contact angles on polymer substrate (images shown in insets) of PTFE are color-coded (wetable: gray-purple, intermediate: blue-green, repelling: yellow-red). The projection of contact angles to the δ_H - δ_D and δ_H - δ_P planes is drawn in the same color as that in the pseudo 3D plots; the data-deficient region was interpolated using graphing software. The surface HSPs of polymers determined via linear regression using the least-squares method between experimental contact angles and estimated ones (for various δ_D , δ_P , and δ_H values) are plotted as those for ideally wettable liquids with a contact angle of 0° (in gray) (reprinted with permission from ACS [198]).

Experimental contact angles were measured using the sessile drop method on polymer films or plates corresponding to materials for which bulk HSP have been determined. It is essential to distinguish bulk HSP, which describe cohesive energy density within the material volume from effective surface HSP, which reflect only the outermost molecular layers probed in wetting experiments. Surface HSP values were obtained by fitting contact angle data using least-squares regression, adjusting the δ_D , δ_P , and δ_H values to define an “ideally wetting” condition (i.e., a contact angle of 0° as shown in gray) (Fig. 42). Although this approach involves approximations, it provides a practical route to map surface-affinity trends within the same Hansen framework used for bulk materials, thereby enabling a unified interpretation of PTFE’s low wettability in terms of both cohesive and interfacial energetics.

By correlating contact angle measurements of probe liquids on PTFE with their Hansen parameters, this representation provides a structured way to interpret PTFE’s surface affinity, within the same energetic framework used for bulk interactions. Rather than describing actual solubility behavior, the approach provides a relative scale of interfacial compatibility, highlighting PTFE’s position at the extreme low-polarity and low-hydrogen-bonding edge of Hansen space.

To extend this framework to interfacial phenomena, several formulations have been proposed to estimate liquid and solid surface energies, as well as their interfacial energy, from surface energy components. Among these, the geometric-mean approach of Owens and Wendt [200] proposed the surface free energy as the sum of dispersive and polar contributions and remains widely used due to its simplicity, while more recent treatments extend this logic to the three-component HSP framework described above. Contact angles predicted from such relations, using bulk HSPs derived from solubility or swelling data, have been compared with experimentally measured values obtained using sessile-drop methods. The generally good correlations observed across diverse polymer–liquid systems suggest that, despite the conceptual gap between bulk cohesive parameters and surface properties, HSP-based approaches can serve as a useful semi-empirical tool for rationalizing trends in wettability and interfacial energy. Nevertheless, these models do not explicitly account for surface reconstruction, chemical heterogeneity, or roughness effects, which can significantly influence contact-angle measurements. As such, HSP-based predictions should be regarded as a complementary interpretative framework rather than a substitute for direct surface characterization.

8. Electrical and dielectric properties of PTFE

8.1. Position of PTFE among polymer dielectrics

From an electrical standpoint, PTFE represents an extreme case among polymer dielectrics (Fig. 43). Unlike most organic polymers, whose dielectric behavior results from a combination of dipolar orientation, segmental mobility, and free-volume fluctuations, PTFE exhibits an almost purely electronic polarization mechanism. Its fully fluorinated $-\text{CF}_2-$ backbone suppresses permanent dipoles and rotational degrees of freedom, leading to a dielectric response that remains essentially invariant with frequency and temperature [201,202].

Consequently, PTFE exhibits a remarkably stable relative permittivity (ϵ_r) between 2.0 and 2.1 with extremely low dielectric losses ($\tan \delta < 10^{-4}$ over a broad frequency range). Its dielectric breakdown strength E_{bd} typically ranges from 40 to 60 $\text{kV}\cdot\text{mm}^{-1}$ for bulk specimens with thicknesses of 0.5–1 mm ([203,204]).

When normalized to permittivity, the normalized dielectric strength (E_{bd} / ϵ_r) reaches ca. 25 $\text{kV}\cdot\text{mm}^{-1}$ per unit ϵ_r , significantly higher than those of common insulating polymers such as PE

($\approx 12 \text{ kV}\cdot\text{mm}^{-1}$) or polyimide ($\approx 8 \text{ kV}\cdot\text{mm}^{-1}$). This combination of low polarizability and high breakdown strength places PTFE among the most efficient polymeric insulating materials.

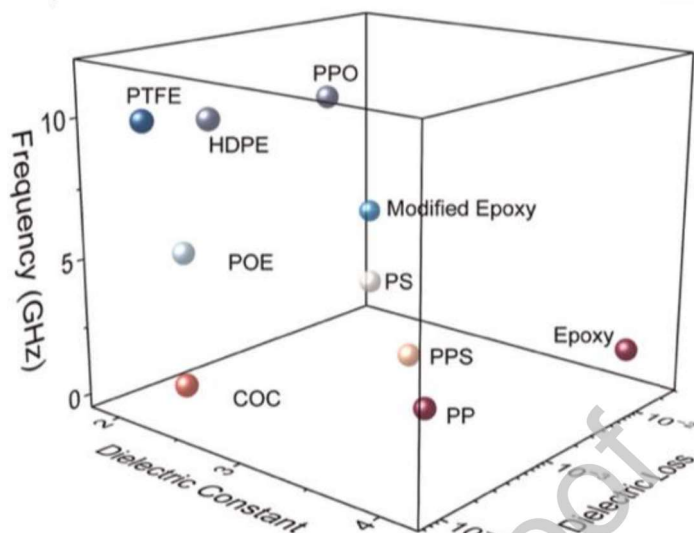


Fig. 43 : Comparative dielectric properties of different polymers (reprinted with permission from ELSEVIER [205]).

Compared with other polymer families, the contrast is pronounced. PE and polypropylene (PP) have slightly higher permittivity ($\epsilon_r \approx 2.3\text{--}2.4$) but stronger temperature dependence due to increased chain mobility above 80°C . Polymers containing polar functional groups, such as polyimides or polyetherimides (PEI), exhibit higher permittivity ($\epsilon_r \approx 3.2\text{--}3.5$) and significantly higher dielectric losses resulting from dipolar relaxation processes [202,205,206].

Among fluoropolymers, the dielectric behavior varies widely. PVDF exhibits ferroelectric polarization associated with its β phase, leading to ϵ_r values up to 12–13 and a pronounced frequency dispersion [207]. By contrast, melt-processable fluoropolymers such as FEP and PFA retain moderate permittivity values ($\epsilon_r \approx 2.1\text{--}2.3$) but generally show slightly higher dielectric losses due to reduced crystallinity and structural defects.

The molecular origin of the exceptional dielectric stability of PTFE lies in the highly symmetric helical conformation of its chain and the high bond energy of the C–F bond (ca. $485 \text{ kJ}\cdot\text{mol}^{-1}$), which suppresses orientational polarization and limits molecular mobility. Combined with its high crystallinity ($>90\%$) and density (ca. $2.2 \text{ g}\cdot\text{cm}^{-3}$), this structure yields a nearly ideal non-polar dielectric medium.

