

Review

## Overview of the Development of the Fluoropolymer Industry

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**Abstract:** The present review briefly describes the development of the fluoropolymer industry in the past 70 years. Discussed are industrial fluoropolymers including polytetrafluoroethylene, polychlorotrifluoroethylene, polyvinylidene fluoride, polyvinyl fluoride, ETFE, ECTFE, FEP, PFA, THV, Teflon AF and Cytop. Nafion is included as a special functional fluoropolymer material. These industrial fluoropolymers are introduced in the order of their discovery or time of first production, included are their chemical structures, thermal properties, mechanical properties, electrical and electronic properties, optical properties, chemical resistance, oxidative stabilities, weather stabilities, processabilities and their general applications. The main manufacturing companies for the different types of fluoropolymer products are also mentioned.

**Keywords:** fluorine chemistry; fluoropolymer; fluorine industry

### List of Abbreviations

CTFE	chlorotrifluoroethylene
Cytop	homopolymer of PBVE
ECTFE	copolymer of ethylene and CTFE
ETFE	copolymer of ethylene and TFE
FEP	copolymer of fluorinated ethylene and propylene
HFP	hexafluoropropylene
Nafion	TFE and perfluoro-3,6-dioxa-4-methyl-7-octenesulfonic acid copolymer
PBVE	perfluoro-3-butenyl-vinyl ether
PCTFE	polychlorotrifluoroethylene
PDD	perfluoro-2,2-dimethyl-1,3-dioxole
PE	polyethylene
PFA	copolymer of TFE and PPVE

PPVE	perfluoropropylvinylether
PTFE	polytetrafluoroethylene
PVDF	polyvinylidene fluoride
PVF	polyvinyl fluoride
Teflon AF	copolymer of TFE and PDD
TFE	tetrafluoroethylene
THV	poly(TFE-co-HFP-co-VDF)
VDF	vinylidene fluoride

## 1. Introduction

Fluoropolymers are the polymer materials containing fluorine atoms in their chemical structures. From general organic polymer concepts, there are two types of fluoropolymer materials, *i.e.* perfluoropolymers and partially fluorinated polymers. In the former case, all the hydrogen atoms in the analogous hydrocarbon polymer structures were replaced by fluorine atoms. In the latter case, there are both hydrogen and fluorine atoms in the polymer structures. The fluoropolymer industry discussed here is mainly concerned with the perfluoropolymers, although in some cases the partially fluorinated polymers are included. In the latter case, there are both hydrogen and fluorine atoms in the polymer structures, along with additional elements in selected cases, such as polyvinylidene fluoride (PVDF) and polychlorotrifluoroethylene (PCTFE).

Fluoropolymers possess excellent properties such as outstanding chemical resistance, weather stability, low surface energy, low coefficient of friction, and low dielectric constant. These properties come from the special electronic structure of the fluorine atom, the stable carbon-fluorine covalent bonding, and the unique intramolecular and intermolecular interactions between the fluorinated polymer segments and the main chains.

Due to their special chemical and physical properties, the fluoropolymers are widely applied in the chemical, electrical/electronic, construction, architectural, and automotive industries. The world consumption of fluoropolymers is growing tremendously. Worldwide sales of fluoropolymers in 2000 exceeded \$2.0 billion compared with \$1.5 billion in 1994. Even though the fluoropolymer industry was affected in the same way as other industries because of the economic downturn after 2008, there will be a turnaround along with the recovery of the world economy for fluoropolymer markets, especially in the motor vehicles, wire and cable, advanced batteries, fuel cells and photovoltaic modules.

This review discusses the development of the most popular industrial fluoropolymers along with their chemical structures, basic properties, and general applications. For additional details, previously published books and journals would be helpful for monomer activities, polymerization methods, processing methods, polymer properties, and the applications [1–8].

## 2. The Development of the Fluoropolymer Industry from 1930s ~ 1990s

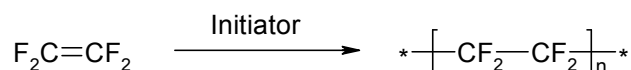
### 1930s

The development of the fluoropolymer industry began with the discovery of the

accident opened the magic door to one of the most important applied chemistry areas—the fluoropolymer industry—which greatly influenced the whole world in the following 70 years.

