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Teflon[®] AF: A Family of Amorphous Fluoropolymers with Extraordinary Properties

PAUL R. RESNICK and WARREN H. BUCK

2.1. INTRODUCTION

Since the discovery of Teflon[®] by Roy Plunkett in 1937 a number of fluorinated plastics have reached commercial status. These plastics, exemplified by polytetrafluoroethylene (PTFE), have outstanding electrical, chemical, and thermal properties. All these commercial materials are either crystalline or semicrystalline. Teflon[®] AF is a family of amorphous copolymers that retain the desirable electrical, chemical, and thermal properties of semicrystalline fluorinated plastics and also have such properties associated with amorphous materials as optical clarity, improved physical properties, and solubility in selected fluorinated solvents.

The Teflon[®] AF family consists of copolymers of tetrafluoroethylene, (TFE) and 2,2-bis-trifluoromethyl-4,5-difluoro-1,3-dioxole, (PDD), whose structure is shown in Figure 2.1.¹ The properties of these amorphous copolymers vary with the relative amounts of the comonomers. At present the two commercial grades of Teflon[®] AF are AF-1600 and AF-2400 with glass transition temperatures of 160 and 240°C respectively. The variation of glass transition temperature with composition is shown in Figure 2.2. Thus AF-1600 and AF-2400 contain 64 and 83 mol % PDD, respectively.

PAUL R. RESNICK · DuPont Fluoroproducts, Fayetteville, North Carolina 28306.
WARREN H. BUCK · Ausimont USA, Thorofare, New Jersey 08086.

Fluoropolymers 2: Properties, edited by Hougham *et al.* Plenum Press, New York, 1999

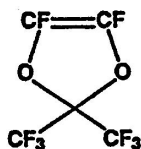


Figure 2.1. Teflon[®] AF: A family of amorphous fluoroplastics, $T_g = 80 - 300^\circ\text{C}$.

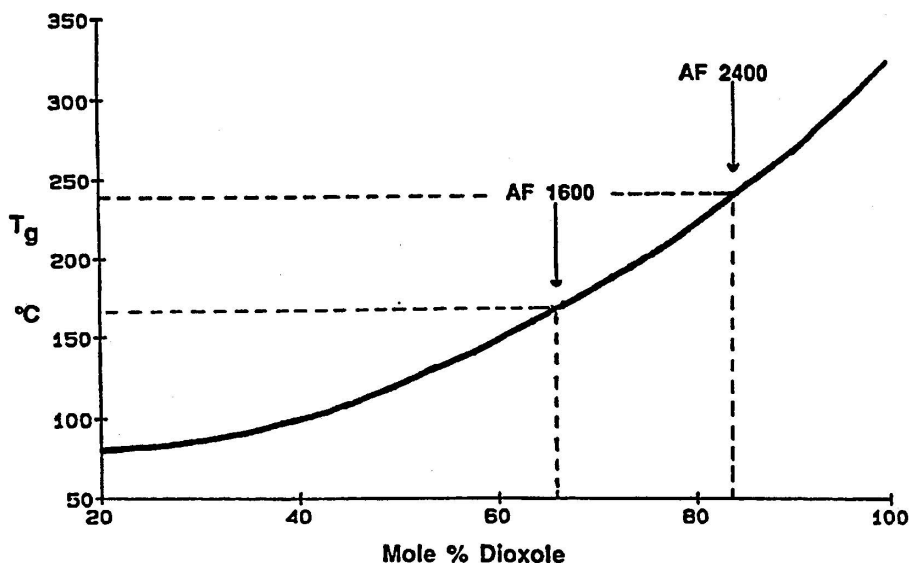


Figure 2.2. Mol % dioxole vs. T_g for Teflon[®] AF.

2.2. PREPARATION METHODS

PDD monomer can be prepared in four steps starting from hexafluoroacetone (HFA) and ethylene oxide (EO), as shown in Figure 2.3. Condensation of HFA and EO yields, 2,2-bis-trifluoromethyl-1,3-dioxolane, which is successively chlorinated, fluorinated, and dechlorinated to give PDD monomer. This monomer is highly reactive and will copolymerize with TFE in all proportions as well as form a homopolymer. This high reactivity is believed to be a function of the steric accessibility of the double bond. The PDD monomer undergoes a number of unusual chemical reactions including the facile addition of iodine to give a stable vicinal diiodide and thermal rearrangement to an isomeric epoxyacyl fluoride (Scheme 1).²

Other dioxole monomers and polymers have been prepared from halogenated dioxoles with different substituents in the 2,4, and 5 positions of the dioxole ring.

