



TECHNICAL WHITEPAPER

## Introduction to Fluoropolymers

### Introduction

Fluorine is one of the most reactive elements in nature and is even more reactive than its halogen relatives such as chlorine, bromine and iodine (these are all Group 17 elements or, if you prefer the older notation, Group VII). This high, and sometimes explosive, reactivity delayed research on the material for a long time because scientists simply couldn't find any material to contain elemental fluorine, not to mention that it was difficult doing research under those conditions. Two of the first researchers of fluorine chemistry were Ruff and Bretschneider of Germany in the 1930s, first synthesizing the gas tetrafluoroethylene. This was considered to be a topic of purely academic concern and few people paid much attention to their work. It was also in Germany that the first of the fluoropolymers was created and the IG Farben conglomerate patented PCTFE in 1934.

Despite this, it was the discovery of PTFE that accelerated the development of the fluoropolymers. As mentioned in a previous newsletter ("Focus on: PEEK"), the discovery of PTFE was purely accidental. In 1938, Roy Plunkett and his team at DuPont were working on the chemistry of tetrafluoroethylene and noticed that a 'full' cylinder of the gas appeared to have nothing in it when the valve was opened. Intrigued by the missing tetrafluoroethylene, they cut the cylinder open and a white residue (Polytetrafluoroethylene) was found on the inside of the cylinder. PTFE was born!

PTFE may have remained a laboratory curiosity except for the onset of World War II. Fluorine chemistry in all its forms suddenly became a vital topic of research across the world in the race to build the first atomic bomb. Concentration of the fissile component (Uranium-235) from natural uranium required the preparation of uranium hexafluoride gas – what had once been of simple academic interest suddenly had the attention of the world and almost unlimited finance and personnel.

The polymer chemists were a little faster in attempting to develop useful polymers from the basic structure, and Carothers carried out some of the first work in the development of nylon in the 1930s. This basic research continued, and in the 1970s, Rose and his team at ICI began constructing polymers almost from the first reported principles. Their work was based on previously successful materials such as the polysulfones, and one of their first products was the aromatic polyether ketone family.

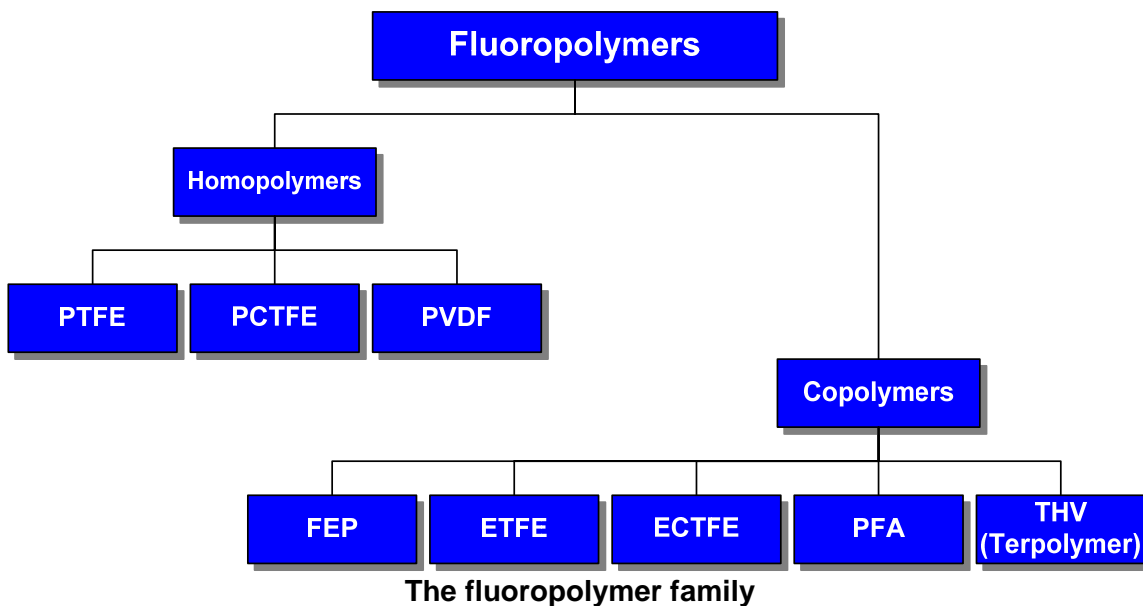
The result was that a small amount of white residue in a gas cylinder suddenly found itself the center of considerable scientific attention as researchers attempted to find out

more about this new material. For a new and accidental material, PTFE had remarkable properties. It was resistant to almost every known chemical, had excellent heat and electrical resistance properties, an extremely low coefficient of friction, and a surface energy so low that it was almost impossible to get anything to stick to it. A fortuitous set of circumstances for the birth of the fluoropolymer family.

