Journal of the Korean Nuclear Society
Vol. 2, No. 3, Sept. 1970

《Review》

Fluorine Containing Polymers

Dal Jho Park*

Korean Institute of Science and Technology, Seoul, Korea

(Received July 8, 1970)

Prior to the serendipic discovery of "Teflon" by Dr. Ray J. Plunkett of the duPont Co. in the late "thirties" the theory of polymerization confined itself to the following structure:

$$\rangle C = C \langle^{H}$$

as being susceptible of undergoing polymerization. The presence of a vinylic hydrogen in a monomer was considered essential. However, when $CF_2 = CF_2$ underwent polymerization, the old theory had to undergo revision. In its broadest sense, one can say that any π-bonded molecule has the potential of undergoing chain propagation to yield oligomers and polymers, be they homologues of carboolefins or hetero-olefins.

The outstanding properties of "Teflon" *eventually* "triggered off" a series of studies leading to the wide range of fluoro-polymers now available. "Eventually" in this context meant a lapse of several years before the inherent properties of "Teflon" overcame the conventional thinking, practices and preconceived prejudices of the then "status quo" "experts" in polymer chemistry.

One outstanding "defect" as the "experts" saw at that time, was "Teflon's" insolubility in any solvent. The practice then was to either extrude or cast polymers from a melt, suspension or solution. This was the status until the technique of powdered-metal technology was applied. Today, one takes for granted the myriads of ways in which polymers of this type are handled. The greatest deterrent to a more rapid adaptation and use of "Teflon" may be laid to the inflexible attitude of many "experts". On the hand, the greatest impetus was given to "Teflon's" exploitation by the chemical needs of World War II for a product possessing the properties of "Teflon".

One learns an important economic lesson from this case. Many companies look with envy at the expansive market opened up by "Teflon" and its family of fluoropolymers. They wrongfully attribute most or all of them to the genius and versatility of the duPont chemists and engineers. They are also prone to give up difficult projects or problems at the initial stages. To them, a study of the history of the development of "Teflon", "Kynar", "Dulite", etc. should be enlightening not only from the chemical viewpoint but also from the economic standpoint.

The question can logically be asked, "Why is "Teflon" and other fluoropolymers so important and valuable?"

Some of these points can be answered by stating some of their outstanding physical, thermal and electrical properties.

1) Excellent low-temperatures properties, down to -200°C. (cryogenic regions)
2) High-temperature properties (200° to 350°C)

*On leave from and now at the Department of Chemistry, Colorado University

3) Relative insolubility in most organic solvents and corrosive chemicals
4) High resistance to air oxygen and other oxidizing mediums (HNO_3, NO_2, etc.)
5) Non-inflammability in air
6) Low free surface energy which result in very low friction, high lubricity and low adhesion and cohesion.
7) Good electrical properties-low dielectric loss and high dielectric strength
8) Low moisture absorption

Some of their disadvantages may be enumerated as follows:

1) Tendency to undergo plastic flow
2) Relatively high cost
3) Complex procedures for the making of the monomers and polymers
4) Specialty types of fabrication

However, all of these difficulties have been eased and great progress made in generally over-coming them by ingenious fabrication, mechanical implementation and advances in chemical syntheses.

Today, the most important uses for the fluoropolymers are in the field of thermoplastics and elastomers.

1) Polytetrafluoroethylene-$(CF_2—CF_2)$-$_n$ (PTFE) is known by the following trade names.

"Teflon"—duPont (U.S.A.)
"Halon"—Allied (U.S.A.)
"Tetran"—Pennwalt (U.S.A.)
"Fluon"—I.C.I. (England)
"Algoflon"—Montedison (Italy)
"Daiflon"—Daikin (Japan)
"Hostaflon TFE"—Hoechst (W. Germany)

Polychlorotrifluoroethylene (PCTE)

$—(CF_2—CFCl)_n—$

"KEL-F"—3-M Co.
"Plaskon" (pellet)—Allied Chemical
"Aclar" (film)—Allied Chemical
"Hosteflo n"—Hoechst

Perfluorinated Ethylene-Propylene (FEP)

$$—(CF_2—CF_2—\underset{\displaystyle CF_3}{\underset{|}{CF}}—CF_2)$$

"FEP"—duPont

Fluorinated Ethylene-Propylene ("technoflon")—Montedison

Vinylidene fluoride-Hexafluoropropene Copolymer

$$—(CF_2—CH_2—\underset{\displaystyle CF_3}{\underset{|}{CF}}—CF_2)_n—$$

"VITON"—duPont
"Fluorel"—3-M Co.

