

FLUOROCARBON ELASTOMERS

Introduction

Fluorocarbon elastomers are fluorine-containing, cross-linked amorphous polymers with a carbon-carbon backbone. They are designed for demanding service applications in hostile environments characterized by broad temperature ranges and contact with industrial chemicals, oils, or fuels.

Military interest in the development of fuel- and thermal-resistant elastomers for low temperature service created a need for fluorinated elastomers. In the early 1950s, the M.W. Kellogg Co., in a joint project with the U.S. Army Quartermaster Corps, and 3M Co., in a joint project with the U.S. Air Force, developed two commercial fluorocarbon elastomers. The copolymers of vinylidene fluoride ($\text{CF}_2=\text{CH}_2$) and chlorotrifluoroethylene ($\text{CF}_2=\text{CFCl}$) became available from Kellogg in 1955 under the trademark of Kel-F (1-3), and a polymer based on poly(1,1-dihydroperfluorobutyl acrylate) was marketed in 1956 as 3M brand fluororubber 1F4 (4). The poor acid-, steam-, and heat-resistance of the latter limited its commercial use (see also VINYLIDENE FLUORIDE POLYMERS).

In the late 1950s, the copolymers of vinylidene fluoride and hexafluoropropylene ($\text{CF}_2=\text{CFCF}_3$) were developed on a commercial scale by 3M (Fluorel) and by DuPont (Viton) (5-7). In the 1960s, terpolymers of vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene ($\text{CF}_2=\text{CF}_2$) were developed (8) and commercialized by DuPont as Viton B. At about the same time, Montedison developed copolymers of vinylidene fluoride and 1-hydropentafluoropropylene as well as terpolymers of these monomers with tetrafluoroethylene marketed as Tecnoflon polymers (9,10) (see also PERFLUORINATED POLYMERS).

In the 1960s and 1970s, DuPont introduced polymers containing perfluoro (methyl vinyl ether), $\text{CF}_2=\text{CFOCF}_3$. With tetrafluoroethylene and a cure-site monomer, it gives a perfluoroelastomer, and when it is used as a comonomer with vinylidene fluoride and/or tetrafluoroethylene, improved low temperature properties are obtained (11,12).

Peroxide cure-site monomers, typically iodine- or bromine-containing fluoroolefins, have also been polymerized with the above monomers for improved steam- and amine-resistance (13–20).

Copolymers of propylene and tetrafluoroethylene were introduced in the early 1980s by Asahi Glass Co., Japan (21–26). 3M introduced bisphenol/onium cured copolymers of vinylidene fluoride, tetrafluoroethylene, and propylene in the late 1980s (27–30).

The principal commercial fluorocarbon elastomers are given in Table 1.

Of the approximately 10,000 t consumed worldwide per year, ca 40% is used in the United States, 30% in Europe, and 20% in Japan, and 10% APAC (excl. Japan); 2000 prices were \$44–\$4000/kg.

Properties

The characteristics of vulcanizates prepared from commercially available fluorocarbon elastomer gumstocks are given in Table 2.

Thermal Stability. The retention of elongation after thermal aging is an indication of the thermal stability of fluorocarbon elastomers. As shown in Figure 1, fluorocarbon elastomers are far superior to hydrocarbon elastomers. A more severe test at 205°C shows that a typical molding compound retains 90% of initial elongation after 1 year. Retention of tensile strength is another important characteristic of fluorocarbon elastomers. Figure 2 demonstrates the effect of long-term heat aging on a typical O-ring compound made from vinylidene fluoride–hexafluoropropylene copolymer; 90% of the initial tensile strength is retained after

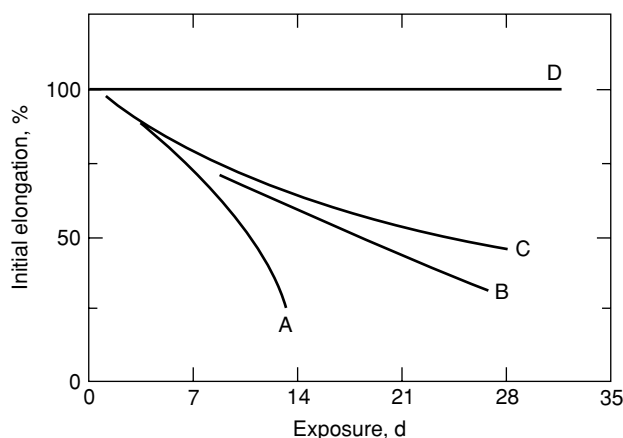


Fig. 1. Elongation retention of vulcanized elastomers at 150°C: A, nitrile; B, ethylene–propylene–diene monomer (EPDM); C, acrylate; D, fluorocarbon (31).