8.2. Intrinsic dielectric response of bulk PTFE

The dielectric response of bulk PTFE has been investigated for more than seven decades, with a remarkable consistency across studies despite variations in processing route, crystallinity, and molar mass [118,201,205,208].

Early measurements established a relative permittivity ϵ_r close to 2.05 and dielectric losses below 2×10^{-4} over the frequency range 50 Hz–3 MHz [201,209]. Later, broadband dielectric spectroscopy extending to gigahertz frequencies confirmed the absence of dipolar or space-charge relaxation within the accessible measurement window [210].

Minor variations reported in the literature (ϵ_r ranging from 2.00 to 2.15) are mainly attributed to microstructural heterogeneity, such as porosity or incomplete sintering. Samples containing residual voids may exhibit slightly higher apparent permittivities due to local electric-field distortions [210] (Fig. 44). Conversely, highly dense, crystalline PTFE consistently exhibits $\epsilon_r \approx 2.05$ [201,202].

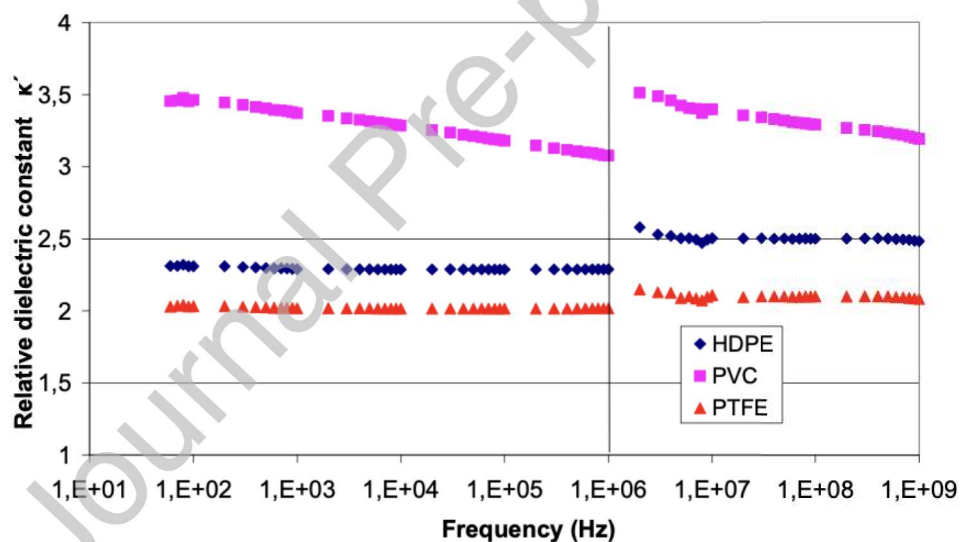


Fig. 44 : Relative dielectric constant results vs. frequency of PTFE and compared to HDPE and PVC. The vertical line at 1 MHz marks the boundary between the two measurement setups (reprinted with permission from IEEE [210]).

The absence of dielectric dispersion over a wide frequency range reflects the lack of orientational polarization. In PTFE, the only available polarization mechanisms are electronic ($\approx 10^{15}$ Hz) and vibrational ($\approx 10^{13}$ Hz), both occurring well beyond the frequency range typically explored in dielectric spectroscopy.

Temperature has only a minor influence on the dielectric response. Measurements between $-100\text{ }^{\circ}\text{C}$ and $+250\text{ }^{\circ}\text{C}$ show that ϵ_r varies by less than 2 %, while $\tan \delta$ remains below 10^{-4} until temperatures approaching the melting point [206,208].

This stability reflects the predominance of electronic polarization, described by:

$$P_e = \epsilon_0 (\epsilon_r - 1) E \quad (\text{eq 4})$$

where P_e is the electronic polarization density ($\text{C}\cdot\text{m}^{-2}$), ϵ_0 the permittivity of free space ($8.85 \times 10^{-12} \text{ F}\cdot\text{m}^{-1}$), ϵ_r the relative permittivity of the material, and E the applied electric field [202,206].

8.3. Breakdown strength and electrical aging

The dielectric breakdown strength, E_{bd} , of PTFE has been extensively investigated because it reflects both the intrinsic electronic stability of the polymer and the influence of microstructural defects. For dense bulk specimens (thickness 0.5–1.0 mm), typical values range between 40 and 60 $\text{kV}\cdot\text{mm}^{-1}$ [203,204]. However, reported values vary significantly across the literature, from about 20 $\text{kV}\cdot\text{mm}^{-1}$ in porous or heterogeneous samples to more than 200 $\text{kV}\cdot\text{mm}^{-1}$ in thin films ($<50\text{ }\mu\text{m}$) [118,211,212].

These variations highlight the composite nature of dielectric breakdown, which depends not only on the intrinsic electronic properties but also on the defect density, surface morphology, and testing conditions.

8.3.1. Thickness dependence and measurement dispersion.

Breakdown measurements performed according to IEC 60243 reveal a weak inverse dependence on sample thickness, approximately following a power-law dependence:

$$E_{bd} \propto t^{-0.15} \quad (\text{eq 5})$$

where t denotes the sample thickness [206].

This trend reflects the statistical probability of defect initiation rather than a fundamental material limit: thicker samples contain a higher density of structural heterogeneities, such as voids, inclusions, or surface defects, that can concentrate the electric field.

Consequently, direct comparison of breakdown values across studies without reporting sample thickness or measurement geometry often leads to misleading conclusions. Thin PTFE films

(20–50 μm) commonly reach 150–220 $\text{kV}\cdot\text{mm}^{-1}$, whereas sintered blocks of 1–2 mm thickness rarely exceed 50 $\text{kV}\cdot\text{mm}^{-1}$, even when produced from identical polymer grades [203,204,212] (Fig. 45).

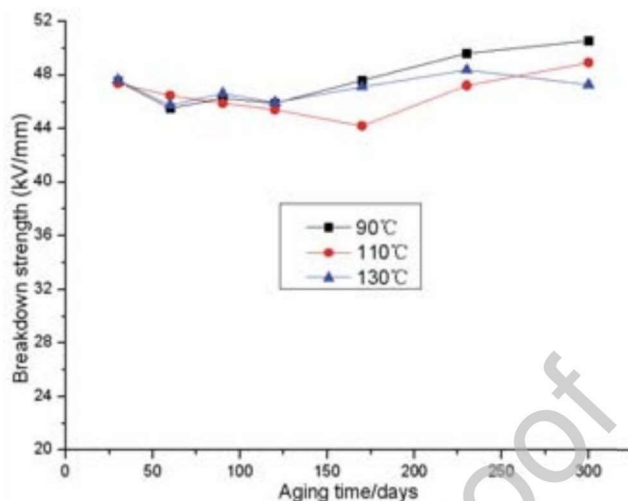


Fig. 45 : Breakdown field strength of PTFE films (thickness = 0.5 mm) *versus* aging time under three aging temperatures (reprinted from IEEE [204]).