Poly (vinylidene fluoride) (PVDF)

$—(CF_2\text{-}CH_2)_n—$

"Kynar"—Pennwalt
"Dulite"—duPont

Poly (vinyl fluoride) (PVF)

$—(CHF—CH_2)_n—$

"Tedlar"—duPont
"Dalvor"—Diamond Shamrock

Nitroso-rubber (NR)

$$—(\overset{\displaystyle CF_3}{\overset{|}{N}}—O—CF_2—CF_2)_n—$$

"CNR"—Thiokol (Terpolymer)

Fluorosilicone Elastomer (Poly-trifluoropyl methyl siloxane)

$$—(O—\overset{\displaystyle C_2H_4CF_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{Si}}}}—O)_n—$$

Silastic LS-53.—Dow-Corning

Fluoroethers

$$—(\overset{\displaystyle CF_3}{\overset{|}{CF}}—CF_2—O)_n—$$

"Krytox"—duPont
"Fomblin"—Montedison

The estimated values of the above products were in excess of $110 million with the major portion of the business being concentrated in PTFE. In the next five years, the polyfluoroethers may contribute a major portion of the total value.

In the U.S. a major portion of the uses of the fluoropolymers may be distributed over the following use patterns in the electrical, chemical, mechanical and aerospace industries covering such diverse things as coatings, packaging, cryogenics, labware, medical and automotive parts.

1. Polytetrafluoroetylene (PTFE)

When first produced and sold in 1942~43 by duPont the price of PTFE was in the range of \$140 per pound. This was reduced to \$18–20/1b in 1944. Today granular PTFE sells for about \$3.00–\$3.25/1b when bought in large quantities.

From the early difficulties encountered in its fabrication, technology has made great advances. PTFE is now available in various forms:

1) granular molding powder
2) extrusion pastes
3) dispersions or suspensions
4) monofilaments
5) telomer dispersions or suspensions

The granular molding powder is by far in largest production and is used for molded components in high performance electrical and mechanical equipments. Quite frequently it is filled with graphite, fluorspar, inorganic salts, etc to increase compressive strength and to reduce cold flow. Tapes are made by skiving from a billet in a manner similar to the making of plywood sheets. DuPont, still a leader in this field, offers 6 grades of granular PTFE (1, 1B, 5, 5B, 8, 9) with particle sizes ranging from 30–650 microns.

Paste extrusions are made from poly TFE powders (particle sizes ranging from 400–500 microns) suspended in naphtha, aromatic or mineral spirits. These are used for the manufacture of tubings, wire coatings, hose and pipe, lining of chemical equipment, tapes, etc.

Aqueous PTFE dispersions are utilized in the manufacture of low frictional coatings, cost films, cookware coatings and other industrial coatings.

PTFE monofilaments are used in fabric manufacture for use in filters, pump packings, bearings, clothing and medical implants.

A number of telomer dispersions are used as excellent lubricants, release and antistick materials. This type of material has been used ("Vydax") to coat razor blade edges and as thickening agents for fluorinated oils in the manufacture of greases.

Chemistry

The monomer ($CF_2{=}CF_2$) is obtained from the high temperature pyrolysis of $CHClF_2$

$$2\ CHClF_2 \longrightarrow CF_2{=}CF_2+2HCl$$

This is generally carried out in a platinum lined tube at temperature ranging from 600–750°C under 25% conversion with recycling of the unconverted $CHClF_2$.