Table 1. Commercial Fluorocarbon Elastomers

Copolymer	Trademark	Supplier
Poly(vinylidene fluoride- <i>co</i> -hexafluoropropylene)	Dai-el	Daikin
	Dyneon	LLC ^a
	Tecnoflon	Ausimont
	Viton	DuPont Dow ^b
Poly(vinylidene fluoride- <i>co</i> -hexafluoropropylene) plus cure-site monomer	Dyneon	LLC
Poly(vinylidene fluoride- <i>co</i> -hexafluoropropylene- <i>co</i> -tetrafluoroethylene)	Dai-el	Daikin
	Dyneon	LLC
	Tecnoflon	Ausimont
	Viton	DuPont Dow
Poly(vinylidene fluoride- <i>co</i> -hexafluoropropylene- <i>co</i> -tetrafluoroethylene) plus cure-site monomer	Dai-el	Daikin
	Dyneon	LLC
	Tecnoflon	Ausimont
	Viton	DuPont Dow
Poly[vinylidene fluoride- <i>co</i> - tetrafluoroethylene- <i>co</i> -perfluoro(methyl vinyl ether)] plus cure-site monomer	Dai-el	Daikin
	Tecnoflon	Ausimont
	Viton	DuPont Dow
Poly[tetrafluoroethylene- <i>co</i> -perfluoro(methyl vinyl ether)] plus cure-site monomer	Dai-el	Daikin
	Dyneon	LLC
	Kalrez	DuPont Dow
	Tecnoflon	Ausimont
Poly(tetrafluoroethylene- <i>co</i> -propylene)	Aflas	Asahi Glass
	Dyneon	Dyneon
Poly(vinylidene fluoride- <i>co</i> -tetrafluoroethylene- <i>co</i> -propylene)	Aflas	Asahi Glass
	Aflas	Asahi Glass
	Dyneon	LLC
	Viton	DuPont Dow
	Aflas	Asahi Glass
Poly(tetrafluoroethylene- <i>co</i> -ethylene- <i>co</i> -perfluoro(methyl vinyl ether) plus cure-site monomer	Viton Extreme	DuPont Dow

^aWholly owned subsidiary of 3M.

^bJoint venture between DuPont and Dow Chemical Co.

1 year at 205°C. Perfluoroelastomers [copolymers of tetrafluoroethylene and perfluoro (alkyl vinyl ethers)] are more thermally stable yet. Some of these polymers are stable up to 320°C.

Chemical Resistance. The resistance of fluorocarbon elastomer compounds to chemicals is given below:

- (1) *Excellent resistance, may be used without reservation*, eg, automotive fuels and oils, hydrocarbon solvents, aircraft fuels and oils, hydraulic fluids, and certain chlorinated solvents.

Table 2. Properties of Fluoroelastomers

Property	ASTM test method	Value/description
Physical properties		
Tensile strength, MPa ^a	D412	9–20
100% modulus, MPa ^a		2–16
Elongation at break, %		100–500
Hardness, Shore A	D2240	45–95
Compression set, %	D395 ^b	
70 h at 25°C		9–16
70 h at 200°C		10–30
1000 h at 200°C		50–70
Specific gravity of gumstock	D297	1.80–2.04
Low temperature flexibility, °C		
T _g	E1356	0 to –30
TR10	D1329	0 to –30
Brittle point, °C	D2137	–18 to –50
Thermal degradation temperature, °C	E1131	400–550
General characteristics		
Gas permeability		Very low
Flammability		Self-extinguishing or nonburning ^d
Radiation resistance		Good to fair
Abrasion resistance		Good and satisfactory for most uses
Weatherability and ozone resistance		Outstanding ^e

^aTo convert MPa to psi, multiply by 145.

^bMethod B for 5-mm O-ring.

^cHighly dependent on material grade.

^dWhen properly formulated.

^eUnaffected after 200-h exposure to 150-ppm ozone.

- (2) *Good to excellent resistance, gum and compound must be chosen with care, eg, highly aromatic solvents, polar solvents, water and salt solutions, Aqueous acids, dilute alkaline solutions, oxidative environments, and amines.*
- (3) *Not recommended, to be used only with perfluoro and TFE/propylene elastomers, eg, ammonia, strong caustic, 50% sodium hydroxide above 70°C, and, certain polar solvents, eg, low molecular weight ketones, esters, and ethers.*

However, Viton Extreme (32) is resistant to ammonia, strong caustic, and certain polar solvents.

In the past 10 years fluoroelastomers containing 70–72% fluorine have been introduced. These highly fluorinated elastomers are resistant to the new oxygenated fuels now used in the automobile industry and meet the stringent permeation requirements (33–35) (see Fig. 3).