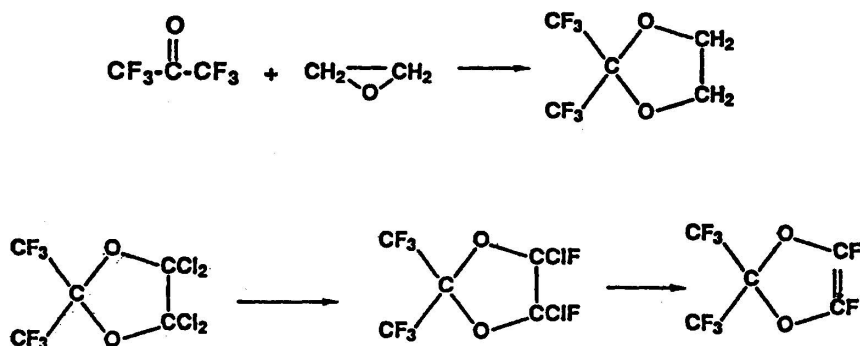
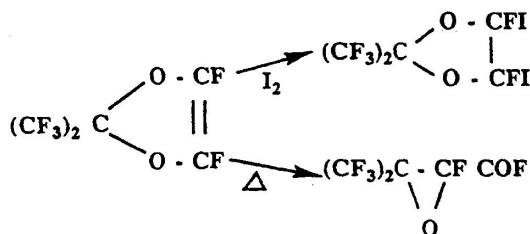


Figure 2.3. Synthesis of PDD.

PDD as well as other dioxoles have been copolymerized with monomers such as vinyl fluoride, vinylidene fluoride, trifluoroethylene, perfluoroalkylethylenes, chlorotrifluoroethylene, hexafluoropropylene, and perfluorovinyl ethers, some of which contain functional groups.



Scheme 1

Table 2.1 lists a number of dioxole monomers and indicates their ability to homopolymerize and/or copolymerize with TFE in CFC-113 solution. The copolymerization of dioxoles with chlorine in the 4 and 5 position of the dioxole ring further demonstrates the very high reactivity of this ring system. Thus an almost infinite number of dioxole polymers can be prepared with one or more comonomers in varying proportions. We have chosen to focus our present work on copolymers of TFE and PDD to preserve the outstanding thermal and chemical properties of perfluorinated polymers. At this point it should be noted that fully fluorinated ethers are nonbasic and effectively possess the same chemical inertness as fluorinated alkanes. Perfluorinated ether groups in polymers are even less reactive as a result of their inaccessibility to chemical reagents.

Table 2.1. Radical Polymerization in CFC-113 at 40–100°C

Dioxole		Homopolymer	TFE-copolymer
X	Y		
Cl	Cl	—	+
Cl	F	—	+
Cl	H	—	+
H	H	+	+
H	F	+	+
F	F	+	+

2.3. PROPERTIES

The excellent chemical stability of Teflon[®] AF is the same as that of the other Teflon[®] types (PTFE, PFA, FEP). To date we have not found a reagent that differentiates Teflon[®] AF from the other Teflons[®]. The good thermal stability of AF-1600 is shown in Table 2.2. Note the very small weight loss at 400°C. The bulk of the weight loss is due to particulate formed by random cleavage of the polymer backbone. Little if any unzipping of the polymer chain to yield PDD monomer has been observed. In this respect Teflon[®] AF differs from PTFE. When heated in vacuum Teflon[®] AF ablates and recondenses to give a polymer with the same structure as the starting material.³ Toxic materials may be formed when Teflon[®] AF is heated at very high temperatures. Adequate ventilation is needed during high-temperature processing of Teflon[®] AF or other fluoropolymers.