PTFE is obtained from $CF_2{=}CF_2$ by aqueous suspension polymerization in the presence of various free radical polymerization catalysts.

2. Fluorinated Ethylene-Propylene-FEP

This copolymer of $CF_2{=}CF_2$ and $CF_3CF{=}CF_2$ has a melt viscosity low enough to permit fabrication by conventional techniques used for ordinary thermoplastic materials. This material however suffers in some of its properties compared to poly TFE, e.g. it has a maximum service temperature for continuous application of 400°F, compared to 500°F for PTFE and a relatively higher cost.

Chemistry

Both of the monomers, $CF_2{=}CF_2$ and $CF_3CF{=}CF_2$ are available from the pyrolysis of $CHClF_2$. The major product is $CF_2{=}CF_2$ with

$CF_3CF=CF_2$ as a by-product. The latter monomer may be obtained in higher yields by subjecting $CF_2=CF_2$ to further pyrolysis

$$3\ CF_2=CF_2 \longrightarrow 2\ CF_3CF=CF_2$$

The copolymerization of these two monomers is carried out in a manner analogous to that of PTFE.

3. Poly (chlorotrifluoroethylene)-PCTFE

PCTFE was first reported by I.G. Farben in 1937 and it was this disclosure that decided duPont to concentrate on PTFE rathert han on PCTFE.

Today, only 3-M Co. and Allied are in this field and supply materials for molding and extrusion, elastomers, resins for coatings and film. The market is quite limited and its use is concentrated in a narrow range where clarity of the film is essential and where its superior cryogenic properties may be utilized.

Chemistry

a) $CCl_2=CCl_2+Cl_2+HF \xrightarrow{Sb^V} CClF_2-CCl_2F$

b) $CClF_2-CCl_2F \xrightarrow[ROH]{Zn} CF_2=CFCl+ZnCl_2$

Polymerization (both homo-and copolymers) of PCTFE may be carried out in a bulk, suspension or emulsion system in a free radical system.

4. Poly (vinylidene fluoride)-PVDF

This polymer was first produced and patented by duPont in 1948 and has been utilized for the production of "Dulite" a high performance metal coating system.

Pennwalt (formerly Pennsalt) has been producing and marketing PVDF since 1965 under the "Kynar" trade name. They offer various grades of resins, pellets and dispersions.

PVDF has properties which are typical of the family of fluoropolymers. They possess outstanding moisture, chemical, oxidation and weathering resistance along with excellent dielectric properties.

Second to PTFE, this family of polymers has found a broad spectra of uses in the chemical, electrical and aerospace industries, of special interest is its application in the metal coating field where coil strip, roller, knife coatings and spary may be used. A great field of research may be found in studying the applicability of this and other similar polymers and copolymers in the field of organic semi-conductors and uses in the preparation of wafers for use in resistors, transisters and microelectronics.

"Kynar" has been utilized to a large extent in the marking pen industry for porous pen tips to the tune of 30–50 million pounds per year.

Chemistry

a) $CH_3CCl_3 \longrightarrow CH_3CClF_2 \longrightarrow CH_2=CF_2$

b) $CH_2Cl-CCl_3 \longrightarrow CClF_2-CH_2Cl \longrightarrow CF_2=CH_2$

c) $CH\equiv CH+2HF \longrightarrow CHF_2-CH_3 \xrightarrow{-H_2} CF_2=CH_2$

any or all three of the above methods may be utilized for the production of the monomer, vinylidene fluoride (VF_2)

PVDF polymers can be produced by bulk, suspension and emulsion polymerization similar to that used for the production of PCTFE. These reactions can be carried under pressure with peroxides or a redox system.

5. Poly (vinyl fluoride)-PVF

This polymer is thermoplastic and is an interesting member of the fluoropolymer family.

It was first patented in 1937 by I.G. Farben

Presently, duPont markets PVF as a film ("Tedlar") and as a dispersion powder by Diamond-Shamrock under the trade name of "Dalvor".

PVF film is a chemically inert and insoluble (in most solvents below 100°) high melting material. It possesses excellent weathering and oxidative properties along with excellent abrasion resistance and gloss retention. Its resistance to UV is outstanding.