Compression-Set Resistance. Fluorocarbon elastomers are used in the sealing industry because of their resistance to compression set under extreme

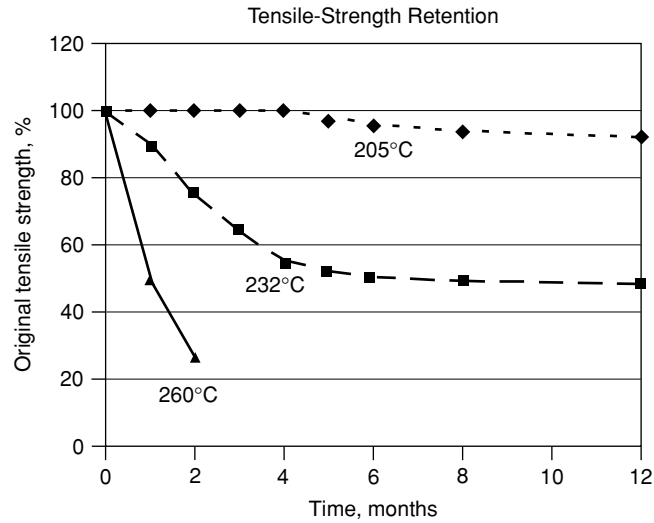


Fig. 2. Tensile-strength retention in continuous service for fluorocarbon elastomers, compound 1 (see Table 5).

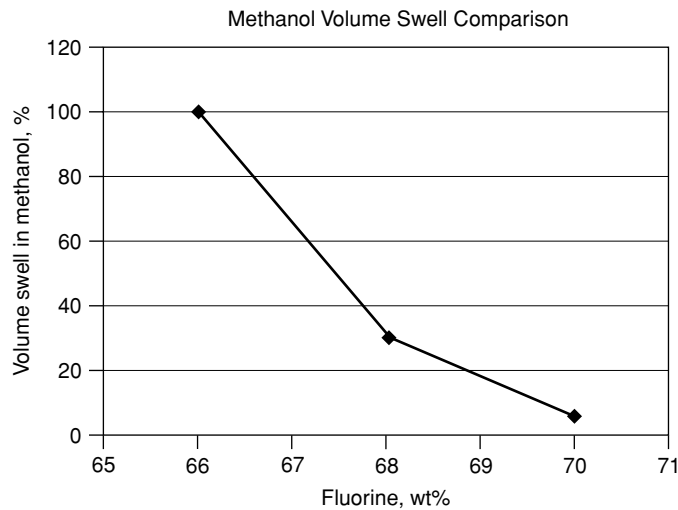


Fig. 3. The percent volume swell in methanol for 7 days at 21°C compared with the weight percent of fluorine in fluorocarbon elastomers: 66%, dipolymer of vinylidene fluoride–hexafluoropropylene; 68% and 70%, terpolymers of vinylidene fluoride–hexafluoropropylene–tetrafluoroethylene.

conditions. Plots of compression set vs time are shown in Figure 4 for compounds prepared especially for compression-set resistance (O-ring grades).

Manufacture

The elastomers listed in Table 1 are typically prepared by high pressure, free-radical, aqueous emulsion polymerization (5,8,36,37). The initiators are organic or

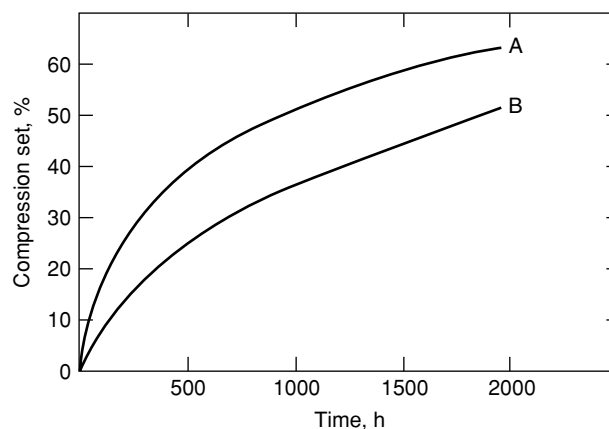


Fig. 4. Compression-set values of fluorocarbon elastomers at 200°C (ASTM D 395), 3.5-mm O-rings: A, compound 1 (see Table 5); B, compound 2 (see Table 5).

inorganic peroxy compounds, such as ammonium persulfate, and the emulsifying agent is usually a fluorinated acid soap. The temperature ranges from 30 to 125°C and the pressure from 0.35 to 10.4 MPa (50–1500 psi). The molecular weight of the polymer is controlled by the ratio of initiator to monomer or choice of chain-transfer agent, or both. Typical chain-transfer agents are ethyl acetate, methanol, acetone, diethyl malonate, and dodecylmercaptan (38–40). A typical polymerization recipe is given in Table 3.