The dielectric constant of Teflon[®] AF is the lowest of any known solid polymer, ranging from 1.89 to 1.93. (Figure 2.4) Increasing the amount of PDD in the copolymer as well as raising the temperature results in a lower dielectric

Table 2.2. Thermal Stability of Teflon[®] AF 1600 in Air

Temperature (°C)	Weight loss (%)	Time (h)
260	None	4
360	0.29	1
380	0.53	1
400	1.94	1
420	8.83	1

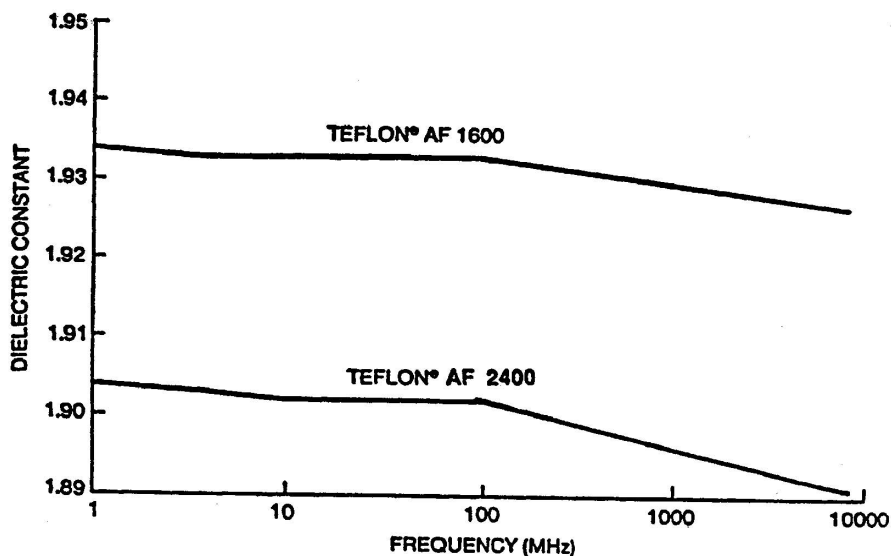


Figure 2.4. Dielectric constant of Teflon[®] AF at 23°C.

constant. Dissipation factors are very low, ranging from 1.2×10^{-4} at 1 MHz to 8.0×10^{-5} at 100 MHz. Breakdown voltages are 522 and 495 V/mil for AF-1600 and AF-2400, respectively.

Amorphous polymers characteristically possess excellent optical properties. Unlike all the other commercially available fluoropolymers, which are semicrystalline, Teflon[®] AF is quite clear and has optical transmission greater than 90% throughout most of the UV, visible, and near-IR spectrum. A spectrum of a 2.77-mm-thick slab of AF-1600 is shown in Figure 2.5. Note the absence of any absorption peak. Thin films of Teflon[®] AF have UV transmission greater than 95% at 200 nm and are unaffected by radiation from UV lasers.⁴ The refractive indexes of Teflon[®] AF copolymers are shown in Figure 2.6 and decrease with increasing PDD content. These are the lowest refractive indexes of any polymer family. It should be noted that the abscissa could also be labeled as glass transition temperature, T_g , since T_g is a function of the PDD content of the AF copolymer. Abbe numbers are low: 92 and 113 for AF-1600 and AF-2400.⁵

The volume coefficient of expansion of Teflon[®] AF is linear with temperature and quite low. The coefficients are 280 ppm/°C and 300 ppm/°C for AF-1600 and AF-2400, respectively. Above the glass transition temperature these values increase sharply. Thermal conductivity is quite low, increasing from only 0.05 W/mK at 40°C to 0.2 W/mK at 260°C. Many of these properties are believed to be related to the very low (1.7–1.8 g/ml) densities of these dioxole

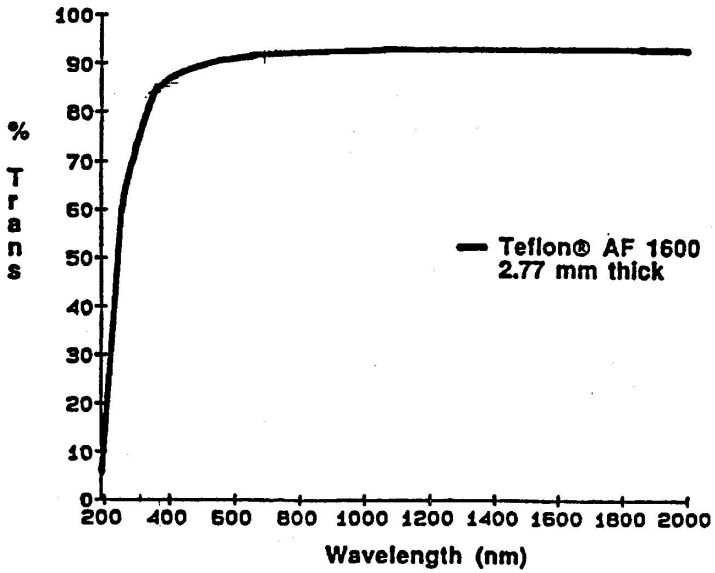


Figure 2.5. Percent transmission vs. wavelength for Teflon® AF 1600, Lot P29-3034F, 2.77 mm thick.