Experimental conditions also influence the measured values. Flat electrodes generally produce lower breakdown fields than spherical electrodes due to edge effects, whereas air gaps at the electrode–polymer interface can initiate premature discharge. When measurements are performed in insulating oil or under vacuum, breakdown strengths may increase by 10–20%, illustrating the sensitivity of PTFE to local-field amplification [118].

8.3.2. *Electronic versus thermal breakdown mechanisms.*

Breakdown mechanisms in PTFE differ significantly from those observed in hydrocarbon polymers. Because of its large electronic band gap ($\approx 8\text{--}9$ eV) and low charge-carrier mobility, pure electronic avalanche breakdown is relatively unlikely under normal conditions. Instead, failure often follows a thermo-electronic mechanism, in which localized Joule heating at defect sites initiates partial bond scission within the polymer backbone [204,212].

Decomposition of C–F bonds produces volatile fluorocarbon fragments, such as CF_2 and CF_3 radicals, which facilitate the formation of a conductive channel. Post-mortem analyses typically reveal localized carbonization cones confined to regions of 10–50 μm around the discharge site, without an extensive macroscopic cracking [203].

The high crystallinity of PTFE (>90 %) further restricts electron transport. Charge carriers remain largely confined to amorphous interlamellar regions, where conduction processes are thermally activated rather than electronic in nature [118,202,206].

At extremely high electric fields ($>150 \text{ kV}\cdot\text{mm}^{-1}$), impact ionization can occur, leading to a rapid increase in current and thermal runaway within nanoseconds [118,206]. However, such conditions are rarely encountered in practical applications due to PTFE's low permittivity and moderate thermal conductivity (ca. $0.25 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), which limit the local energy density.

Generally, dielectric breakdown in PTFE should therefore be regarded not as a single intrinsic constant but as a statistically distributed property governed by defect population, microstructure, sample thickness, and testing protocol [118,203,212].

8.3.3. Aging mechanisms: corona and humidity effects

Long-term electrical endurance is one of the distinguishing features of PTFE relative to most engineering polymers. Under prolonged alternating current stress or corona discharge, degradation generally remains superficial. For example, Wei et al. [204] reported that after 300 days of exposure at 130°C under an electric field of $20 \text{ kV}\cdot\text{mm}^{-1}$, the breakdown strength decreased by less than 10 %. In comparison, epoxy insulation systems under identical conditions induced reductions exceeding 60 %.

Similarly, repetitive arc discharges produce only a thin carbonized surface layer, while the bulk polymer retains most of its insulating properties [212]. This behavior reflects PTFE's chemical inertness and low surface energy, which limit charge accumulation and inhibit the propagation of electrical treeing.

Moisture has a negligible influence on PTFE dielectric properties. Owing to its extremely low surface energy (ca. $18 \text{ mJ}\cdot\text{m}^{-2}$) and strong hydrophobicity (water contact angle $\approx 115\text{--}120^\circ$), water uptake remains below 0.01 wt.%. Consequently, dielectric losses remain largely unchanged even under high-humidity conditions, unlike in polar polymers such as polyimides or polyamides [231].

8.4. Temperature and radiation effects on dielectric stability

8.4.1. Thermal dependence and phase transitions.

The outstanding dielectric performance of PTFE is maintained over an exceptionally wide temperature range, from cryogenic conditions to temperatures near its melting point (ca. 327 °C). Unlike most organic polymers, whose dielectric properties are strongly influenced by dipolar relaxation or thermally activated conduction, PTFE exhibits only minor variations in permittivity and dielectric losses with temperature. Dielectric measurements performed between -200 °C and +300 °C show that the real permittivity, ϵ' , varies by less than 2 %, while the loss tangent remains below 10^{-4} over most of this range [201,206,208,209]. This remarkable stability arises from the absence of permanent dipoles and the predominance of electronic polarization in PTFE.

A weak dielectric anomaly is nevertheless observed near 19 °C, corresponding to the well-known crystalline phase transition from phase II to phase IV (see section 2). During this transition, the helical pitch of the $-\text{CF}_2-$ chain slightly changes, producing only a small increase in permittivity (<1 %) while dielectric losses remain essentially unaffected [120,201,208].

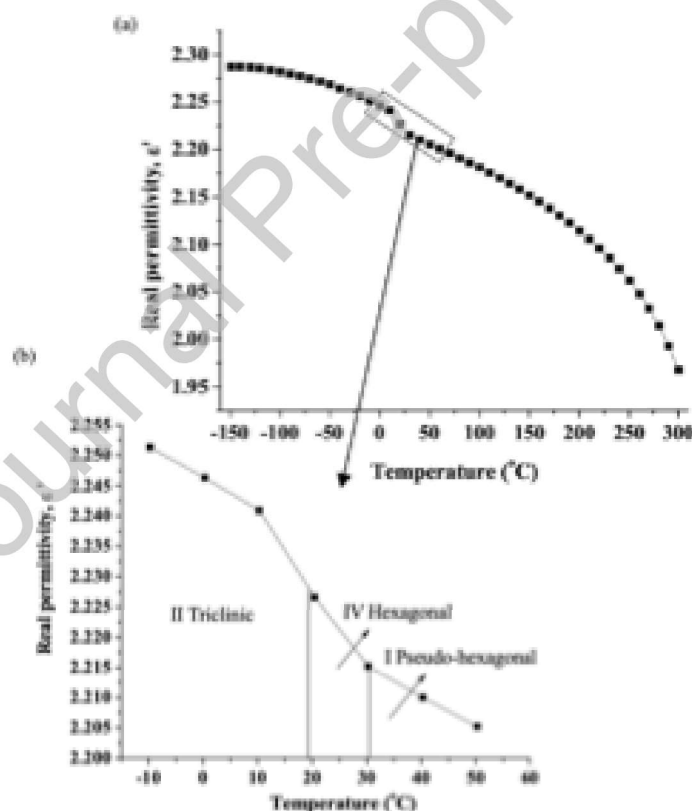


Fig. 46 : Real permittivity of PTFE as a function of temperature at 1.15 kHz. (a): -150 to 300 °C; (b): -10 to 50 °C (reprinted with permission from IEEE [208]).

At higher temperatures (100–250 °C), PTFE retains extremely low dielectric losses despite structural rearrangements such as lamellar thickening or limited chain mobility detected by

DSC and X-ray diffraction [101,110]. Only when temperatures approach the melting point does the electrical conduction begin to increase significantly, leading to a rapid rise in dielectric losses.

This thermal stability exceeds that of most polymer dielectrics. For example, PE and polyimide typically exhibit dielectric losses that increase by one to two orders of magnitude above 150–200 °C due to dipolar relaxation and thermally activated conduction processes.

8.4.2. Radiation-induced modifications.

The dielectric behavior of PTFE under ionizing radiation has been extensively studied in the context of nuclear and aerospace insulation [108,109,118]. Radiation exposure generates a combination of chain scission, crosslinking, and defluorination reactions that alter the polymer microstructure and local electronic density.