PTFE is a linear polymer of tetrafluoroethylene (TFE) (Figure 1). The preparation of PTFE is hazardous because of the chemical properties of TFE. Therefore, special production equipments and processing conditions are required [10,11].

**Figure 1.** The polymerization of TFE.



The chemical structure of PTFE is similar to that of polyethylene (PE), except that the hydrogen atoms are completely replaced by fluorine. Unlike the planer zigzag chain confirmation of PE, PTFE has a helical chain confirmation due to the larger fluorine volume. The rigid helical polymer chains can crystallize very easily and result in a high crystallinity (up to 98%). Because of the compact crystalline structure and the dense fluorine atoms, PTFE is the heaviest polymer material with a density of 2.1 g/cm<sup>3</sup>. The rigid polymer chain structure also caused a high melting temperature (~320 °C) and a high melt viscosity for PTFE, which made it difficult to process PTFE with the traditional methods for polymer materials. For quite a long time after the discovery of PTFE, scientists kept working on the different approaches to process PTFE materials, and it can be processed into all kinds of shapes for almost every application area.

PTFE is available in granular, fine powder and water-based dispersion forms. The granular PTFE resin is produced by suspension polymerization in an aqueous medium with little or no dispersing agent. Granular PTFE resins are mainly used for molding (compression and isostatic) and ram extrusion. The fine PTFE powder is prepared by controlled emulsion polymerization, and the products are white, small sized particles. Fine PTFE powders can be processed into thin sections by paste extrusion or used as additives to increase wear resistance or frictional property of other materials. PTFE dispersions are prepared by the aqueous polymerization using more dispersing agent with agitation. Dispersions are used for coatings and film casting.

One of the most distinguishing properties of PTFE is its outstanding chemical resistance, except for some extreme conditions such as molten alkali metals or elemental fluorine. Basically, PTFE is not soluble in any organic solvents. PTFE exhibits high thermal stability without obvious degradation below 440 °C. PTFE materials can be continuously used below 260 °C. The combustion of PTFE can only continue in a nearly pure oxygen atmosphere, and it is widely used as an additive in other polymer materials as a flame suppressant. PTFE has an extremely low dielectric constant (2.0) due to the highly symmetric structure of the macromolecules.

The conventional PTFE has some limitations in its applications, such as poor weldability, low creep resistance, low radiation resistance, and high microvoid content. Therefore, research efforts were mainly trying to modify PTFE in different ways to overcome the shortcomings of the conventional PTFE. Modified PTFE significantly reduced melt viscosity by lowering the crystallinity through the incorporation of bulky comonomers into the polymer main chain. Modified PTFE has the advantages such as lower microvoid content and reduced permeation, better weldability and easier bonding

treatment, better sealing properties, excellent electrical insulation properties, smoother surface finishes and higher gloss.

Even after modification, PTFE materials still have low tensile strength, wear resistance and creep resistance compared to other engineering polymers. The properties of the PTFE products are strongly dependent on the processing procedure, such as polymer particle size, sintering temperature and processing pressure. Therefore, other fluoropolymers are still needed for some specific applications where PTFE is not completely suitable.

### 1940s

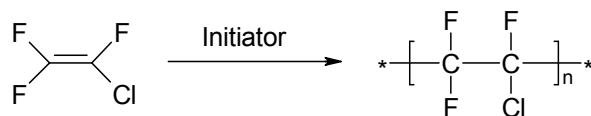
In the beginning, PTFE polymers found no use for any application due to its insolubility, high melting temperature and extremely high melt viscosity. During World War II people realized the importance of this new material. At the time, the Manhattan Project was carrying out the development of the atomic bomb. Practically, U-235 needs to be separated from U-238 using differential diffusion of  $UF_6$ .  $UF_6$  is highly corrosive to most metals and it was difficult to purify this material. As a result, the Manhattan project was looking for new corrosion resistant materials to meet the novel needs of purifying  $UF_6$ . The then strange new material and its resistance to chemicals proved that PTFE could survive the extremely corrosive purification conditions. Therefore, PTFE got its first business order from the Manhattan project. After the war, PTFE was commercially available in 1947 with the trademark Teflon from DuPont to meet the growing market needs of the US and the world. The rate of market growth for PTFE has been 3%–5% per year for the past 30 years. In the late 1990s, annual consumption worldwide for PTFE was over 55,000 tons, which is almost doubled now. Some typical commercially available PTFE products are Teflon (DuPont), Polyflon (Daikin), Dyneon PTFE (Dyneon), and Fluon (Ashai Glass).