Studies are in progress to compare the relative properties of PVF and PVDF along with their costs in order to decide what product or products from the above may return the greater financial return for the capital and research efforts expended

Chemistry

a) $HF + CH{\equiv}CH \xrightarrow{Hg^{++}} CHF{=}CH_2$

b) $CH_2{=}CHCl + HF \longrightarrow CH_3CHClF \xrightarrow{-HCl} CH_2{=}CHF$

c) $CH{\equiv}CH + 2\,HF \longrightarrow CHF_2 - CH_3 \xrightarrow[Cr^{3+}]{-HF} CH_2{=}CHF$

d) $CH_3{-}CCl_3 + HF \longrightarrow CH_3 - CCl_2F \xrightarrow{-HCl} CH_2{=}CClF \xrightarrow[\text{Cat.}]{H_2} CH_2{=}CHF$

Vinyl fluoride is normally polymerized by aqueous suspension procedures under pressure in the presence of free radical catalysis conditions generally utilizing peroxides or azo initiators in a buffered medium.

6. Copolymer of Vinylidene fluoride and hexafluoropropene-P (VDF-HFP)

This type of copolymer is generally made by emulsion polymerization procedures with the use of fluorinated surfactants in the presence of peroxides or persulfates.

This copolymer is elastomeric in nature and is known in the trade as "Viton" (duPont) or "Fluorel" (3M).

These specialty elastomers possess excellent high temperature properties when used in contact with chemicals, jet fuels, hydraulic fluids and jet engine lubricants.

"Technoflon"

This elastomeric material is a copolymer of $CH_2 = CF_2$ and $CF_3\,CF{=}\,CHF$ produced and sold by Montecatini-Edison of Milan, Italy.

Its chemistry and properties are similar to that of the "Vitons" or "Fluorels". However, one of monomers is different and its preparation is worthy of mention

a) $CF_3{-}CF{=}CF_2 + H_2 \xrightarrow{\text{Catalyst}} CF_3 - CFH{-}CHF_2 \xrightarrow{-HF} CF_3{-}CF{=}CHF$

Nitroso Rubber

This nitroso rubber, copolymers and terpolymers, based on TFE and CF_3-$N{=}O$ were the result of a combined effort by University and industrial research men, particularly the efforts of the 3-*M* Co., the University of Colorado (Prof. Park) and the University of Florida (Prof. Tarrant) research teams.

Hazeldine first reported the reaction between CF_3-$N{=}O$ and $CF_2 = CF_2$ but did not obtain any polymers and the method of preparation of CF_3-$N = O$ was tedious, expensive and of low overall yield of less than 5%.

It was the task of the team of industrial and university researchers under the sponsorship of the Natick Laboratories to find a breakthrough, and this it did.

Over thirty or more methods were expolored and studied resulting finally in the following

a) $2CF_3COOH \longrightarrow (CF_3CO)_2O \xrightarrow{N_2O_3} CF_3COONO \longrightarrow CF_3-N=O$

b) $CF_3-NO+C_2F_4 \longrightarrow -(\underset{CF_3}{\underset{|}{N}}-O-CF_2-CF_2)_n-$

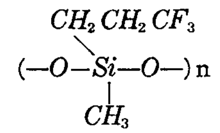
Step (b) iss carried out in batch-wise process using an aqueous suspension polymerization at -25°C in a nonaqueous medium.

This elastomer is able to perform in a fuel line system at temperatures as low as -65°F and capable of withstanding pump diaphragm embrittlement and maintain reliable elctrical insulating properties at low temperatures.