At moderate irradiation doses (10–100 kGy), chain scission predominates, particularly in amorphous regions [117]. The formation of radical species ($-\text{CF}_2\bullet$ and $-\text{CF}\bullet$) slightly increases permittivity and dielectric losses as localized polar groups or defects appear within the material. Under these conditions, ϵ_r typically increases from about 2.05 to approximately 2.15, while $\tan \delta$ may reach values close to 5×10^{-4} [108,109,118] (Fig. 47).

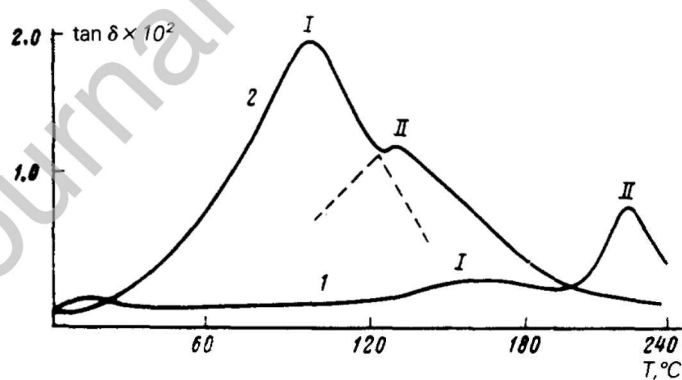


Fig. 47 : Plot of $\tan \delta$ vs temperature for irradiated PTFE at 300Hz. (1) γ -Irradiation in vacuum, dose 150 kGy; (2) γ -irradiation in air, dose 100 kGy (reprinted with permission from ELSEVIER [118]).

At higher doses (>500 kGy), crosslinking reactions compete with chain scission. Infrared and ESR analyses reveal the formation of $-\text{CF}_3$ end groups and carbon–carbon crosslinks, producing a denser but more defective crystalline texture [207,210] (Fig. 48). These structural changes generally lead to a moderate decrease in dielectric breakdown strength (20–30 %) due to the accumulation of defect sites that facilitate the charge injection.

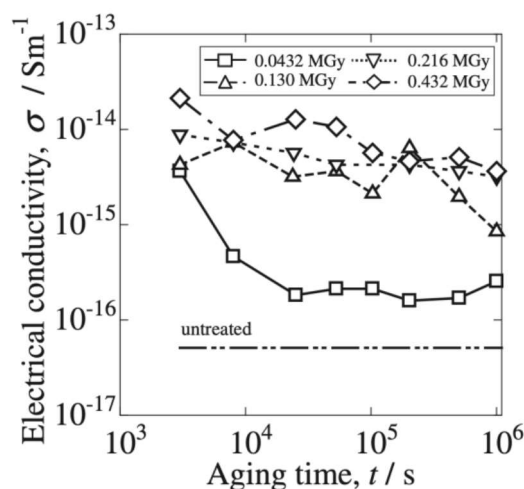


Fig. 48 : Effects of aging time on electrical conductivity of electron beam irradiated PTFE samples at various doses (reprinted with permission from the Japan Institute of Metals [207]).

Interestingly, part of the radiation-induced damage can be reversed by thermal annealing at temperatures above 300 °C. Under these conditions, volatile fluorocarbon fragments are removed, and recrystallization of partially degraded regions can occur, restoring part of the initial dielectric properties [118,204].

8.4.3. Coupled thermo-radiative degradation mechanisms

In environments such as nuclear reactors or space systems, PTFE may be exposed to simultaneous elevated temperatures and ionizing radiation. Under such combined conditions, radical mobility increases, and chain scission processes can accelerate. Studies report moderate increases in dielectric losses ($\tan \delta \approx 10^{-3}$) and permittivity values approaching $\epsilon_r \approx 2.3$ after very high radiation doses (ca. 10^6 Gy), although these values remain lower than those observed in most hydrocarbon polymers under similar conditions.

The dominant degradation pathway involves localized depolymerization of the PTFE chain. Polymer-bound $-\text{CF}_2\cdot$ radicals that undergo β -scission to form highly reactive difluorocarbene ($:\text{CF}_2$), which rapidly recombines to produce volatile TFE molecules, which diffuse out of the matrix [117].

Despite these structural modifications, PTFE generally retains its insulating character even under severe irradiation. The limited impact on dielectric properties reflects the fundamental electronic origin of polarization in PTFE, which is relatively insensitive to moderate changes in molecular topology.

8.5. Composite and filled PTFE systems

Although pristine PTFE is one of the most stable dielectric materials known, its relatively low permittivity ($\epsilon_r \approx 2.05$) and poor thermal conductivity (ca. $0.25 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) restrict its use in certain electronic and microwave devices. Consequently, numerous studies have led to the development of PTFE-based composites incorporating ceramic or carbon fillers in order to tailor their dielectric and thermal properties while maintaining their insulating performance. In such heterogeneous systems, the dielectric response is governed not only by the intrinsic permittivity of the filler or its loading fraction but also by the morphology of the composite and the quality of the filler-matrix interface.

Because PTFE is chemically inert and non-polar, untreated fillers generally interact weakly with the polymer matrix, which may lead to interfacial voids and local electric-field amplification. These heterogeneities promote interfacial charge accumulation, often described as Maxwell–Wagner–Sillars polarization, thereby increasing dielectric losses.

For this reason, the design of PTFE composites relies heavily on interface engineering. Surface functionalization of fillers using silane coupling agents, titanates, or bio-inspired coatings such as polydopamine has proven particularly effective in improving dispersion and interfacial adhesion [213–216]. When interfacial compatibility is improved, moderate increases in permittivity can be achieved while maintaining low dielectric losses.

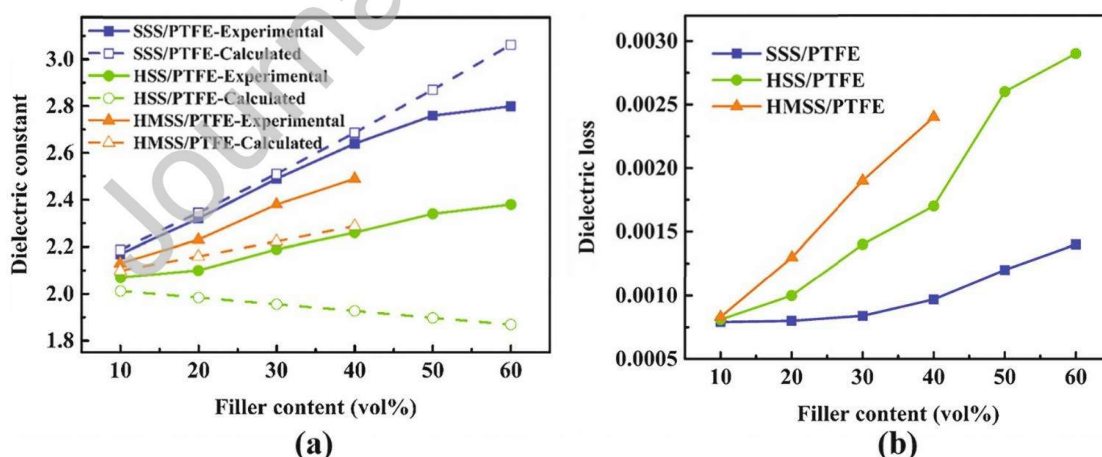


Fig. 49 : Dielectric properties variations of SiO₂/PTFE composites with different SiO₂-based filler contents: a) dielectric constants, b) dielectric losses, where HSS, HMSS, and SSS stand for hollow silica spheres, hollow mesoporous silica spheres, and solid silica spheres, respectively (reprinted with permission from Springer Nature [215]).

