

## Teflon<sup>®</sup> AF Amorphous Fluoropolymers

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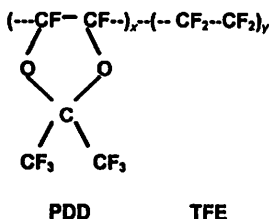
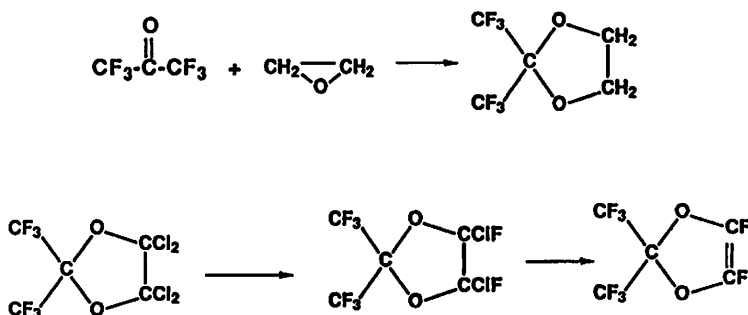
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Teflon<sup>®</sup> AF is a family of amorphous fluoropolymers based on copolymers of 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole (PDD) which retain the outstanding chemical, thermal and surface properties associated with perfluorinated polymers while also having unique electrical, optical and solubility characteristics. This combination of properties makes them useful for a large variety of applications.

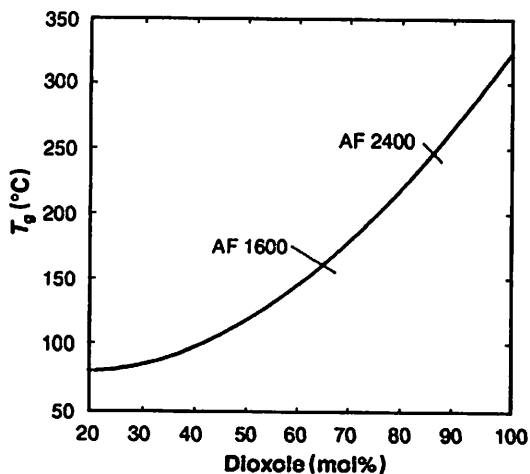
All previously commercialized perfluorinated polymers such as Teflon<sup>®</sup> PTFE, FEP or PFA are semicrystalline materials. The first commercial perfluoropolymer, Teflon<sup>®</sup> PTFE, is highly crystalline and was discovered by Roy Plunkett in 1938 [1]. Its extremely high molecular weight estimated to be between 5 and  $100 \times 10^6$  Daltons and melt viscosity of the order of  $10^{13}$  Pa . s at 380 °C make it difficult to process. The introduction of hexafluoropropylene and perfluoroalkylvinyl ethers into the polymer chain to give Teflon<sup>®</sup> FEP and Teflon<sup>®</sup> PFA respectively, lower both the crystallinity and molecular weight allowing these polymers to be melt processed. These semicrystalline polymers do not possess good optical transparency and in general have poor solubility. Amorphous polymers usually have excellent optical properties and solubility characteristics. Teflon<sup>®</sup> AF is an amorphous fluoropolymer family which have both the properties expected of amorphous plastics and the properties expected of perfluorinated polymers. The PDD dioxole monomer in Teflon<sup>®</sup> AF yields polymers which have even further unexpected properties. Teflon<sup>®</sup> AF is a copolymer of PDD and tetrafluoroethylene, TFE. Its structure is shown in Figure 22.1 [2-5].

The dioxole monomer, PDD, is synthesized in four steps from hexafluoroacetone and ethylene oxide as shown in Figure 22.2. Hexafluoroacetone

**Figure 22.1.** Structure of Teflon® AF**Figure 22.2.** Synthesis of PDD

condenses with ethylene oxide to form a highly chemically stable dioxolane ring in quantitative yield. Exhaustive chlorination followed by chlorine-fluorine exchange yields 2,2-bistrifluoromethyl-4,5-dichloro-4,5-difluoro-1,3-dioxolane in greater than 90% yield. Dechlorination of this dioxolane with magnesium, zinc or a mixture of titanium tetrachloride and lithium aluminum hydride gives PDD monomer. PDD is a clear colorless liquid boiling at 33°. It is highly reactive and is stored at low temperature with a trace amount of radical inhibitor. Free radical initiated polymerization and copolymerizations of PDD or other fluorinated dioxoles may be carried out in either aqueous or non-aqueous media.

PDD readily polymerizes with tetrafluoroethylene and other fluorine containing monomers such as vinylidene fluoride, chlorotrifluoroethylene, vinyl fluoride and perfluoroalkylvinyl ethers. It can also homopolymerize to give an amorphous polymer with a glass transition temperature,  $T_g$ , of 335°C. Thus the number of potential polymers of PDD is very large. This number becomes even larger when one considers the many other dioxoles with different substituents in the 2-, 4- and 5-position of the dioxole ring that can and have been prepared and polymerized. At present the commercial Teflon® AF products are copolymers of PDD and tetrafluoroethylene and have glass transition temperatures of 160 and 240°C for Teflon® AF-1600 and Teflon® AF-2400 respectively.

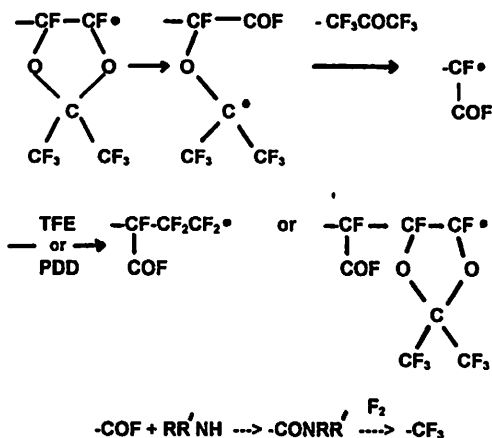


**Figure 22.3.** Composition of Teflon® AF vs  $T_g$

Copolymers may be prepared which have any proportion of tetrafluoroethylene and PDD. The  $T_g$  of these polymers is a function of the PDD content and is shown in Figure 22.3. The lower limit for  $T_g$  is approximately  $80^\circ$  corresponding to 20 mol% PDD. Copolymers with less PDD are no longer amorphous due to the presence of tetrafluoroethylene runs of sufficient length to result in crystallization of the polymer. As noted the  $T_g$  of PDD homopolymer is  $335^\circ$ , but it is difficult to fabricate since it possesses limited melt flow below its decomposition temperature and is soluble to only a few tenths of 1%. Teflon® AF-1600 and 2400 contain 65 and 87 mol% PDD respectively. In general, the glass transition temperature of a PDD copolymer decreases when the PDD concentration in the polymer is lowered by addition of any comonomer.