### Developing the fluoropolymer family

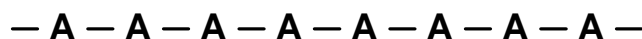
The high thermal stability of the fluorine-carbon bond and excellent chemical resistance of the fluoropolymers means that the PTFE and PCTFE polymers have unique properties. Polymer technologists have continued to develop the fluoropolymer family to improve melt processability, reduce cost and improve other properties. Technology may have a history but polymer technologists have no past - they have to constantly invent new things to improve and modify.

Today the fluoropolymer family consists of a range of homopolymers and copolymers to meet the demands of the industry.

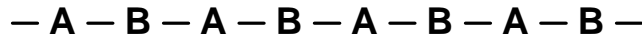


### Homopolymers and copolymers – What’s the difference?

Homopolymers consist of a single monomer (A) that is repeatedly joined together to form the long chain of the polymer molecule:



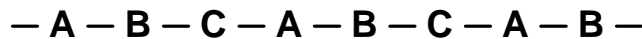
Copolymers consist of two different monomers (A and B) that are alternated when joined together to form the long chain of the polymer molecule:



Graft copolymers are copolymers with a branched structure in the long chain of the polymer molecule:



Terpolymers consist of three different monomers (A, B and C) that are alternated when joined together to form the long chain of the polymer molecule:



### Fluoropolymer classification

The fluoropolymers can all be classified as semi-crystalline high performance thermoplastics. This means that they have a random molecular orientation when in the molten phase but have densely packed crystallites in the solid phase. The degree of crystallization varies within the fluoropolymer family but all semi-crystalline plastics have some general common properties.

The high performance semi-crystalline thermoplastics tend to have the following properties (in comparison to amorphous plastics):

- Higher specific gravity
- Higher tensile strength and tensile modulus
- Lower ductility
- Tend to be translucent or opaque rather than transparent
- Higher fatigue resistance
- More difficult to bond using adhesives and solvents

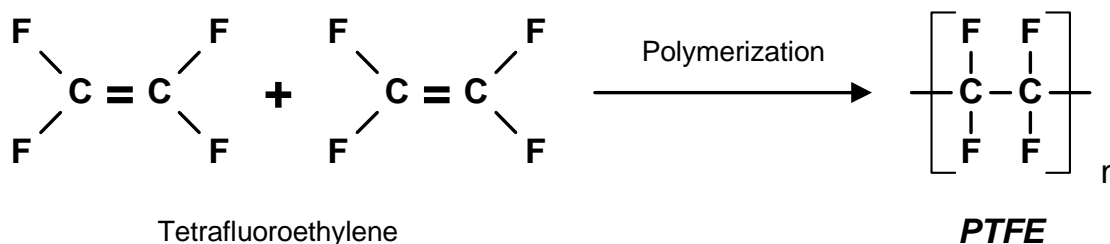
These plastics also tend to have the following properties (in comparison to other plastics):

- Outstanding temperature resistance
- Outstanding electrical properties
- Outstanding chemical resistance
- Lower coefficient of friction
- Better toughness

### Types of fluoropolymers – the homopolymers

#### PTFE – Polytetrafluoroethylene

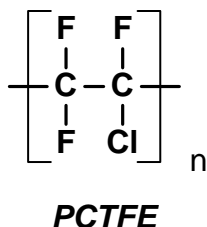
PTFE is one of the few fully fluorinated polymers and is made by polymerizing TFE. The repeat unit of PTFE is shown below:



PTFE was the first fluoropolymer to be manufactured and used by both Germany and the U.S. during World War II. PTFE was used extensively in the Manhattan Project to handle corrosive compounds such as uranium hexafluoride. Due to its full fluorination, it still has some of the best properties of the family today. The major disadvantage with PTFE is the very high melt viscosity that makes processing difficult by the normal methods of extrusion and injection molding. Processing technologies have more similarity to those of powder metallurgy than those of traditional plastics processing. This led to a search for melt-processable fluoropolymers and the development of other members of the family.

#### **PCTFE – Polychlorotrifluoroethylene**

PCTFE is a partially fluorinated polymer and is made by polymerizing CTFE monomer in a very similar manner to that for PTFE. The repeat unit is shown below:



The introduction of the Cl atom distorts the symmetry of the crystal packing and leads to a lower softening point and reduced electrical and chemical resistance properties. It also results in a harder polymer with higher tensile strength. PCTFE is melt-processable but it is still difficult to process because of the high melt viscosity (brand names are Kel-F<sup>®</sup> and Neoflon<sup>®</sup>).