8.5.1. Oxide and silicate fillers

Silica-based composites are among the most extensively investigated PTFE dielectric systems because they offer a favorable compromise between permittivity enhancement and low dielectric losses. For example, Chen et al. [82] reported that PTFE–SiO₂ composites containing nanoscale silica increased ϵ_r from approximately 2.1 to about 2.35 while maintaining dielectric losses near 6×10^{-4} at microwave frequencies.

Surface functionalization of silica particles further improves composite performance by reducing interfacial porosity and promoting homogeneous dispersion. Various treatments using silane coupling agents or related modifiers have been reported to yield ϵ_r values of 2.5–2.6, with $\tan \delta$ typically below 10^{-3} (Fig. 49) [213,215,217,218].

More recently, fluorinated interfacial layers have been proposed to enhance compatibility between PTFE and oxide fillers. Jin et al. [219] demonstrated that surface fluorination of SiO₂ particles using pentafluorostyrene significantly reduces interfacial porosity and lowers dielectric losses to approximately 1.5×10^{-3} at 40 GHz while maintaining $\epsilon_r \approx 2.38$ (Fig. 50).

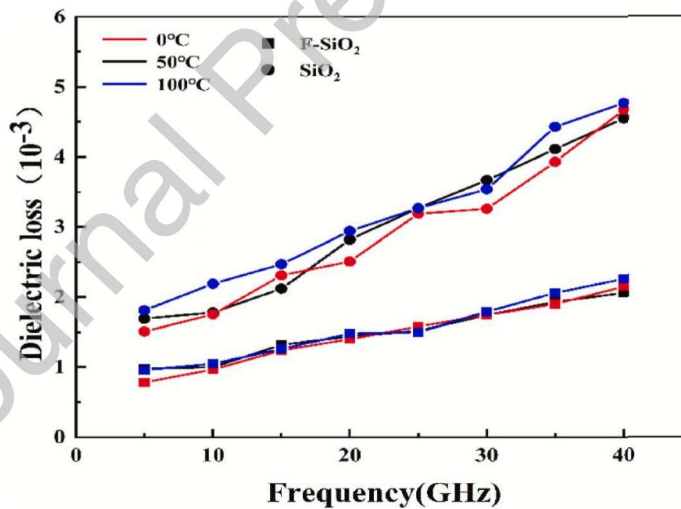


Fig. 50 : Dielectric properties of F–SiO₂/PTFE composite with 5 wt.% pentafluorostyrene (PFS) varying with temperature (reprinted with permission from ELSEVIER [219]).

8.5.2. Thermally conductive nitrides

In recent years, electrically insulating but thermally conductive fillers such as boron nitride (BN) and aluminum nitride (AlN) have attracted considerable attention [86]. These materials combine moderate dielectric constants ($\epsilon_r \approx 4$ –5) with very high thermal conductivity.

Hybrid PTFE composites containing BN and AlN can increase thermal conductivity up to $1.5 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, nearly six times higher than that of neat PTFE, while maintaining relatively low dielectric losses ($\tan \delta \approx 8 \times 10^{-4}$) and breakdown strengths above $40 \text{ kV} \cdot \text{mm}^{-1}$ [86,220].

The success of these systems lies in their ability to enhance phonon transport without introducing electrically conductive pathways.

8.5.3. *Conductive fillers*

Conductive nanofillers such as carbon nanotubes (CNTs), graphene, or metallic nanoparticles can significantly increase permittivity even at low loadings. However, these materials rapidly approach the percolation threshold.

For example, CNT contents above ca. 1 vol% typically produce dramatic increases in dielectric losses and a sharp decrease in breakdown strength due to the formation of conductive networks [221]. Surface-modified CNTs coated with silica or polydopamine can partially suppress this effect, allowing moderate permittivity enhancement ($\epsilon_r \approx 3.2$) while keeping $\tan \delta$ close to 10^{-3} [216].

Nevertheless, the trade-off between permittivity enhancement and dielectric stability remains a fundamental limitation of conductive fillers.

8.5.4. *Role of the interphase*

In PTFE composites, the interfacial region between filler and polymer matrix plays a decisive role in determining the dielectric behavior. Because PTFE lacks reactive functional groups, a strong interfacial bonding must be engineered through the surface treatments such as plasma activation, sodium–naphthalene etching, or coupling agents.

Experimental and modeling studies suggest that an interphase layer with a thickness of 5–20 nm and intermediate permittivity often occurs around the functionalized fillers [215,219]. This interphase acts as a dielectric buffer that reduces electric-field concentration and suppresses the charge trapping. For instance, Luo et al. [214] demonstrated that adding a titanate coupling agent to $\text{Li}_2\text{Mg}_3\text{TiO}_6$ (LMT)-filled PTFE improved ϵ_r uniformity (2.4–2.6) and reduced $\tan \delta$ by 50 % (Fig. 51).

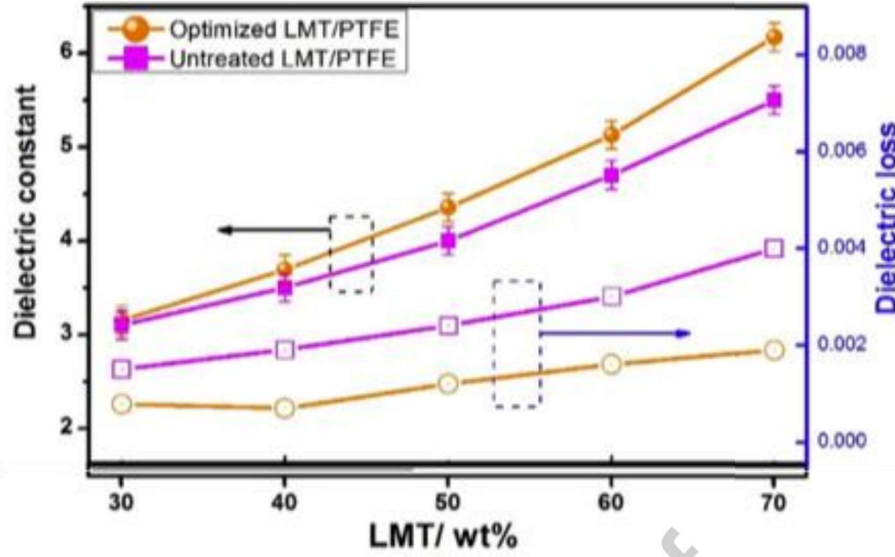


Fig. 51 : The variation of dielectric properties with LMT loading content for optimized and untreated LMT/PTFE composites (reprinted with permission from ELSEVIER [214]).