Aqueous polymerization of PDD and tetrafluoroethylene is usually carried out in the presence of a fluorinated surfactant and ammonium persulfate or other metal persulfate initiators. Under these conditions small amounts of acid fluoride or carboxylic acid chain ends may be produced by ring opening during the polymerization. For some applications these unstable ends are removed and converted to trifluoromethyl groups by first treating the polymer with ammonia or alkyl amines followed by high-temperature fluorination with elemental fluorine. (Figure 22.4) [6].

The  $T_g$  of dioxole copolymers with tetrafluoroethylene is highly sensitive to the structure of the dioxole monomer. Replacing the trifluoromethyl groups at the 2-position of the dioxole ring with either fluorine or large fluoroalkyl groups dramatically changes the  $T_g$  of the polymer and the reactivity of the monomer (Figure 22.5). One rationale for the high  $T_g$  of Teflon® AF (Fig. 22.5, X = F;  $R_1 = R_2 = CF_3$ ) is that steric interactions involving the two trifluoromethyl



**Figure 22.4.** Ring opening during polymerization and removal of carboxylate side chains

Bp (°C)	R <sub>1</sub>	R <sub>2</sub>	X	T <sub>g</sub> (°C)
33	CF <sub>3</sub>	CF <sub>3</sub>	F	335
16	CF <sub>3</sub>	F	F	212
0	F	F	F	180
40	CF <sub>3</sub> CF <sub>2</sub>	F	F	150
42.5	CF <sub>3</sub> CF <sub>2</sub>	CF <sub>3</sub>	F	118-139
52	CF <sub>3</sub> CF <sub>2</sub>	CF <sub>3</sub> CF <sub>2</sub>	F	a
44	CF <sub>3</sub>	CF <sub>3</sub>	H	256
42	CF <sub>3</sub>	CF <sub>3</sub>	Cl	a
55	CF <sub>3</sub>	CF <sub>3</sub>	CF <sub>3</sub>	a
105 49.5/101 torr			F	292[7,8]
24	F	F	OCF <sub>3</sub>	162 [9]

**Figure 22.5.** Glass transition temperature of dioxole homopolymers (a = does not form homopolymer) [7,8,9]

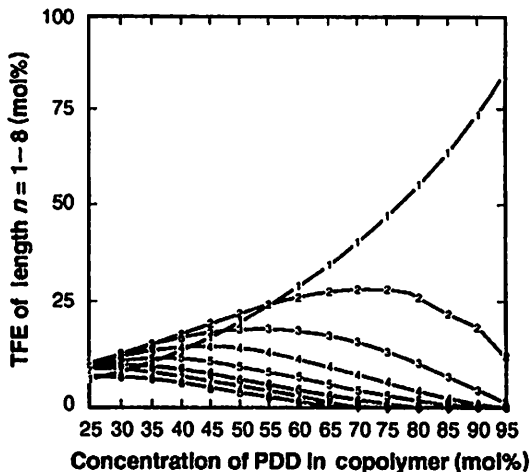
groups in these dioxole polymers lead to a highly congested chain structure with limited mobility. These interactions and hence the  $T_g$  of these polymers is highly sensitive to differences in substituents at the 2-position of the dioxole ring of the monomer. Note especially the difference in  $T_g$  of the homopolymer of PDD, 335°, and that of its isomer, 2-pentafluoroethyl-2,4,5-trifluoro-1,3-dioxole, 150° [10].

Teflon® AF copolymers share many characteristics of other Teflon® types, but also have significant differences. Figure 22.6 lists some of these similarities and differences. All of the polymers in the Teflon® family have high-temperature stability due to their perfluorinated structure. This also accounts for their excellent chemical resistance, low surface energy, and low water absorption. The limiting oxygen index, LOI, of all of the Teflon® polymers is greater than 95, meaning that they require an atmosphere of greater than 95% oxygen to sustain combustion. Teflon® PTFE, FEP, and PFA are all semicrystalline. Since Teflon® AF polymers are completely amorphous, they have different properties. The semicrystalline Teflons® have high melting points and are only soluble in high boiling perfluoro-carbon solvents at temperatures near their melting points. Teflon® AF polymers are soluble in several perfluorinated solvents at room temperature. The crystallites in semicrystalline Teflon® scatter light and consequently have low optical transmission. Teflon® AF is free of crystallites and absorbing functional groups and thus has high optical transmission across a broad wavelength region from the near infrared to the ultraviolet. Teflon® AF polymers also have unusually low refractive indices and dielectric constants. The stiffness imparted by the in-chain ring structure of the dioxole unit also causes Teflon® AF to be stiffer and exhibit a higher tensile modulus than other Teflons®. Finally the Teflon® AF family of polymers have extraordinarily high gas permeability compared to other polymers, both fluoropolymers and non-fluoropolymers.

Figure 22.7 shows the TFE sequence length distribution in PDD-TFE copolymers as a function of composition. These sequence lengths were calculated from

Similarities	Differences
High-temperature stability	Non-crystalline, amorphous
Excellent chemical resistance	Soluble at ambient temperature in fluorinated solvents
Low surface energy	Transparent
Low water absorption	Lower refractive index
Limiting oxygen index (LOI) > 95	Stiffer
	High gas permeability

**Figure 22.6.** Teflon® AF. Comparison to other Teflon® polymers



**Figure 22.7.**  $-\text{CF}_2\text{CF}_2-$  (TFE) sequence length distribution for PDD-TFE copolymers

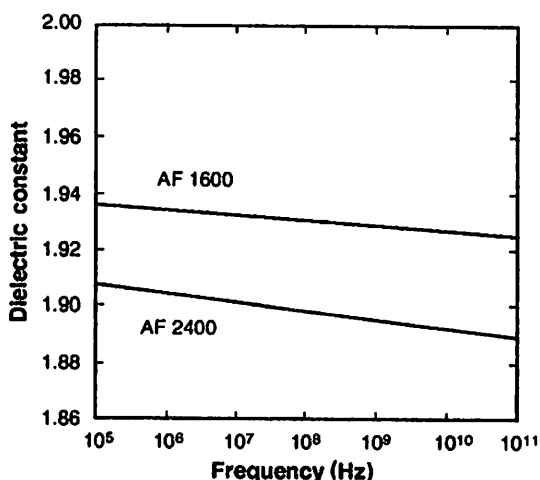
the experimentally measured reactivity ratios [11]. The numbers in Figure 22.7 represent the mol% of TFE present in run lengths of 1, 2, 3, etc. For example Teflon® AF-1600 has 65 mol% PDD and about 30% of the TFE present has a run length of one, i.e. as single  $-\text{CF}_2\text{CF}_2-$  units flanked on both sides by dioxole units. It can also be seen from Figure 22.7 that about 25% of the TFE in AF 1600 has run length 2, 15% run length 3, 10% run length 4, 5% run length 5, and the remaining 15% has run length greater than 5. For Teflon® AF-2400, 75% of the TFE has run length 1, 20% run length 2, nearly 5% run length 3, and virtually no TFE run lengths greater than 3. Since the barrier to rotation of the carbon-carbon bond in a TFE residue is much less than that of the carbon-carbon bond in the dioxole ring, increasing TFE content should lead to the observed decrease in glass transition temperature and to increased solubility. The presence of a significant number of TFE sequences greater than five or six is necessary for TFE crystallinity to be observed. When PDD content is less than 55 mol% most of the TFE is present in runs of two or longer and when PDD content is less than 20 mol% TFE crystallinity is observed.