7. Fluorosilicone elastomers-(Silastics)

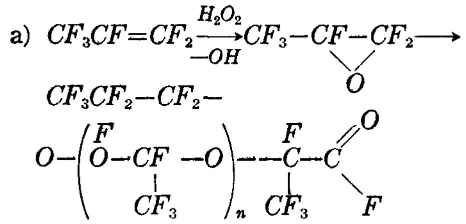
This study is the "marriage" of the chemistry of fluorine and silicon in an effort to combine many of the best properties of fluoropolymers and silicones. These vulcanized gums possess unusual properties in that they are resistant to immersion in various solvents, jet fuels, lubricants and hydraulic fluids. They can also maintain elastomeric properties at temperatures below -80°C, with concomitant high temperature performance (350°F or higher) without too great a loss in tensile and detrimental increase in elongation. However, these polymers have several major shortcomings, cured rubbers are attacked quite readily by certain ketones and phosphate esters and tend to revert to the gum stage at high temperatures approaching 450°F.

These materials are made from the hydrolysis of α-trifluoropropyl, methyl dichlorosilanes followed by hydrolysis to the siloxane.



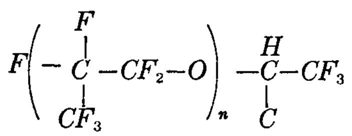
Fluorinated Polyethers

DuPont has been active in this field with their low molecular weight polymers obtained from hexafluoropropeneoxide (HFPO). This epoxide is made by the oxidation of HFP with alkaline hydrogen peroxide at -30 °C.



(n=1−6)

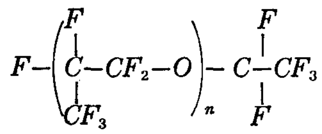
The duPont Co.'s "Freon Products Divison" also markets a "Freon-E" series of fluorocarbons which are HFPO oligomers, end-capped with fluorocarbon agents;



These have been developed for uses as dielectric coolants (transformer, power supplies) electronic gear test bath liquids, laser coolants, gyroscopic fiuids, stable hydraulic fiuids, etc. Montecatini-Edison has also introduced a similar liquid perfluorinated polyether under the trade name of "Fomblin". These are prepared by the UV induced reaction between HFP and molecular oxygen at low temperatures.

The structure of these polymers can be better controlled by the Montecatini-Edison than by the duPont process and is also more versatile. The applications are similar to those of the duPont materials.

DuPont also markets HFPO polymers in the medium molecular weight ranges under the Krytox tradename. These are completely fluorinated polyethers of the following structure



Similar compounds or homologously similar compounds are also available from the Montecatini-Edison sources.

These fully fluorinated ethers have a molecular weight range from 2000-7000 and have high thermal and oxidative stability, are good lubricants and hydraulic fluids. They are also non-inflammable and generally radiation resistant with good dielectric properties.

Du Pont also makes Krytox greases by thickening Krytox oils with Vydax (PTFE telomer solids). These possess excellent resistance to chemicals and solvents and are insoluble in sulfolane extraction solvent, inert to chlorine and bromine and generally usable as lubricants in petroleum refinery equipment. In the textile industry they are used as lubes in high speed spinning equipment.

It becomes evident from a short survey such as this, how fluorine chemistry once an unwanted "step-child" has blossomed into a modern "Cinderella" courted by every type of modern chemical "Prince" to solve the problems of his kingdom be it mechanical, chemical, electrical and even biological*. Korea has a stake in the rapidly expanding kingdom of fluorine by virtue of her large reserve of fluorspar deposits. The challenge is yours-Will the scientists, engineers and business men in Korea rise up to it? You and you alone have the answer.

*Fluorocarbons have been used successfully as substitute blood plasma in animals. They have been found to be excellent oxygen carrier as well as CO_2 carrier so necessary for the maintenance of animal life.

The author of this paper is presently Professor of Chemistry at the University of Colorado, Boulder, Colorado. He has been active in fluorine chemistry since 1929. Presently, on IESC assignment to KIST, he has been advisor on various problems. This paper was written at KIST at the invitation of Dr. H.S. Choi, President of KIST.

Born in Hawaii of immigrant Korean parents from Taegu, Korea, he has spent most of his life in the U.S.A. Strangely, at the height of an active career now approaching its end, the request to contribute to Korea's future became so strong that the requests of Korean friends essentially became commands and demands so urgent that several visits of various durations have resulted.