As a result, the macroscopic dielectric properties of PTFE composites cannot be described solely by simple mixture rules but instead emerge from the complex interplay between filler morphology, interface structure, and microstructural continuity.

8.5.5. Comparative evaluation

When data are compiled, several quantitative tendencies emerge and can be summarized in Table 8.

These results clearly indicate that interface-controlled systems, such as $\text{SiO}_2/\text{PDA}/\text{PTFE}$ or BN/AlN hybrids, offer the optimal balance between permittivity enhancement and loss suppression. In contrast, high-k ceramics ($\epsilon_r > 20$) rarely yield practical advantages because interfacial mismatch introduces parasitic conduction and reduces the breakdown field.

8.6. Frequency and high-frequency behavior

8.6.1. Frequency dispersion in pristine PTFE

The dielectric response of PTFE remains remarkably stable over an exceptionally broad frequency range. From a few hertz up to several tens of gigahertz, PTFE preserves an almost constant permittivity ($\epsilon' \approx 2.04\text{--}2.06$) together with extremely low dielectric losses (i.e., $\tan \delta < 10^{-4}$) [201,202,208,222,223] (Fig. 52).

Table 8 : Non-exhaustive list of fillers in PTFE

Filler type	ϵ_r (10 GHz)	$\tan \delta$ ($\times 10^{-4}$)	E_{bd} ($\text{kV}\cdot\text{mm}^{-1}$)	Remarks	Ref
None (Neat PTFE)	2.05	< 1	50–60	Reference	[201–204,209,222]
SiO ₂ (20 vol %)	2.4–2.6	3–8	45–55	Low-loss, stable	[82,215]
Al ₂ O ₃ (20 vol %)	3.0–3.3	10–20	40–50	Increased loss	[224,225]
Mg ₂ SiO ₄ (40 vol %)	4.5–4.8	20	35–45	High ϵ_r , degraded Ebd	[143]
BN + AlN hybrid (30 vol %)	3.0	8	40–50	High thermal conductivity	[86,220]
CNT (0.5 vol %)	3.2	10–50	20–30	Onset of percolation	[216,221]
SiO ₂ /PDA (20 vol %)	2.6	5	55–60	Best compromise	[215,216,219]

where PDA stands for polydopamine.

This frequency independence reflects the absence of dipolar relaxation processes in PTFE. Because polarization arises almost exclusively from electronic displacement of electrons within the C–F bonds, the characteristic relaxation frequencies lie in the optical range and remain far beyond the frequency window typically explored in dielectric spectroscopy.

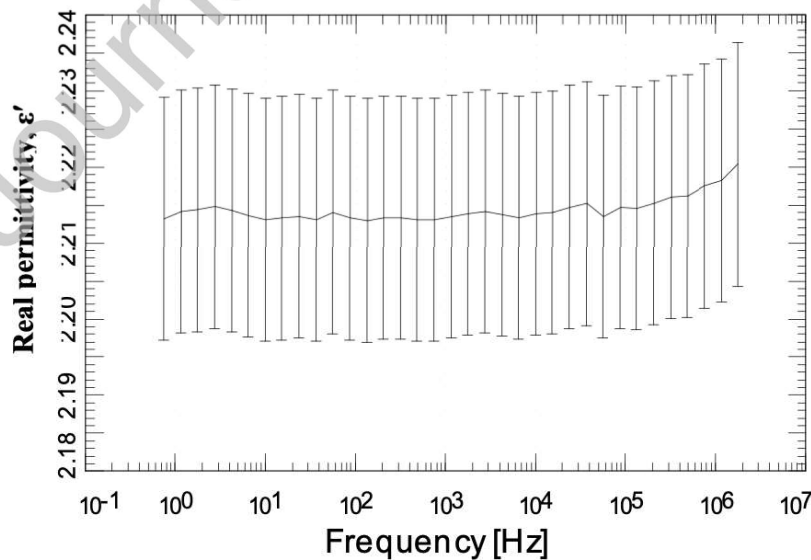


Fig. 52 : Real permittivity of PTFE as a function of frequency at room temperature (reprinted with permission from IEEE [208]).

Even at microwave frequencies approaching 100 GHz, only very small variations in permittivity are observed, generally below $\Delta\epsilon \approx 0.02$. These changes are associated with weak lattice-vibration contributions rather than with classical dielectric relaxation.

8.6.2. High-frequency performance of PTFE composites

The introduction of ceramic fillers slightly modifies the dielectric response of PTFE but generally preserves its remarkable frequency stability. In oxide- or nitride-filled systems, the relative permittivity typically increases from about 2.1 to 2.5-3.0 while remaining nearly frequency-independent across the microwave range [215,225].

Dielectric losses increase only moderately in these composites, with $\tan \delta$ values typically ranging from 4×10^{-4} to about 1.5×10^{-3} at 10 GHz. These values remain significantly lower than those observed in most engineering polymers containing polar functional groups, such as polyetherimide, polysulfone, polycarbonate, or polyetheretherketone (Fig. 43) [206,222]. By contrast, composites containing high-permittivity ceramic fillers often exhibit stronger dispersion and higher dielectric losses at microwave frequencies. For instance, BaTiO₃-based composites may exhibit decreases in ϵ' of several percent between 1 and 10 GHz, accompanied by increased losses due to interfacial polarization processes [143,224,226].

8.6.3. Millimeter-wave and emerging communication frequencies

Recent developments in high-frequency electronics, including 5G communication systems and radar technologies, have extended the characterization of PTFE composites to millimeter-wave frequencies above 60 GHz.

Recent laminate systems incorporating nano-Al₂O₃ or BN fillers exhibit permittivities of $\epsilon_r \approx 2.8$ and dielectric losses of 6×10^{-4} up to frequencies of about 110 GHz [225]. Such results confirm that moderate ceramic loading does not significantly degrade the intrinsic frequency stability of PTFE.

By comparison, conventional epoxy-glass or cyanate-ester laminates typically exhibit greater permittivity dispersion and significantly higher dielectric losses in the same frequency range [219,222,227,228].

Because signal propagation in microwave circuits depends directly on the square root of permittivity, the exceptional stability of PTFE ensures minimal phase distortion and group-delay dispersion across wide bandwidths, which explains its widespread use as a substrate material in high-speed communication systems.

8.7. Perspective and outlook

The PTFE dielectric behavior illustrates how a chemically simple polymer can achieve exceptional electrical stability through an unusual combination of molecular symmetry, high crystallinity, and minimal dipolar activity. Because polarization in PTFE is dominated by instantaneous electronic displacement, its dielectric response remains remarkably insensitive to temperature, frequency, and environmental perturbations. This intrinsic stability explains why PTFE has remained a benchmark dielectric material for more than seven decades.