Amorphous Teflon® AF is a unique family of polymers. Its structure is characterized by microvoids which have been examined using positron annihilation lifetime spectroscopy [12]. These voids result in lower than expected polymer density, low dielectric constant, low refractive index, high gas permeability and low thermal conductivity. Most likely the origin of these microvoids is loose chain packing caused by the high energy for rotation and reorientation of the dioxole ring containing polymer chain. The densities of some fluoropolymer resins are shown below. The densities of Teflon® AF vary with composition or  $T_g$  and are

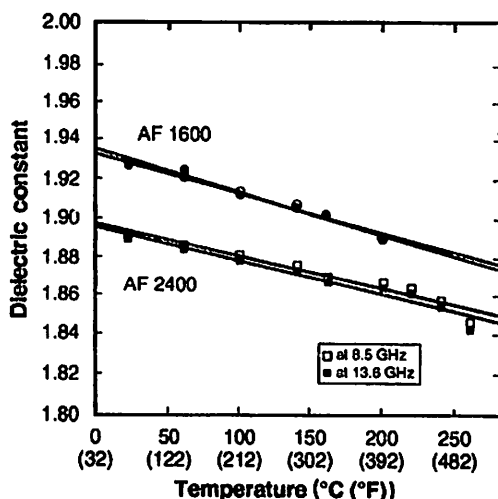
lower than the other fluoropolymers. The densities of these other semicrystalline polymers will vary due to differences in their degree of crystallinity.

Densities of fluoropolymers	
Polymer type	Density (g/cc)
AF-1600	1.8
AF-2400	1.7
PTFE	2.15–2.20
FEP	2.12–2.17
PFA	2.12–2.17

The dielectric constant for Teflon® AF is unaffected by humidity, and is believed to be the lowest dielectric constant known for a solid organic polymer and is appreciably lower than that of Teflon® PTFE. Given its low dielectric constant even very thin coatings have good insulating characteristics. Figure 22.8 shows the dielectric constant,  $\epsilon$ , of Teflon® AF 1600 and 2400 as a function of frequency at 22°C. The dielectric constant data were measured at the Massachusetts Institute of Technology Laboratory for Electromagnetic and Electronic Systems by W. B. Westphal using a method similar to ASTM D-150. The dielectric constant of AF 1600 has a nearly constant value of 1.93 over a frequency range of 1 MHz to 10 GHz. Similarly, AF 2400 has a dielectric constant of 1.90 over the same frequency range. For comparison, Teflon® PTFE has a dielectric constant of 2.0 and Teflon® FEP and PFA both have dielectric constants of 2.1. Figure 22.9 shows the dependence of Teflon® AF dielectric

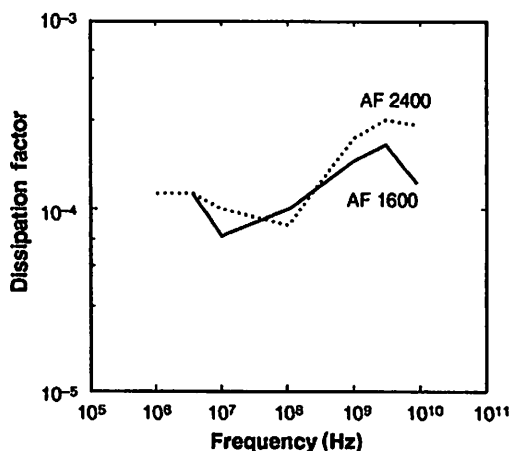


**Figure 22.8.** Dielectric constant of Teflon® AF at 22°C



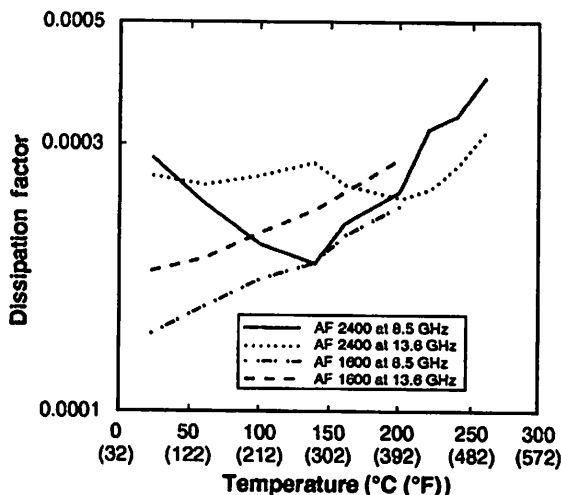
**Figure 22.9.** Dielectric constant of Teflon® AF vs temperature

constant on temperature at 8.5 and 13.6 GHz. The change is only approximately 0.05 units from room temperature to the glass transition temperature for both Teflon® AF 1600 and AF 2400. At temperatures above the  $T_g$  the dielectric constants decrease more rapidly. The change in  $\epsilon$  with temperature for Teflon® AF is only about one-half the change seen for crystalline Teflon®. This is probably due to changes in the degree of crystallinity with temperature for the latter polymers. Figure 22.10 shows the dissipation factor of Teflon® AF as a function



**Figure 22.10.** Dissipation factor of Teflon® AF at 22 °C



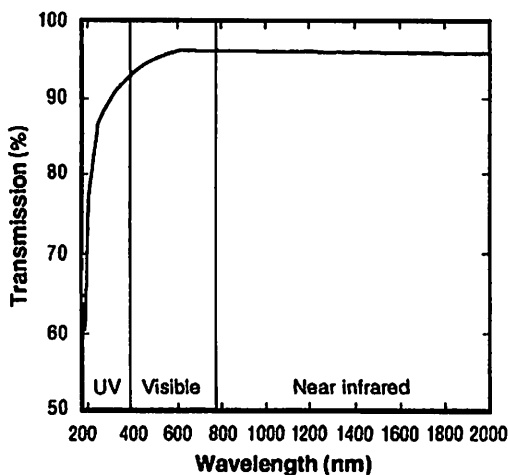


**Figure 22.11.** Dissipation factor of Teflon® AF vs temperature

of frequency at room temperature. Values range from  $8 \times 10^{-5}$  to  $3 \times 10^{-4}$  for AF 2400 and  $8 \times 10^{-5}$  to  $2 \times 10^{-4}$  for AF 1600. These values are essentially equivalent to the reported dissipation factor of  $2 \times 10^{-4}$  for PTFE [13]. Figure 22.11 shows the temperature dependence of the dissipation factor of Teflon® AF at two fixed frequencies. There is little change,  $2 \times 10^{-4}$  units, from room temperature to above the polymer  $T_g$  at low frequency. The  $T_g$  of 160 and 240 °C respectively for Teflon® AF 1600 and 2400, refer to values measured by differential scanning calorimetry, which has an effective measurement frequency of  $10^{-2}$  Hz. At the GHz frequency range used for these measurements,  $T_g$  will be appreciably higher. The dissipation factor is maximum at  $T_g$ , so the increasing dissipation factor in Figure 22.11 indicates the approach to  $T_g$  at the measurement frequencies.