The aqueous emulsion polymerization is conducted by batch, semicontinuous, or a continuous process (Fig. 5). In a simple batch process, all the ingredients are charged to the reactor, the temperature raised, and the polymerization run to completion.

In a semicontinuous process all the recipe ingredients are added to the reactor and the vessel is pressurized with the monomers. The reaction is started and the consumed monomers are continuously replenished in order to maintain constant reactor pressure.

In a continuous process (37), feeding of the ingredients and removal of the polymer latex are continuous. The discharge of latex from the reactor is controlled by a pressure-control or relief valve. The polymer latex is coagulated into a crumb

Table 3. Typical Fluorocarbon Elastomer Polymerization Recipe

Component	Grams
Vinylidene fluoride	61
Hexafluoropropylene	39
Diethyl malonate	0.13
Ammonium persulfate	0.35
Ammonium perfluorooctanoate	0.90
Potassium phosphate, dibasic	0.85
Water	225

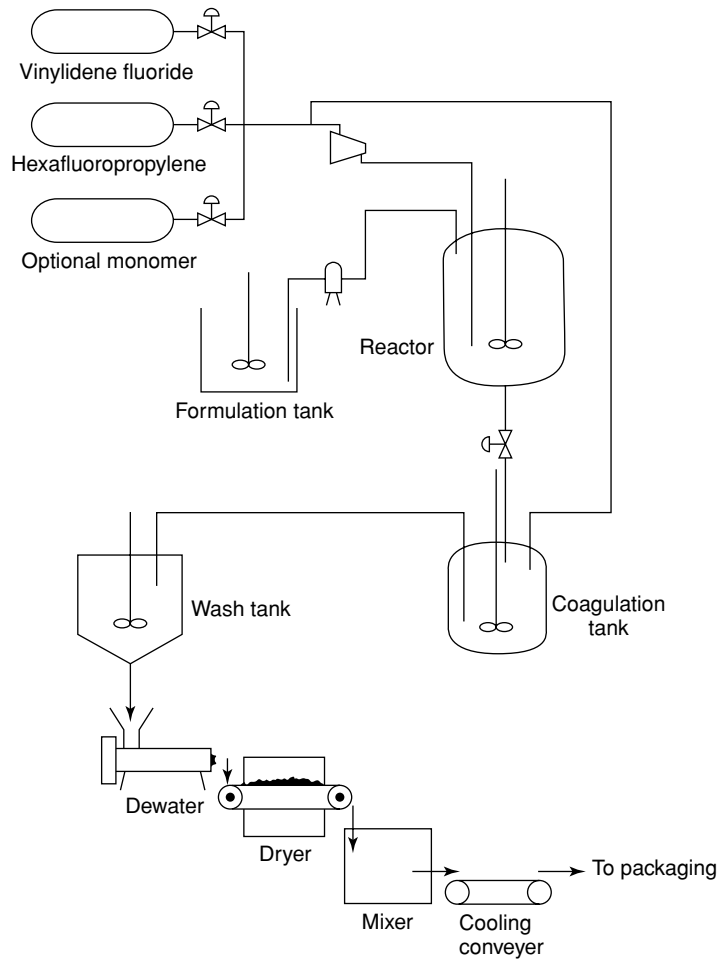


Fig. 5. Production of fluorocarbon elastomers.

by adding salt or acid, a combination of both, or by a freeze-thaw process. The crumb is washed, dewatered, and dried.

Most fluorocarbon elastomer gums contain a cure system, and, in the final step, the cure additives are incorporated in a two-roll mill, in an internal mixer, or in a mixing extruder. The cure system comprises an organic onium cure accelerator, such as triphenylbenzylphosphonium chloride, and a bisphenol cross-linking agent, such as hexafluoroisopropylidenediphenol. These cure systems improve compression-set performance and processing safety and accelerate cure cycles.

For complete formulation, reinforcing fillers and metallic oxides are added, the latter as acid acceptors (41–46). Raw gums contain no curative, and cure ingredients such as diamines, bisphenols, or peroxides (47) must be added in addition to formulation (compound) ingredients. Diamines were the first commercially important curing agents; they give good thermal resistance but poor scorch resistance. Bisphenol/onium cure systems yield very low compression set and good processing

safety. Peroxide cure systems improve steam and water resistance and give fair compression-set resistance; no water is produced during cure.