However, modern electronic technologies increasingly require materials that simultaneously combine low dielectric losses, tunable permittivity, and enhanced thermal management. In this context, PTFE composites represent a particularly promising strategy. By incorporating carefully selected ceramic fillers and controlling the structure of the filler–polymer interphase, it is possible to increase permittivity while preserving the polymer's intrinsic low-loss character.

Future developments will likely focus on the precise control of interfacial polarization mechanisms, particularly in nanostructured composites designed for millimeter-wave and sub-, terahertz communication technologies. In such systems, the challenge is no longer merely to maximize permittivity but to maintain dielectric homogeneity at the nanometer scale to avoid local-field amplification and energy dissipation. PTFE-based materials, therefore, continue to offer a unique platform for exploring the interplay between polymer structure, interfacial physics, and high-frequency dielectric performance.

9. Applications

9.1. Introduction

PTFE is widely used across numerous technical sectors, from electrical and medical equipment to clothing and even pyrotechnics (Fig. 53). As the applications of PTFE have already been extensively discussed by Puts et al. [11] and Dhanumalayan et Joshi [16], this section focuses on highlighting emerging applications of PTFE, rather than reiterating an exhaustive overview

of its past and established uses. The aim is to emphasize its contemporary relevance and the evolution of its uses in the context of current science and technology.

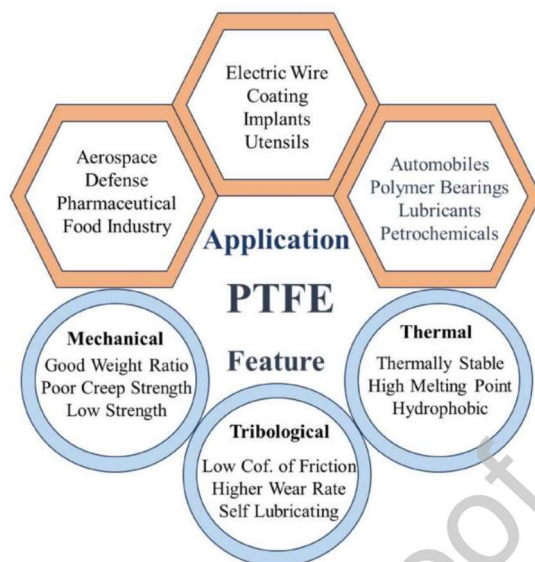


Fig. 53 : Brief overview of PTFE applications and features (reprinted with permission from WILEY [144]).

Thanks to its remarkable combination of chemical inertness, thermal stability, and low friction, this highly stable polymer has become indispensable in many industries. In recognition of its growing importance and status as the most widely produced and utilized fluoropolymer, global PTFE production reached 228,33 Kilotons in 2025 [229]. This was driven by increased demand from sectors such as chemical processing, surface coatings, specialty textiles, aerospace, automotive, medical devices, and advanced electronics (Fig. 53) [4,11,144,229].

9.2. PTFE in coating applications

PTFE is best known for its use as the non-stick coating on cookware and has long been used in the food industry for its chemical inertness, ease of cleaning, and non-stick properties. Its widespread adoption in consumer products, particularly non-stick cookware, stems from its excellent water- and fat-repellent properties that effectively prevent food from adhering during cooking [230]. The non-stick cookware sector alone accounted for 12,000 tons of PTFE consumption in 2023. When used under normal conditions, PTFE coatings are considered safe (section 10). However, overheating to temperatures above 380 °C for extended periods can lead to the formation and release of invisible gases (section 10).

PTFE is also used to coat textiles or fabrics to provide waterproofing [4,231]. In particular, expanded PTFE is used as a waterproof yet breathable membrane in clothing (commercially

known as Gore-Tex® (Fig. 54)). Additional applications of PTFE coatings include release coatings on molds, pipe liners, and vessel and thermocouple coatings in the pharmaceutical and chemical industries. These uses extend to pipe liners in acid plants, non-fouling coatings in heat exchangers, and anti-corrosion coatings for machinery housings [1,11]. It is common to find PTFE-coated magnetic stirring bars in virtually every chemistry laboratory. Besides, thanks to its essential tribological properties (section 6), PTFE also serves as a low-friction surface coating in various applications where reduced wear and smooth interaction are critical. For example, ultra-thin PTFE coatings have been applied to razor-blade cutting edges to reduce friction and provide a smoother shave [1,11].



Fig. 54 : Resistance of Gore-Tex® waterproof Shoes (photo taken by B. Ameduri).

Moreover, due to its exceptionally high limiting oxygen Index ($\text{LOI} > 95\%$), PTFE exhibits auto-extinguishing behavior, making it an outstanding material for cable coatings in aircraft applications, enhancing fire safety and reliability (e.g., electrical insulation in aerospace wiring systems) (Fig. 55) [226,232]. Furthermore, PTFE insulation is widely used in cable coatings within the oil and gas industry, particularly in deep-well environments, due to its excellent chemical resistance, low permeability, and broad thermal stability [233].

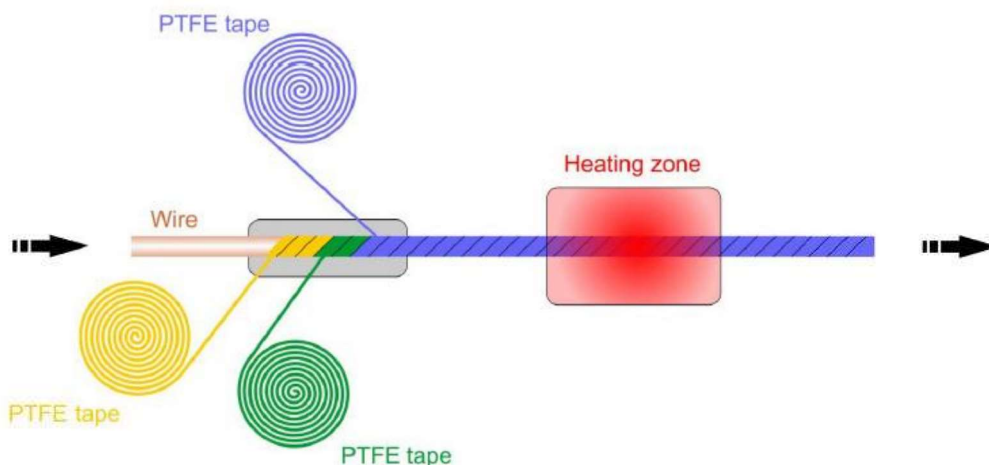


Fig. 55 : Cable insulated based on applying a PTFE three-layer coating around a wire to induce safety in airplanes, thanks to the excellent features of PTFE (reprinted with permission from M. Schlipf [232]).