Starkweather *et al.* [14] investigated the low-temperature dielectric properties of Teflon® AF and other Teflon® polymers. They found that the  $\gamma$  relaxation found at  $-186^\circ\text{C}$  for PTFE is only one-third the intensity for AF 1600 and AF 2400. This relaxation is attributed to the cooperative motion of the four carbon atoms of a TFE dimer unit. Since the total TFE content and concentration of TFE units of length greater than one is small for both AF compositions, this explains the reduced intensity of the  $\gamma$  relaxation. Teflon® AF exhibits a very weak maximum in the low temperature dissipation factor at  $-200^\circ\text{C}$  which is attributed to rotation of the perfluoromethyl group on the dioxole ring.

The optical properties of Teflon® AF are outstanding and quite unique as one would expect from a perfluorinated amorphous material. Figure 22.12 shows the transmission spectrum of Teflon® AF from 200 to 2000 nm. The polymer has high transmission from the deep ultraviolet through the near infrared spectral regions. Note that the spectrum shown is for a 0.22 mm (0.009 in.) thick sample.



**Figure 22.12.** Transmission of Teflon® AF (0.22 mm thick sample)

Rothschild and Sedlacek [15] found that Teflon® AF 1600 films of thickness between 0.2 and 2  $\mu\text{m}$  showed no absorbance at 200 nm. They also showed that a Teflon® AF pellicle, which had been optimized for use at 248 nm, could withstand irradiation at 193 nm for the equivalent of 10 years of full-time exposure in a semiconductor manufacturing environment.

The refractive index of Teflon® AF shown in Figure 22.13 is the lowest known for any solid organic polymer. The refractive index of AF 1600 at 20 °C at the sodium D line is 1.31 and that of AF 2400 is 1.29. The indices were measured by an Abbe refractometer using  $\alpha$ -bromonaphthalene as contact liquid. The refractive index of AF 2400 is near the theoretical lower limit predicted by Groh and Zimmermann [16] based on group contribution calculations. The Abbe number is a measure of dispersion or the change in refractive index with wavelength. It is defined at the bottom of Figure 22.13, where  $n_D$  is the refractive index at the sodium D line (589 nm),  $n_F$  is the refractive index at the hydrogen F line (486 nm), and  $n_C$  is at the hydrogen C line (656 nm). These Abbe numbers for Teflon® AF shown in Figure 22.13 are extremely high

AF	$n_D$	Abbe no.*	$dn_p/dT$ (ppm/°C)	
			Below $T_g$	Above $T_g$
1600	1.31	92	-77	-329
2400	1.29	113	-78	-378

**Figure 22.13.** Refractive index of Teflon® AF. Abbe number =  $(n_D - 1)/(n_F - n_C)$

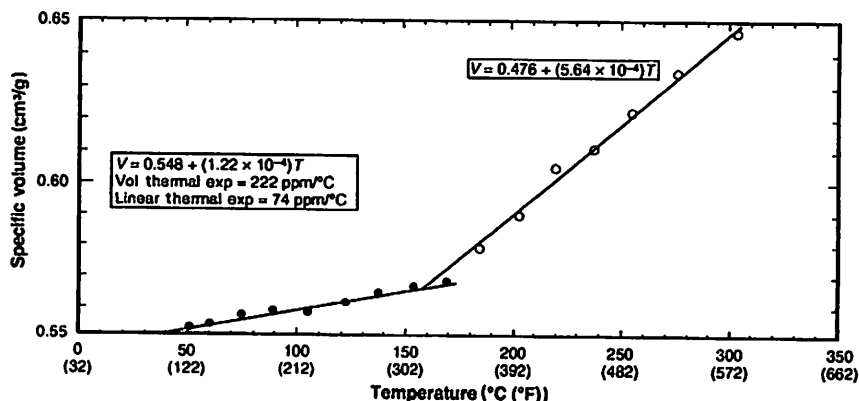
## Stress optical coefficient (SOC)

Polymer	SOC (Brewster)
Teflon® AF-1600	4.5
Polystyrene	10
Poly(methyl methacrylate)	4.0

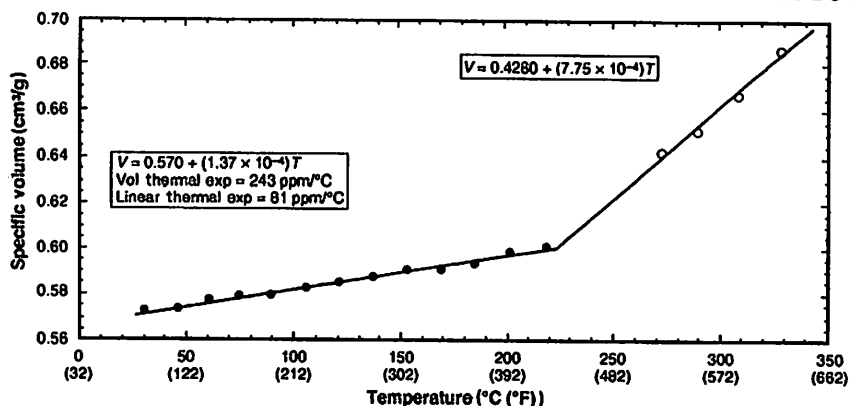
**Figure 22.14.** Stress optical coefficient (SOC). Brewster =  $10^{-13}$  cm<sup>2</sup>/dyn

by comparison with other materials [17]. The Abbe number for acrylics is 57, for polycarbonate 34, for styrene 31, and for BK-7 glass 64. The variation in refractive index with temperature below  $T_g$  is  $-77$  ppm/°C for AF 1600 and  $-78$  ppm/°C for AF 2400. However, above their glass transition temperatures the variations in refractive index with temperature for AF 1600 and 2400 are  $-329$  and  $-378$  ppm/°C respectively. Other amorphous polymers have values between 300 and 500 ppm/°C above their  $T_g$  [18]. These reduced variations in refractive index with temperature are a consequence of the relatively low coefficient of thermal expansion for Teflon® AF. The values of the stress optical coefficient (SOC), of Teflon® AF 1600 [19] and several other optical polymers are shown in Figure 22.14 [20]. The SOC is a measure of the change in refractive index in different directions as a material is stressed. Low values of SOC are desirable for optical components subjected to stress during use.