Processing

Compounding. Compared with the large number of ingredients required in a conventional rubber recipe, fluorocarbon elastomer compounding seems simple (Table 4) (see RUBBER COMPOUNDING).

O-Rings. In O-ring applications, the primary consideration is resistance to compression set. The choice of a fluorocarbon elastomer gum is based on gum viscosity, cross-link density, and cure system. Formulations are given in Table 5 (compounds 1 and 2).

Long-term compression-set resistance is described in Figure 4. Values are reduced by using gumstock of higher viscosity at comparable cross-link densities. Compression-set resistance also depends on the cure system. The bisphenol/onium cure system offers the lowest compression-set resistance, as shown in Table 6.

Table 4. Typical Fluorocarbon Elastomer Compound

Component	phr
Elastomer	100
Magnesium oxide or calcium hydroxide	6–20
Filler, reinforcing or nonreinforcing	0–60
Accelerators or curatives	0–6
Process aids	0–2

Table 5. Fluorocarbon Elastomer O-ring Compounds

	Compound 1	Compound 2
Typical formulation, phr		
Poly(vinylidene fluoride-co-hexafluoropropylene)		
ML ^a 1 + 10 at 121°C = 40 ^b	100	
ML ^a 1 + 10 at 121°C = 100 ^b		100
Hexafluoroisopropylidenediphenol	2.1	2.1
Triphenylbenzylphosphonium chloride	0.45	0.45
Magnesium oxide	3	3
Calcium hydroxide	6	6
MT Black (N-990)	30	30
Physical properties ^c		
Tensile strength, MPa ^d	15	15
Elongation at break, %	200	200
Hardness, Shore A	75	75
Compression set, ^e %	15	10
Specific gravity	1.8	1.8

^aMooney viscosity, large rotor.

^bFKM 2230 and 2178 (Dyneon).

^cPress cure, 5 min at 177°C; postcure, 24 h at 260°C.

^dTo convert MPa to psi, multiply by 145.

^eASTM D395, method B (O-ring) for 70 h at 200°C.

Table 6. Effect of Cure System on Processing Safety and Compression-Set Resistance

	Amine	Bisphenol	Peroxide
Formulation, phr			
Poly(vinylidene fluoride-co-hexafluoropropylene) plus cure-site monomer ^a			
ML ^b 1 + 10 at 121°C = 60	100	100	100
<i>N, N'</i> -Dicinnamylidene-1,6-hexanediamine	2.5		
Hexafluoroisopropylidenediphenol		2.1	
Triphenylbenzylphosphonium chloride		0.5	
Triallylisocyanurate			3.0
2,5-Dimethyl-2,5-bis- <i>t</i> -butylperoxyhexane			1.25
MT Black (N-990)	30	30	30
Magnesium oxide	15	3	
Calcium hydroxide		6	
Zinc oxide			3
Mooney scorch ^c			
Minimum	67	53	43
Time to 18-point rise, min	11	<60	37
Compression set, %	45	15	35

^aFKM 2260 Dyneon.^bMooney viscosity, large rotor.^cSmall rotor at 121°C.^dASTM D395, method B (3.5-mm O-rings) for 70 h at 200°C.

Molded Articles. In the compounding of molded articles, the most important physical property of the vulcanizate is elongation to break. Compression set is a secondary consideration. Since complex shapes are often required, compound flow is also important. These objectives are best met by using a gum with the lowest initial viscosity and a low cross-link density to permit high elongation compared with O-ring formulations.

Comparison of viscosities and properties of a molding compound (see Table 7) with an O-ring compound (see Table 5) shows differences in elongation due to lower cross-link density. Special formulations give even higher elongations and exceptionally high tear strengths in the press-cure state. Fillers (48) are of special importance for water- and acid-resistant compounds. The supplier may make specific recommendations to meet the properties required.

Extruded Articles. In an extruded article, the most important parameters are scorch safety and flow characteristics (49). The bisphenol/onium cure system provides the best scorch resistance. Gum viscosities and process aids affect flow characteristics. Typical formulations for extrusion-grade fluorocarbon elastomers are given in Table 8.