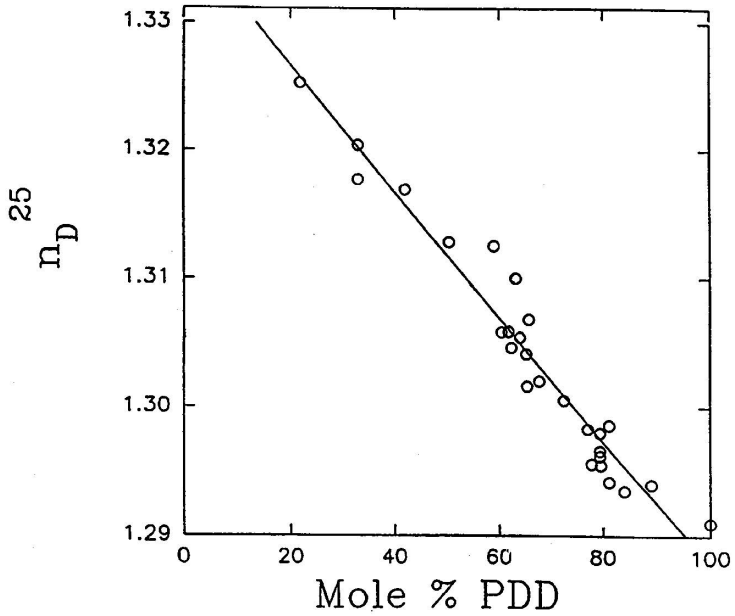


Figure 2.6. Refractive index vs. composition for PDD/TFE copolymers.

copolymers. This suggests that PDD copolymers contain microvoids in the polymer structure associated with the 2,2-dimethyl-1,3-dioxolane ring system.

Gas permeation through Teflon[®] AF thin films is extraordinarily high, with permeation rates increasing as PDD content increases. AF-2400 has an oxygen permeation rate of 99,000 cB (centi-Barrers) and a carbon dioxide permeation rate of 280,000 cB compared to 420 cB and 1200 cB for PTFE respectively.⁶ These unusually high permeation rates are thought to be the direct result of the microvoids present in the copolymer.

The mechanical properties of Teflon[®] AF differ from those of the semicrystalline Teflon[®]. Below the glass transition temperature the tensile modulus is higher (1.5 GPa) and elongation to break lower (5–50%). Similarly, below the T_g , creep is generally less than that normally observed for PTFE and shows much less variation with temperature.

Teflon[®] AF is insoluble in water and “normal” organic solvents. It is swollen by CFC-113 and is soluble in selected perfluorinated solvents such as Fluorinert, Hostinert, Flutec, and Galden liquids. Fluorinert FC-75, b.p. 100°, is a very useful solvent for molecular weight and viscosity measurements. In general the solubility decreases with increasing PDD content and increasing molecular weight. Thus the solubility of AF-1600 in FC-75 is 8–10%, while the solubility of AF-2400, which contains more PDD, is only 2–3%. The solubility of PDD homopolymer is 0.2% at best. Incorporation of polar groups in AF polymers dramatically decreases polymer solubility.

A plot of Brookfield viscosity as a function of concentration for AF-1600 and AF-1601 is shown in Figure 2.7. AF-1601 differs from AF-1600 only in having a lower molecular weight. It is possible to prepare low-molecular-weight polymers with a solubility greater than 30% in FC-75 at room temperature. As one would expect, these lower-molecular-weight polymers have poorer physical properties. AF gives true solutions in FC-75 and many of these can be filtered through 0.2- μ m filters.

The physical properties of PDD polymers can also be varied by substituting all or part of the TFE portion with other monomers. It should be noted that specific polymer properties are not independent variables and other properties in addition to the target one may be altered when different monomers are used in the copolymers.

AF polymers can be extruded, compression and injection-molded, solution or spray-coated as well as spin-coated from solution. A representative plot showing the dry-film thickness obtained by spin-casting from two different concentration AF solutions at different spin speeds is shown in Figure 2.8. It is possible to prepare multiple coats of AF using this technique. Although most of the solvent is removed in the spin-coating step the polymer must be heated above its glass transition temperature to ensure removal of the last traces of solvent.