As noted earlier, the density of Teflon® AF is extremely low in comparison to other perfluorinated polymers. As shown in Figures 22.15 and 22.16 the coefficients of thermal expansion are linear both below and above the glass



**Figure 22.15.** Thermal expansion of Teflon® AF-1600 (Lot P29-3032F). Extrapolated to zero pressure from high-pressure dilatometry



**Figure 22.16.** Thermal expansion of Teflon® AF-2400 (Lot P29-4012F). Extrapolated to zero pressure from high-pressure dilatometry

transition temperature but greater above  $T_g$  [21]. Thus the volume coefficient of thermal expansion for Teflon® AF 1600 below the  $T_g$ , 160°, is 222 ppm/°C and 960 ppm/°C above the  $T_g$ . The values have been extrapolated to zero pressure. For Teflon® AF 2400 the values are 243 ppm/°C below the  $T_g$  and 1280 ppm/°C above the  $T_g$ . These thermal expansion properties are in contrast to those of the semicrystalline fluorinated polymers such as PTFE, FEP and PFA whose coefficients increase, sometimes quite sharply, with increasing temperature. The rapid rate of change near the melting temperature is due to melting of smaller crystallites which are absent in Teflon® AF.

Figure 22.17 shows the extraordinarily high gas permeabilities of Teflon® AF. They are greater than two orders of magnitude higher than those of PTFE and are exceeded only by those of the most permeable polymer known, poly(1-trimethylsilyl-1-propyne). The gas permeability of Teflon® AF increases with

Gas	AF-1600	AF-2400	AF-2400	PTFE	Selectivity gas/N <sub>2</sub>	
		Melt processed	Solution cast		AF-2400	
					Melt processed	solution cast
CO <sub>2</sub>		280 000	390 000	1200	5.7	5.0
O <sub>2</sub>	34 000	99 000	160 000	420	2.0	2.0
He		270 000	360 000		5.5	4.6
H <sub>2</sub>		220 000	340 000	980	4.5	4.4
N <sub>2</sub>		49 000	78 000	140		
Ethylene		35 000				
Methane		34 000	60 000		0.7	0.8
Ethane		18 000	37 000		0.4	0.5
H <sub>2</sub> O (g)	117 000	410 000				

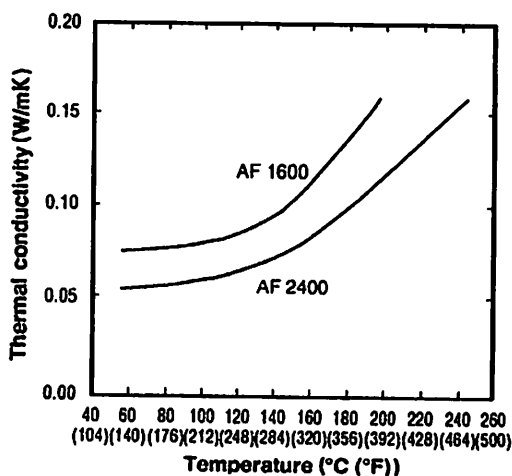
**Figure 22.17.** Gas permeability of Teflon® AF [22,23] (cB) (cB = centi-Barrer =  $10^{-8} \times (\text{cm}^3 \cdot \text{cm})/\text{cm Hg s cm}^2$ )

dioxole content and reaches a maximum with PDD homopolymer. Although PDD homopolymer is extremely difficult to work with due to very limited solubility and melt processability, several thin films have been fabricated and showed high oxygen and nitrogen permeabilities. Permeabilities of small gas molecules in Teflon® AF-2400 are higher than those of large, condensable gases, indicating that the high gas permeabilities result from very high diffusion coefficients. The selectivity shown by Teflon® AF-2400 is a function of the differences in diffusivity of the gases. It has been suggested that the low nitrogen/organic vapor selectivity and the strong dependence of selectivity on vapor activity will severely limit the use of Teflon® AF-2400 as a membrane material for the separation of air from organic vapors [22].

Teflon® AF has very low thermal conductivity [24]. The conductivities of Teflon® AF-1600 and AF-2400 and other materials at room temperature are shown in Figure 22.18. The thermal conductivity of Teflon® AF-1600 has also been shown to have weak absolute pressure and temperature dependencies in comparison with PTFE [25]. Figure 22.19 shows the thermal conductivity

Material	Conductivity (W/mK)
AF-2400	0.05
AF-1600	0.07
Polystyrene	0.12
Polyvinyl chloride	0.16
Teflon® PFA	0.19
Teflon® FEP	0.20
Teflon® PTFE	0.23
Corning glass 7740	1.14

**Figure 22.18.** Thermal conductivity of selected materials at room temperature



**Figure 22.19.** Thermal conductivity of Teflon® AF

Solvent	Boiling point (°C)	Solubility Parameter (J/m <sup>3</sup> ) <sup>1/2</sup> (cal/cm <sup>3</sup> ) <sup>1/2</sup>	
'Fluorinert' FC-72	60	0.0123	6.0
Perfluoromethylcyclohexane	76	0.0129	6.3
Perfluorobenzene	82	0.0123	6.0
Perfluorodimethylcyclohexane	102	0.0139	6.8
Perfluorooctane	103	0.0116	5.8
'Fluorinert' FC-75	103	0.0129	6.3
Perfluorodecalin	142	0.0136	6.6
'Fluorinert' FC-40	155	0.0136	6.6
Perfluoro-1-methyldecalin	160	0.0143	7.0
Perfluorodimethyldecalin	180	0.0147	7.2

**Figure 22.20.** Solvents for Teflon® AF

of Teflon® AF-1600 and AF-2400 below their glass transition temperatures. The conductivity results for Teflon® AF are consistent with a low-density fluoropolymer containing microvoids.

One of the unique properties of Teflon® AF is its solubility in fluorinated solvents. Figure 22.20 lists some of these solvents and their boiling points. All of the known solvents for Teflon® AF are essentially perfluorinated. Like the semicrystalline fluoropolymers, Teflon® AF is insoluble and not swollen in hydrocarbon solvents. 'Fluorinert' FC-75 is a product of the 3M company and is nominally perfluoro(n-butyl-tetrahydrofuran). 'Fluorinert' FC-40 is a perfluoro(alkyl amine). Teflon® AF is also soluble in Ausimont's 'Galden' and Hoechst's perfluorinated ethers. The higher boiling solvents tend to be poorer solvents at room temperature, but solubility at higher temperatures is improved. Teflon® AF 1600 is more soluble than AF 2400. In general, solubility decreases as dioxole content of the polymer increases. At room temperature Teflon® AF 1600 has a solubility limit of 12–15% by weight. This is the concentration at which the solution will not flow when its container is inverted. In contrast, the solubility limit of AF 2400 is only 1.5–2 wt% at room temperature. The homopolymer of PDD is soluble at only a few tenths of 1%. Solubility can be changed by modifications to the polymer structure. Increased solubility may be obtained by substituting other fluorinated monomers such as chlorotrifluoroethylene for tetrafluoroethylene or by lowering the molecular weight of the polymer.