The versatility of PTFE has led to its use in coatings and composites [234]. For example, Nickel-based coatings incorporating modified PTFE particles have been developed to enhance corrosion resistance. Polydopamine functionalization has been shown to facilitate the stable dispersion of PTFE particles in plating solutions, thereby enabling complexation with metal ions and enhancing adhesion and mechanical properties [235,236].

9.3. PTFE applications in the energy sector

The energy sector requires many fluoropolymers. Besides ionomers, copolymers of TFE with *co*-sulfonic acid perfluoroalkyl vinyl ether or perfluorosulfonic acid (PFSA) are used in PFSA membranes. At the same time, PTFE plays a pivotal role in proton exchange membrane fuel cells, serving as a membrane reinforcement and a gas diffusion layer coating that enhances both gas transport and mechanical stability [237,238]. Additionally, the presence of PTFE fibers in catalyst layers (especially at the cathode) facilitates oxygen transport, thereby supporting efficient electrochemical reactions [239] (Fig. 56).

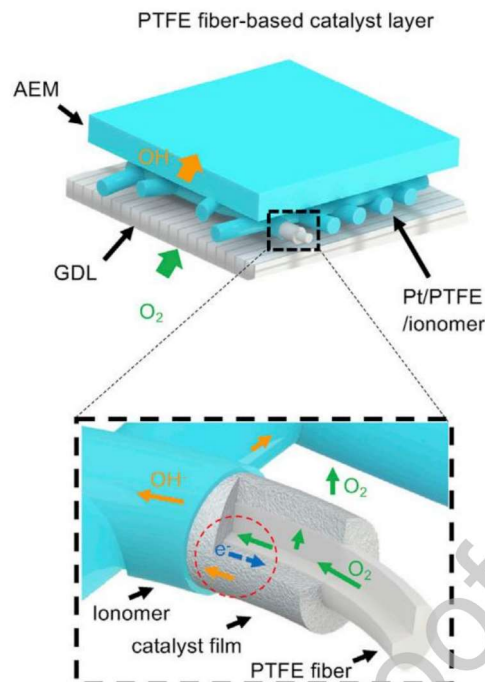


Fig. 56 : PTFE fiber-based catalyst layer for the oxygen reduction reaction (ORR) electrode in alkaline fuel cells. In the former case, gas (green), electron (blue), and hydroxide ion (orange) are transported by the gas pores, electronically conducting support, and ionomer, respectively. In the latter, the PTFE fibers provide an additional transport pathway for O_2 due to their high affinity for nonpolar gases. In both (A) and (B), the red circle denotes a site where electrochemical reactions can happen (reprinted with permission from CellPress [239]).

Additionally, Dong et al. [240] used expanded PTFE (e-PTFE) as a reinforcing framework for PFSA membranes, in which surface modification enhances interfacial compatibility, mechanical strength, and proton conductivity for hydrogen fuel cell applications. In this context, Guo et al. [241] summarized the strategies to control the membrane pore structure as well as the functionalization of PTFE porous membranes. These authors also reviewed the main issues linked to the practical applications of PTFE porous membranes. They suggested the appropriate PTFE membrane production technology to match the variety of well-designed applications.

Though most binders in lithium-ion battery (LIB) cathodes are made of PVDF [242], PTFE has also been shown to improve performance due to its chemical inertness and nonpolar nature [243]. PTFE has been employed as an alternative binder to enhance the electrochemical performance of LIB based on $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathodes. However, owing to the highly nonpolar nature of PTFE, commonly used organic solvents are ineffective at separating cathode materials from PTFE-based lithium-ion batteries. Consequently, effective strategies for separating and recycling cathode materials from these batteries must be developed [244]. Moreover, PTFE has also been utilized as a source of fluorine for the surface fluorination of

reactive anode materials [245]. Upon thermal treatment, PTFE decomposes, generating fluorinated species that react with the anode surface to form a thin, stable fluorinated layer. This surface modification effectively suppresses undesirable side reactions with the electrolyte, enhancing interfacial stability and improving the electrochemical performance and cycling durability of battery anodes, both of which are key features for evaluating LIB efficiency. Thus, the use of PTFE demonstrates its potential beyond conventional binder applications, serving as a functional material for surface engineering in advanced battery systems [245].

It is important to note that PTFE is widely used in the nuclear sector. Thanks to its chemical inertness in HF, F₂, or KF, this exceptional polymer is used for seals, fluid circuits, tubing, elbows, cable insulation, and instrumentation, as well as for high-purity containers employed in nuclear fuel analysis [246].

9.4. Use of PTFE in electronics

In the field of electronics, thanks to a long-term electrical endurance (section 8.3.3), PTFE is a critical component in high-frequency cables, flexible printed circuits, and insulation in 5G (Fig. 57. a) and 6G devices due to its low dielectric loss, thermal stability, and chemical inertness [232,247,248]. Porous PTFE fibers have also been shown to resist and enable terahertz pulse transmission through low-loss channels [247,248] (Fig. 57. b). Furthermore, PTFE has also been involved in robotics and artificial intelligence supercomputers.



Fig. 57 : a) 5G antenna systems made from PTFE [232]. b) Photograph and cross-section of the porous core fiber made of PTFE. The porous fiber has 19 air holes arranged in a hexagonal *lattice*, with air-hole diameter (D), pitch (A), and outer diameter (O.D.). (reprinted with permission from IEEE [248]).

9.5. PTFE in Printing Technologies

Zhang et al. [249] extend PTFE's applications to advanced fabrication techniques, such as 3D micro-printing (μ -printing) (Fig. 58), which is based on digital ultraviolet (UV) lithography. In

this method, PTFE nanoparticles are dispersed in a photocurable polyethylene glycol diacrylate (PEGDA) solution and printed layer by layer into predefined microstructures. Subsequent sintering steps are then employed to remove the polymer matrix, leaving pure PTFE microstructures. The use of this approach has enabled the fabrication of 3D PTFE micro-scaffolds for applications such as droplet lasers and electrostatic-driven biomimetic water striders, thereby underscoring the potential of micro/nano-structured superhydrophobic PTFE surfaces and the versatility of 3D printing in microengineering [250]. Such a study by Nieswic et al. [250] demonstrated an innovative strategy for the 3D printing of PTFE vascular grafts using digital light processing (DLP) of PTFE latex particles. In this process, the PTFE nanoparticles are dispersed in a photocrosslinkable, dimethacrylated Pluronic resin (similar to PEGDA), enabling direct printing in an aqueous environment. Following thermal and chemical post-treatments, the composite structure was transformed into a fully sintered device. The printed materials present excellent mechanical properties, including a Young's modulus of approximately 18 MPa and an elongation at break of ca. 157 %, while maintaining impermeability up to 4 bar due to controlled internal porosity (ca. 27 %). In addition, fibroblast cytotoxicity assays confirmed biocompatibility in accordance with ISO 10993 standards. This two-step printing and conversion process provides a compelling route toward the rapid fabrication of patient-specific PTFE grafts with complex morphologies, overcoming the limitations of traditional paste extrusion and stretching methods [250].