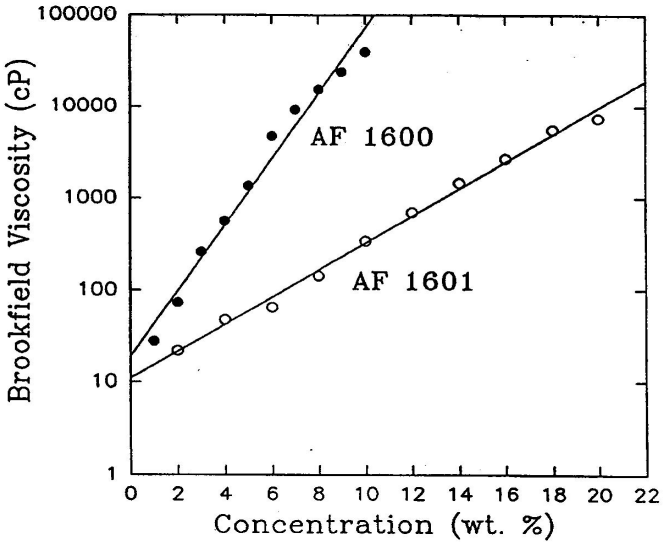


Figure 2.7. Brookfield viscosity vs. concentration in FC-75.

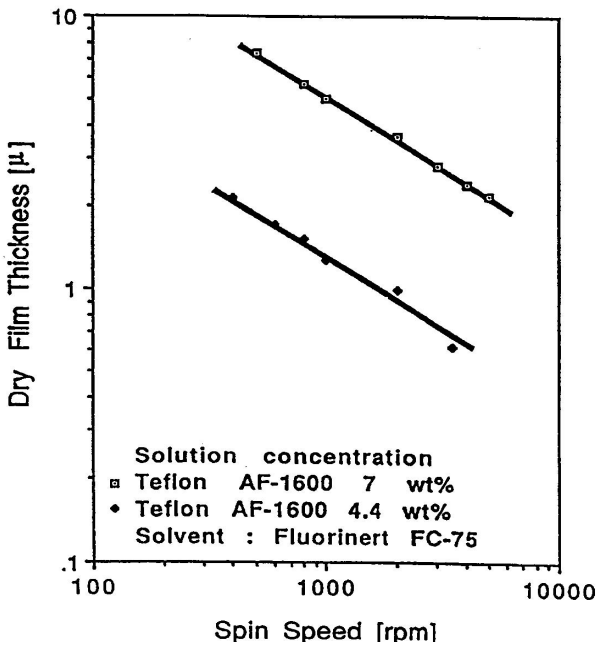


Figure 2.8. Dry film thickness in spin-coating.

Table 2.3. Teflon[®] AF—Comparison to Other Teflon[®]

Similarities	Differences
High temperature stability	No crystallinity—amorphous
Great chemical resistance	Solubility—solvent castable
Low coefficient of friction	High optical clarity
Low water absorption	Low refractive index
High flame resistance	Improved electrical properties
	Low thermal expansion
	Higher creep resistance
	Higher tensile modulus
	High gas permeability

2.4. CONCLUSION

Teflon[®] AF is truly a family of amorphous fluoropolymers with an extraordinary combination of properties. All of the excellent properties of the existing fluoropolymers have either been retained or improved upon and properties arising from the amorphous nature and the presence of microvoids in the AF family of polymers have been added. The similarities and differences of AF and other Teflon[®] polymers are summarized in Table 2.3. This unique combination of properties of Teflon[®] AF amorphous fluoropolymers makes them well suited for applications that had previously precluded polymeric materials,

2.5. REFERENCES

1. P. R. Resnick, U.S. Patent 3865845, 3978030; E. N. Squire U.S. Patent 4754009
2. M-H. Hung and P. R. Resnick, *J. Am. Chem. Soc.* 112, 9671 (1990).
3. T. C. Nason, J. A. Moore, and T. M. Lu, *Appl. Phys. Lett.* 60, 1866 (1992).
4. H. Hiraoka, S. Lazare, and A. Cros, *J. Photopolym. Sci. Technol.* 4, 463 (1991); S. Lazare, H. Hiraoka, A. Cros, and R. Gustiniani, *Mat. Res. Soc. Symp. Proc.* 227, 253 (1991).
5. J. H. Lowry, J. S. Mendlowitz, and N. S. Subramanian, *Proc. SPIE Int. Soc. Opt. Eng.* 1330, 142 (1990).
6. S. M. Nemser and I. C. Roman, U.S. Patent 5051114.