The chemical resistance of Teflon® AF is essentially the same as that of the other Teflon® polymers such as PTFE, FEP or PFA except for its solubility in fluorinated solvents as noted as discussed earlier. Teflon® AF is resistant to attack by most chemicals including hot acids, hot caustic, chlorine, organic esters, ketones and alcohols. Materials known to attack PTFE such as molten alkali metals and sodium naphthalide will also attack Teflon® AF. Figure 22.21 shows the chemical resistance of Teflon® AF 1600 in a variety of organic and inorganic liquids. Measurements were made by drying polymer samples to constant weight, then immersing them in the liquids for seven days. After immersion, the samples

Reagent	Temperature (°C)	% Wt change	Appearance change
Acetone	23	0	None
CCl <sub>4</sub>	23	0	None
CFC-113	23	+6.2	Swollen
12N HCl	60	0	None
Hexanes	23	0	None
50% HF	60	0	None
98% H <sub>2</sub> SO <sub>4</sub>	60	0	None
MEK	23	0	None
10% NaOH	60	0	None
44% NaOH	60	0	None
CCl <sub>3</sub> -CCl <sub>2</sub>	23	+0.1	None
Toluene	23	0	None

**Figure 22.21.** Chemical resistance of Teflon® AF (seven days immersion)

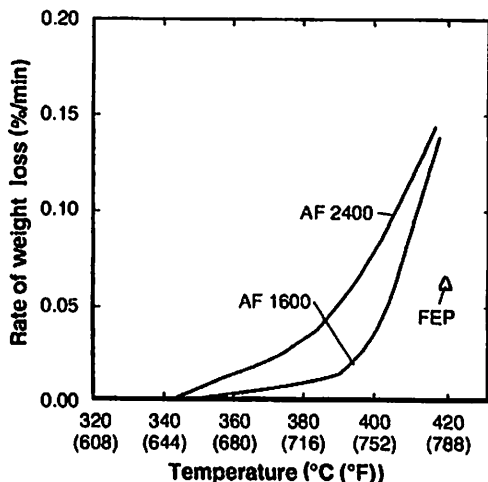
Temperature (°C)	Weight loss (%)	Hours
260	None	4
360	0.30	1
380	0.50	1
400	1.90	1
420	8.80	1

**Figure 22.22.** Thermal stability of Teflon® AF

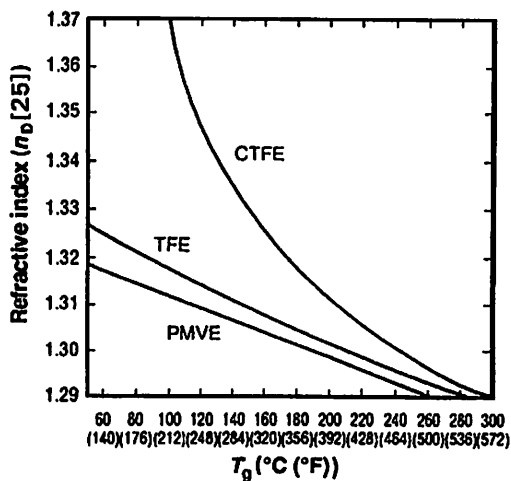
were rinsed with water and dried to constant weight. CFC-113, 1,1,2-trichloro-1,2,2-trifluoroethane, swells Teflon® AF appreciably and is difficult to remove completely. The other liquids have essentially no effect on Teflon® AF.

The thermal stability of Teflon® AF is high and approaches that of other perfluorinated plastics. Figure 22.22 shows the isothermal weight loss data in air for Teflon® AF as a function of temperature. These data were obtained by holding the sample at the indicated temperature for one hour in a thermogravimetric analyzer (TGA) and measuring the rate of weight loss. The rates plotted are the maximum rates observed, which were always seen at the beginning of the experiment. Initial weight loss was observed between 350 and 360 °C (Figure 22.23). At lower temperatures AF 1600 showed lower rates of weight loss than AF 2400, but at 420 °C the rates were equal. The maximum weight of weight loss for Teflon® AF is 0.15%/min at 420 °C. The rate of weight loss for Teflon® FEP at 420 °C is shown for comparison and is slightly less than that of Teflon® AF.

The commercially available grades of Teflon® AF are copolymers of PDD and tetrafluoroethylene. As previously noted many other comonomers have been copolymerized with PDD. The resulting copolymers have differing physical properties. Figure 22.24 shows the effect of changing the structure of the comonomer polymerized with PDD on refractive index. CTFE is chlorotrifluoroethylene and PMVE is perfluoromethylvinyl ether. The physical and chemical properties of



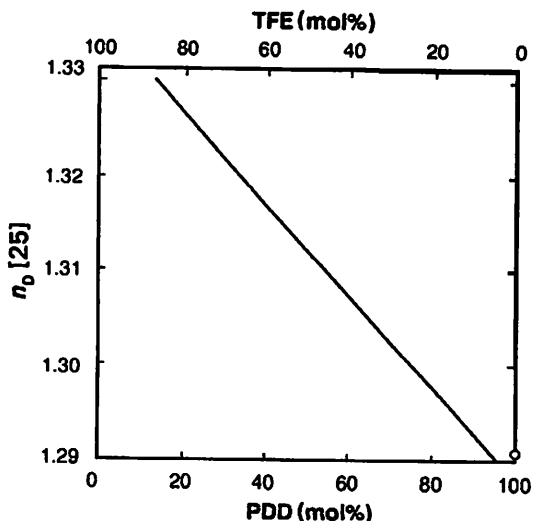
**Figure 22.23.** Thermogravimetric curves for Teflon® AF (FEP is shown for reference)



**Figure 22.24.** Refractive index of copolymers of PDD as a function of composition

these copolymers are generally comparable to the TFE copolymers. The refractive index has been plotted against the glass transition temperature,  $T_g$ , rather than polymer composition;  $T_g$  is related to composition in the same way as are the PDD-TFE (Teflon® AF) copolymers. A plot of polymer composition against refractive index for Teflon® AF is shown in Figure 22.25. The refractive index of PDD-CTFE copolymers changes much more rapidly with  $T_g$  or composition