Formulation. Gum viscosity affects vulcanizate properties, especially compression set. Gums are available with Mooney viscosity (ML 1 + 10, large rotor, at 121°C) values of 0–160. A range of 20–60 gives the optimum combination of flow and physical properties. Mooney viscosity is commonly measured in a Mooney viscometer apparatus (ML = large rotor, MS = small rotor) after preheating the sample for 1 min, followed by heating at 121°C for 10 min, and then taking a reading (these values may vary). Mooney scorch (MS) is determined with a small rotor. Higher viscosities can cause excessive heat buildup during mixing,

Table 7. Fluorocarbon Elastomers for Molding

	Value
Typical formulation, phr	
Poly(vinylidene fluoride-co-hexafluoropropylene) ^a	100
Hexafluoroisopropylidenediphenol	1.7
Triphenylbenzylphosphonium chloride	0.4
Magnesium oxide	3
Calcium hydroxide	6
MT Black (N-990)	30
Postcure physical properties ^b	
Tensile strength, MPa ^c	14.4
Elongation at break, %	265
Hardness, Shore A	74
Compression set, ^d %	20
Specific gravity	1.8

^aFKM 2230 (Dyneon), ML 1 + 10 at 121°C = 40.

^bPress cure, 5 min at 177°C; postcure, 24 h at 260°C.

^cTo convert MPa to psi, multiply by 145.

^dASTM D395, method B (1.27-cm disk) for 70 h at 200°C.

Table 8. Fluorocarbon Elastomer Extrusion-Grade Compound

	Compound 1	Compound 2
Formulation, phr		
FKM 5830Q ^a	100	100
SRF Black (N-762)	15	
MT Black (N-990)		12
XC-72 (conductive black)		10
Magnesium oxide	3	3
Calcium hydroxide	6	5
Calcium oxide	3	6
Dibutyl sebacate		10
Physical properties ^b		
Tensile strength, MPa ^c	9.8	9.5
Elongation at break, %	380	350
Hardness, Shore A	72	72

^aAvailable from Dyneon LLC.

^bPress-cure, 45 min at 160°C.

^cTo convert MPa to psi, multiply by 145.

without improvement in physical strength. Compound viscosity depends on gum viscosity and filler type and loading. A range of 25–60, as measured by MS (121°C), is preferred.

Compound stability and safety are strongly affected by ingredients and cure systems.

The data in Table 6 clearly show the effect of cure system on scorch stability and processing, as determined by standard testing techniques (MS at 121°C). The most workable formulations are compounded with raw gums containing the bisphenol/onium cure systems. These cure systems offer maximum processibility safety.

Mixing. Fluorocarbon elastomers may be compounded by any standard rubber technique. Open mills may be used, since most commercial gums mix well, except very low viscosity gums, which stick to the rolls, and high viscosity gums, which are very tough.

Internal mixing, commonly referred to as Banbury mixing, is widely used with fluorocarbon elastomers. Gumstocks and compounds that are particularly successful fall in the viscosity ranges discussed earlier. A typical internal mix cycle takes 6–8 min with a drop temperature of 100–125°C. The formulations given in Tables 5 and 8 are both well suited to internal mixing.

Preforming. Formulations are easily preformed at cool barrel temperatures with a screw- or piston-type extruder (Barwell). Gums must be in the proper viscosity range and scorching must be avoided.

For routine calendaring operations, warm rolls (40–90°C) are recommended for optimum sheet smoothness. Process aids, such as low molecular weight polyethylene wax, are often used and sheets of 0.5- to 1.3-mm thickness are normally produced.

Molding. Compression molding is generally used to economize on material. Flow requirements are minimal and high viscosity resins may be used.

Little preforming is required for transfer molding, which is used for the production of very small parts. However, this technique often requires excessive amounts of material. Flow requirements are high, but fluorocarbon elastomers are available that can be used with this technique.

Injection molding is increasingly used in the rubber industry and fluorocarbon elastomers are well suited for this technique. Viscosity and cure rheology are very important because of high shear and fast cures (50–54). Molding at 180–200°C allows operations of 5 min or less, depending on part size.

Extrusion. Extrusion techniques are used for tubing, hose, O-ring cord, preforms, and shaped gaskets; typical extrusion conditions are 70–85°C for barrel temperature and 95–110°C for head temperature. The extruded forms are cured in a steam autoclave at 150–165°C. Special grades of peroxide-curable fluorocarbon elastomers may be vulcanized by hot air.

Postcuring. Postcuring for a period of 16–24 h at 200–260°C develops maximum physical properties, eg, tensile strength and compression-set resistance.

Specifications

Commercially available fluorocarbon elastomers meet automotive specifications in the HK section of ASTM D2000 and SAE J200. ASTM D1418 specifies designations of composition; fluorocarbon elastomers are designated FKM, FEPM, or FFKM in the case of perfluoroelastomers.

Some fluorocarbon elastomers meet the O-ring specifications, such as AMS 7276, AMS 7280A, AMS 7259, and MIL-83248 Amendment 1 Type II, Class I and II.

Certain grades and formulations are approved under the Code of Federal Regulations, 21, Food and Drugs, Part 177.2600, for articles intended for contact with food. Elastomer suppliers provide assistance in formulating for specified uses.