Noticeably, even now PTFE still remains the largest type of fluoropolymers with about 70% of the total fluoropolymer market worldwide.

### 1950s

In 1953, a new fluoropolymer, polychlorotrifluoroethylene (PCTFE) was commercialized by M. W. Kellogg Company under the trade mark Kel-F. PCTFE is produced by the free radical polymerization of chlorotrifluoroethylene (CTFE) with a linear polymer chain structure (Figure 2).

**Figure 2.** The polymerization of CTFE.



High molecular weight PCTFE can be prepared by polymerization in bulk, in solution, in suspension and in emulsion forms [12]. Compared to PTFE, only one fluorine atom was replaced by the chlorine in PCTFE. The introduction of chlorine atom in the polymer structure interrupted the crystallization ability of the polymer main chain, and resulted in lower crystallinity, lower melting temperature, better intermolecular interaction, and better mechanical properties of PCTFE compared to

PTFE. PCTFE showed higher hardness, higher tensile strength, higher resistance to creep, and less water vapor and gas permeability. One important advantage of PCTFE is its melt processability.

PCTFE is easily melt processed and the products are more transparent. PCTFE can be used continuously from  $-100\text{ }^{\circ}\text{C}$  to  $200\text{ }^{\circ}\text{C}$ . Especially, its better cold-flow characteristics made it more competitive to PTFE materials. It showed similar flame retardancy and better radiation resistance compared to PTFE. The chemical resistance and electrical properties of PCTFE are not as good as those of PTFE, but still better than most polymer materials.

The price of PCTFE is higher than that of PTFE due to the expensive monomer as well as the small market size. Therefore, its main application is limited to use as a moisture barrier film in packaging and special engineering devices, where PTFE cannot meet the high performance requirements. Some examples are the aeronautical and space applications for cryogenic seals and gaskets. Low molecular weight PCTFE are used as oils, waxes and greases, inert sealants, lubricants for oxygen-handling equipment or corrosive media, plasticizers for thermoplastics and gyroscopic floatation fluids.

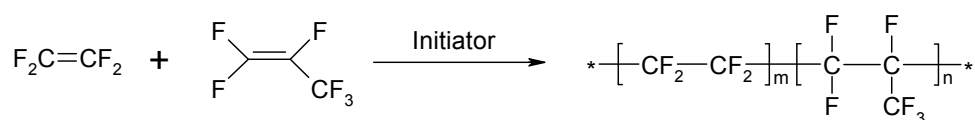
PCTFE was originally produced by M. W. Kellogg and 3M under the trade name of Kel-F [13]. After 3M discontinued the production of PCTFE (1995) [14], Daikin purchased the manufacture rights to PCTFE and produced it under the trade name Neoflon. PCTFE resin is also produced by Honeywell as Aclar and by Arkema as Voltalef.

1960s

Considering the shortcoming of PTFE, researchers looked for new ideas to solve the existing problems. The copolymerization of TFE with other monomers offered many opportunities. The first TFE copolymer was FEP (fluorinated ethylene propylene), which was prepared by the random copolymerization of TFE and hexafluoropropylene (HFP). FEP was commercially introduced to the market in 1960 by DuPont.

The structure of FEP is similar to PTFE except that a trifluoromethyl group was introduced along the side of the polymer main chain (Figure 3). FEP is generally prepared by the copolymerization of TFE and HFP in an aqueous medium with a free radical initiator and a dispersing agent. The comonomer ratio and the polymerization conditions are carefully controlled to achieve the desired copolymer composition and molecular weight, which are closely related to the melt viscosity, the processability and the mechanical properties of the final products [15,16].

**Figure 3.** The preparation of FEP.



Generally, FEP contains about 5 mol% of HFP. The introduction of HFP units in the polymer main chain disrupted the crystallization ability of FEP copolymer compared with the homopolymer of TFE. The crystallinity of FEP is about 70%, and its melting temperature is in the range of  $260\text{--}280\text{ }^{\circ}\text{C}$  depending on the HFP content. It can be used continuously up to  $200\text{ }^{\circ}\text{C}$ . The molecular weight of FEP is much lower than that of PTFE and resulted in a much lower melt viscosity and better processability.

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