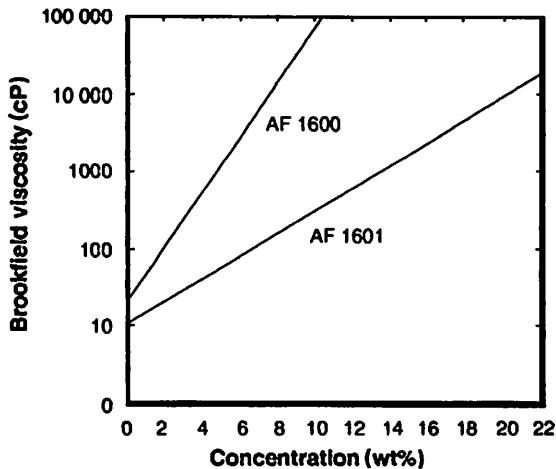


**Figure 22.25.** Refractive index of Teflon® AF polymers

than does the refractive index of the PDD–TFE copolymers. The refractive index of polychlorotrifluoroethylene is 1.42–1.43 [18]. All three curves converge at a refractive index of 1.29 at a  $T_g$  of 335 °C, which is the  $T_g$  of PDD homopolymer. Since PMVE does not readily homopolymerize, it is not possible to obtain the refractive index of polyPMVE. Copolymers of PDD and PMVE have a lower refractive index at a given  $T_g$  than either PDD–TFE or PDD–CTFE copolymers. The change in refractive index with  $T_g$  is also less for PDD–PMVE copolymers than for the other copolymers. Differences in refractive index at a  $T_g$  greater than about 220 °C for these copolymers are small since the amount of comonomer is quite low.

Figure 22.26 shows the effect of the change in molecular weight on the solution viscosity of a copolymer of PDD and TFE with a  $T_g$  of 160 °C. Teflon® AF 1601 has a lower molecular weight than Teflon® AF 1600, but with identical composition. The differences in solution viscosity at room temperature in ‘Fluorinert’ FC-75 at a given concentration are substantial. The Brookfield viscosity of a solution of AF 1601 at 18 wt% concentration is equal to that of a solution of AF 1600 at 6.4 wt%. The lowered molecular weight results in slightly poorer physical properties, but higher solubility as shown in Figure 22.27. Further reductions in molecular weight at this composition lead to further reductions in solution viscosity, but the polymers are likely to be too brittle.

Teflon® AF may be processed by a wide variety of methods. Processing of the polymers have been performed from solution using spin coating, casting, dip coating, spraying and painting. Melt processing by extrusion, compression



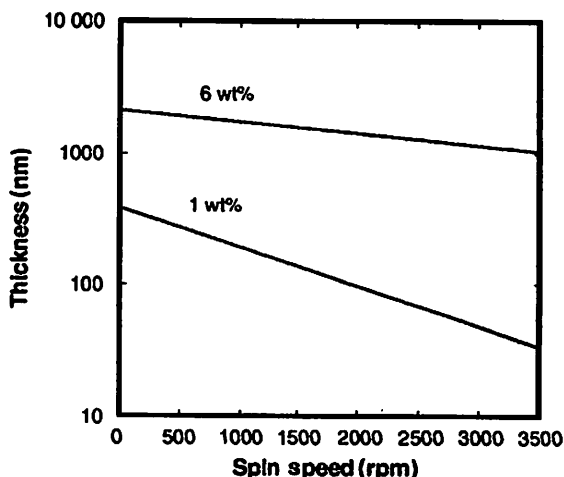
**Figure 22.26.** Brookfield viscosity of Teflon® AF polymers

Property	ASTM method	Units	AF-1600	AF-1601
Glass transition temp.	D3418	°C	160	160
Tensile strength	D638	MPa	27	27
Elongation at break	D638	%	>20	17
Tensile modulus	D638	GPa	1.6	1.55
Vol. coff. thermal exp.	E831	ppm/°C	260	260
Specific gravity	D792		1.78	1.78
Dielectric constant	D150		1.93	1.93
Dissipation factor	D150		0.00012	0.00012
Optical transmission	D1003	%	>95	>95
Refractive Index	D542		1.31	1.31
Contact angle with H <sub>2</sub> O		Degrees	104	104
Critical surface energy		dyne/cm	15.7	15.7
Water absorbtion	D570	%	<0.01	<0.01
Melt viscosity	D3835	250°/s	2657	5000
Solubility in FC-75 (ambient)		%	12-15	25-30
Brookfield viscosity in FC-75		Pa s	5500	5500
			(6.4%)	(18%)

**Figure 22.27.** Physical properties of Teflon® AF polymers

molding and injection molding have also been successful. In addition thin films of Teflon® AF have been prepared by either laser ablation or vacuum pyrolysis.

Solution processing methods are possible due to the room temperature solubility of Teflon® AF in perfluorocarbon solvents. Spin coating is an effective technique for making thin to ultra-thin uniform thickness coatings on flat substrates. Figure 22.28 gives typical data for spin speed and film thickness for Teflon® AF 1600 solutions in ‘Fluorinert’ FC-75 spun onto glass. A 6 wt% solution gives coating thickness between 1 and 3 µm while a 1% solution gives



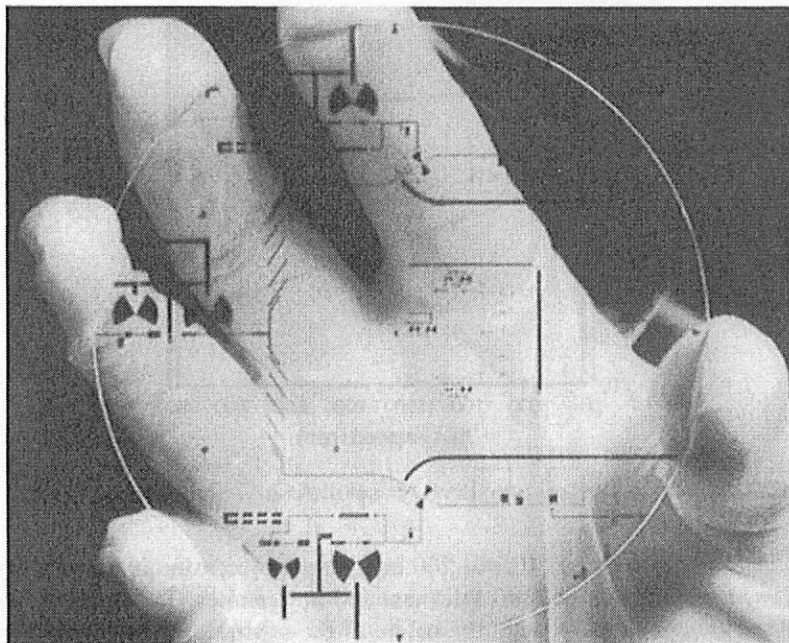
**Figure 22.28.** Spin coating conditions for solutions of Teflon® AF on glass

coating thicknesses between 50 and 200 nm. Microscopic examination of these films show them to have uniform thickness and no pinholes. The film thickness on other substrates will vary with the nature of the substrate, the spin speed and the concentration of the solution.