Test Methods; Health and Safety

The fluorocarbon elastomer raw gums are tested for Mooney viscosity (ASTM D1646) and specific gravity (ASTM D297). When compounded as described above, the stocks are tested for Mooney cure (ASTM D1646), Mooney scorch (ASTM D1646), and vulcanization characteristics (ASTM D2084 and D5289). The vulcanizates are evaluated with respect to original physical properties (ASTM D412, D2240, D1414), aged physical properties (ASTM D573), compression set (ASTM D395), and fluid aging (ASTM D471). Low temperature properties include low temperature retraction TR10 (ASTM D1329), torsional modulus (ASTM D1053), and brittle point (ASTM D2137).

Under normal handling conditions, fluorocarbon elastomers are nontoxic and nonirritating. Safe handling procedures are provided by manufacturers upon request.

Uses

About 45% of U.S. fluorocarbon elastomer consumption is in ground transportation. Typical components include engine oil seals, fuel system components such as hoses and O-rings, and drive-train seals. Growth in this area is expected to continue, considering the increased demands from higher engine temperatures, alcohol-containing fuels, and improved lubricants. Other industries include petroleum and petrochemicals, pollution control, and industrial hydraulic and pneumatic applications. These areas are more dependent upon general industrial production and overall energy demands, and will show slower growth than the automotive segment.

Consumption in Europe and Japan depends more upon the automotive industry. However, with the recent concern about acid rain, the European market is expected to show increased interest in fluorocarbon elastomers for pollution-control applications. In Japan, fluorocarbon elastomers are used for general manufacturing, eg, copiers. Petroleum applications are of little interest outside the United States. The aircraft industry uses less than 10% of the total fluorocarbon elastomer consumed.

Perfluoroelastomer parts are primarily used in the chemical processing industry and are finding increased applications in semiconductor manufacturing equipment, because of their high purity, extreme chemical inertness, and unrivaled thermal stability.

BIBLIOGRAPHY

"Fluorocarbon Elastomers" in *EPSE* 2nd ed., Vol. 7, pp. 257–269, by M. M. Lynn and Allan T. Worm, 3M Co.

1. M. E. Conroy and co-workers, *Rubber Age* **76**, 543 (1955).
2. C. B. Griffis and J. C. Montermoso, *Rubber Age* **77**, 559 (1955).
3. W. W. Jackson and D. Hale, *Rubber Age* **77**, 865 (1955).
4. F. A. Bovey and co-workers, *J. Polym. Sci.* **15**, 520 (1955).
5. U.S. Pat. 3051677 (Aug. 28, 1962), D. R. Rexford.
6. S. Dixon, D. R. Rexford, and J. S. Rugg, *Ind. Eng. Chem.* **49**, 1687 (1957).
7. J. S. Rugg and A. C. Stevenson, *Rubber Age* **82**, 102 (1957).