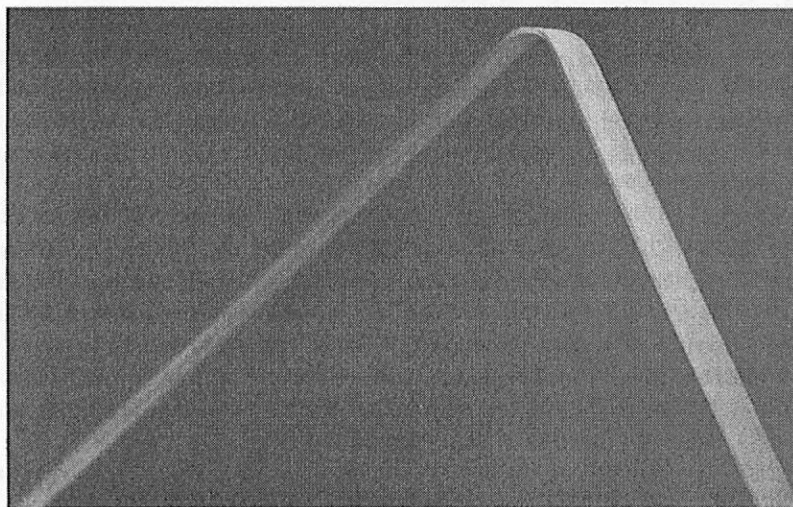
While spin coating is useful for obtaining thin uniform coatings on flat substrates (Figure 22.29), nonplanar surfaces are better coated using dip coating or spraying procedures. Dip coating has been used to produce Teflon® AF 2400 antireflective coatings on lenses [26]. Coating thickness was controlled by solution concentration and the rate of withdrawal of the lens from the polymer solution. Spraying is useful for coating planar and nonplanar substrates where thickness uniformity is not critical. Thick coatings on irregular surfaces may be applied by painting. Teflon® AF is amenable to all methods of application requiring polymer solutions.

In addition to solution-based application methods, Teflon® AF can be melt processed using all of the methods available for other melt fabricable Teflon® polymers. Compression molding is generally done at a temperature 100 °C higher than  $T_g$ . Extrusion and injection molding conditions depend on the part being extruded or molded. Because Teflon® AF is optically clear, special care must be taken to insure a clean, contamination-free environment during the melt fabrication process (Figure 22.30). The low thermal conductivity of Teflon® AF may also require longer heat up times than other polymers.

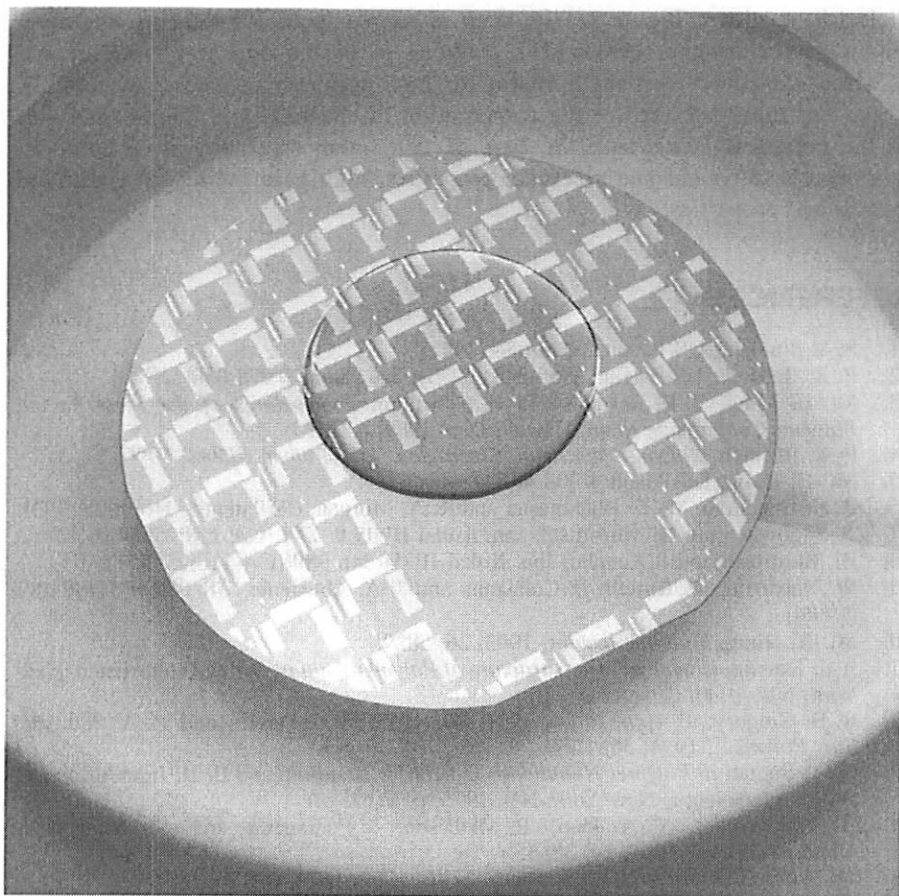
Laser ablation is a technique by which a material is vaporized in a high-vacuum environment by irradiation with a high-powered laser and the vapor directed to a substrate for coating. Advantages are the ability to deposit extremely thin films, of the order of tens of nanometers without the use of solvent. This technique has



**Figure 22.29.** Spin coating of Teflon® AF enables the production of ultra-thin uniform thickness coatings on flat substrates



**Figure 22.30.** Compression Molded Sheet of 1/8" (3.2 mm) thick TEFLON® AF. Note: exceptional clarity is a hallmark of amorphous fluoropolymers



**Figure 22.31.** A spin coater with a solution of Teflon® AF on a silicon wafer

been successfully applied to Teflon® AF using a Nd-YAG laser at  $10^{-7}$  Torr [27]. The copolymers retained their composition during this process. Vacuum pyrolysis is a similar process in which the material is vaporized by thermal rather than laser irradiation. Teflon® AF has also been applied to various substrates using this technique [28,29]. The resulting coatings also retain their composition during this process. Teflon® AF coatings applied by vacuum pyrolysis are claimed to have superior adhesion to the substrate compared to Teflon® AF coatings applied from solution [28].

Teflon® AF is a unique family of amorphous copolymers possessing an unusual combination of properties. The use of these polymers exploit either one or more of these properties since at present the cost of the polymers is quite high. Teflon® AF has many uses including preparation of antireflective coatings [30], low

dielectric coatings (Figure 22.31), deep ultraviolet pellicles used in electronic chip manufacturing processes [31], cladding in plastic optical fibers [32] and as a low dielectric constant insulator for high-performance interconnects [33]. These and other uses utilize the combination of chemical and thermal stability of the polymers along with the ease of fabrication especially from solution, their excellent optical and electrical properties, high permeability to gases and mechanical properties.

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