8. U.S. Pat. 2968649 (Jan. 17, 1961), J. P. Pailthrop and H. E. Schroeder.
9. U.S. Pat. 3331823 (July 18, 1967), D. Sianesi, G. Bernardi, and A. Regio.
10. U.S. Pat. 3335106 (Aug. 8, 1967), D. Sianesi, G. C. Bernardi, and G. Diotalleri.
11. U.S. Pat. 3235537 (Feb. 15, 1966), J. R. Albin and G. A. Gallagher.
12. Ger. Offen. 2457102 (Aug. 7, 1975), R. Baird and J. D. MacLachlan.
13. U.S. Pat. 4035565 (July 12, 1977), D. Apotheker and P. J. Krusic.
14. U.S. Pat. 4418186 (Nov. 29, 1983), M. Yamabe and co-workers.
15. A. L. Barney, G. H. Kalb, and A. A. Kahn, *Rubber Chem. Technol.* **44**, 660 (1971).
16. A. L. Barney, W. J. Keller, and N. M. Van Gulick, *J. Polym. Sci., Part A-1* **8**, 1091 (1970).
17. G. H. Kalb, A. L. Barney, and A. A. Khan, *Am. Chem. Soc. Dev. Polym. Chem.* **13**, 490 (1972).
18. S. M. Ogintz, *Lubr. Eng.* **34**, 327 (1978).
19. U.S. Pat. 4251399 (Feb. 17, 1981), M. Tomoda and Y. Ueta.
20. U.S. Pat. 4263414 (Apr. 21, 1981), A. C. West.
21. Y. Tabata, K. Ishigure, and H. Sobue, *J. Polym. Sci., Part A* **2**, 2235 (1964).
22. G. Kojima and Y. Tabata, *J. Macromol. Sci. Chem.* **5**, 1087 (1971).
23. K. Ishigure, Y. Tabata, and K. Oshima, *Macromolecules* **6**, 584 (1973).
24. G. Kojima and Y. Tabata, *J. Macromol. Sci. Chem.* **6**, 417 (1972).
25. G. Kojima, H. Kojima, and Y. Tabata, *Rubber Chem. Technol.* **50**, 403 (1977).
26. U.S. Pat. 4463144 (July 31, 1984), G. Kojima and M. Hisasue.
27. U.S. Pat. 4 882 390 (1989), W. M. Grootaert and R. E. Kolb.
28. U.S. Pat. 4 912 171 (1990), W. M. Grootaert and R. E. Kolb.
29. W. M. Grootaert, R. E. Kolb, and A. T. Worm, *Rubber Chem. Technol.* **63**, 516 (1990).
30. W. M. Grootaert, *Polymer Materials Encyclopedia*, Vol. **4**, CRC Press, Inc., Boca Raton, Fla., 1996, p. 2495.
31. J. R. Dunn and H. A. Pfisterer, *Rubber Chem. Technol.* **48**, 356 (1975).
32. U.S. Pat. 4694045 (Sept. 1987), A. L. Moore.
33. R. Mastromateo, Performance of Fuel Resistant Elastomers in Alternative Fuels, SAE Technical Paper 900195, 1990.
34. J. R. Blazer and A. L. Edmondson, Effects of Methanol Fuels on Fuel Hose Permeation, SAE Technical Paper 910106, 1991.
35. J. R. Blazer and A. M. Sohlo, Effects of Long-Term Flex Fuel Exposure on Fluorocarbon Elastomers, SAE Technical Paper 900118, 1990.
36. U.S. Pat. 3845024 (Oct. 29, 1974), S. D. Weaver.
37. U.S. Pat. 3053818 (Sept. 11, 1962), F. J. Honn and S. M. Hoyt.
38. U.S. Pat. 3069401 (Dec. 18, 1962), G. A. Gallagher.
39. U.S. Pat. 3080347 (Mar. 5, 1963), C. L. Sandberg.
40. U.S. Pat. 3707529 (Dec. 26, 1972), E. K. Gladding and J. L. Nyce.
41. U.S. Pat. 3655727 (Apr. 11, 1972), K. U. Patel and J. E. Maier.
42. U.S. Pat. 3712877 (Jan. 23, 1973), K. U. Patel and J. E. Maier.
43. U.S. Pat. 3752787 (Aug. 14, 1973), M. R. deBrunner.
44. U.S. Pat. 3857807 (Dec. 31, 1974), Y. Kometani and co-workers.
45. U.S. Pat. 3864298 (Feb. 4, 1975), Y. Kometani and co-workers.
46. U.S. Pat. 3920620 (Nov. 18, 1975), C. Ceccato, S. Geri, and L. Calombo.
47. J. E. Alexander and H. Omura, *Elastomerics* **2**, 19 (1978).
48. *Compounding Fluoroelastomers*, Brochure, Dyneon, Oakdale, Minn.
49. R. Christy, *Rubber World* **184**(6), 38 (1981).
50. U.S. Pat. 5591804 (June 7, 1997) W. D. Coggio, D. H. C. Arren, and A. T. Worm.
51. U.S. Pat. 5654374 (Aug. 5, 1997) D. H. C. Arren, W. D. Coggio, and D. S. Parker.
52. U.S. Pat. 5262490 (Nov. 16, 1993) W. M. Grootaert and R. E. Kolb.
53. D. H. C. Arren, Paper presented at *Europlast*, Paris, France, Oct. 6, 1994.
54. S. Bowers, Paper presented at the *German-French Rubber Symposium*, Trier, Germany, Nov. 15, 1996 (DuPont Dow Elastomers).

GENERAL REFERENCES

- J. Scheirs, ed., *Modern Fluoropolymers*, John Wiley & Sons, Inc., New York, 1997.
- L. E. Crenshaw and D. L. Tabb, *The Vanderbilt Rubber Handbook*, R. T. Vanderbilt Co., New York, 1990, p. 211.
- M. Morton, ed., *Rubber Technology*, Van Nostrand Reinhold Co., Inc., New York, 1973, pp. 407-439.
- W. W. Schmeigel, *Makromol. Chem.* **76/77**, 39 (1979).
- D. Apotheker and co-workers, *Rubber Chem. Technol.* **55**, 1004 (1982); *ACS Symp. Ser.* **260** (1984).
- J. C. Salamone, *Polymeric Materials Encyclopedia*, Vol. **4**, CRC Press, Inc., Boca Raton, Fla., 1996, p. 2495.

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