#### **PVDF – Polyvinylidene fluoride**

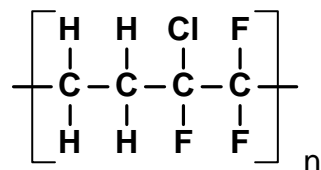
PVDF is a partially fluorinated homopolymer and is made by polymerizing vinylidene monomer. The repeat unit is shown below:



ETFE was first produced by DuPont in 1970 (Tefzel<sup>®</sup>) and is another melt-processable fluoropolymer. ETFE has mechanical properties that approach those of the fully fluorinated polymers but has a lower maximum service temperature. Despite this, ETFE excels in specific applications because of greatly increased cut through and abrasion resistance and impact strength.

### **ECTFE – Ethylene chlorotrifluoroethylene**

ECTFE is a partially fluorinated copolymer made by polymerizing chlorotrifluoroethylene and ethylene, and the repeat unit of ECTFE is shown below:

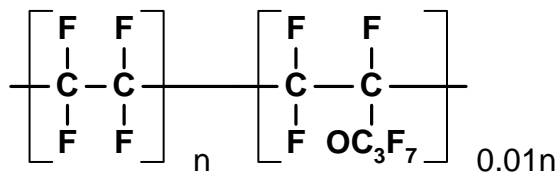


**ECTFE**

ECTFE was first produced by Allied Chemicals (Halar<sup>®</sup>) at the same time as ETFE and the mechanical properties are very similar to those of ETFE. ECTFE also has mechanical properties approaching those of fully fluorinated polymers, with a lower maximum service temperature and the lowest density. As with ETFE, ECTFE has excellent cut through and abrasion resistance and impact strength.

### **PFA – Perfluoroalkoxy**

PFA is a partially fluorinated copolymer made by polymerizing TFE and Perfluoroalkoxy. The repeat unit of PFA is shown below:



**PFA**

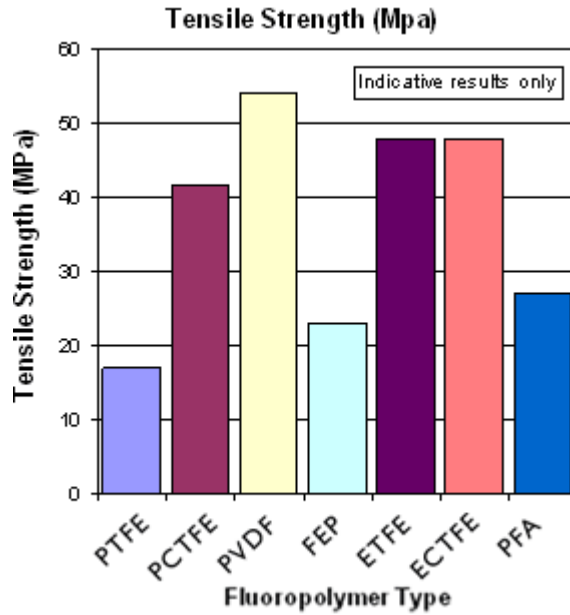
PFA was first produced by DuPont in 1972 (Teflon<sup>®</sup> PFA) and is also melt-processable. In many ways PFA is similar to FEP but generally has better mechanical properties at higher temperatures and a maximum service temperature very similar to that of PTFE. It is considered by some to be the best melt-processable fluoropolymer alternative to PTFE.

### **General properties**

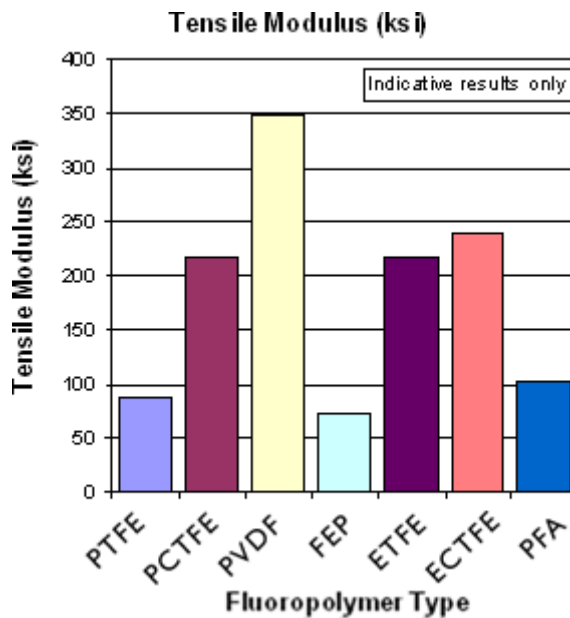
The fluoropolymers have unique properties but the large range of materials within the family can make it difficult to choose between the various materials. Future Whitepapers

will focus on individual material properties in detail but it is useful to present some simple results for a few critical materials properties at this stage. The results are indicative only and are not definitive. The graphs are designed more to show the relative strengths and weaknesses of individual materials.

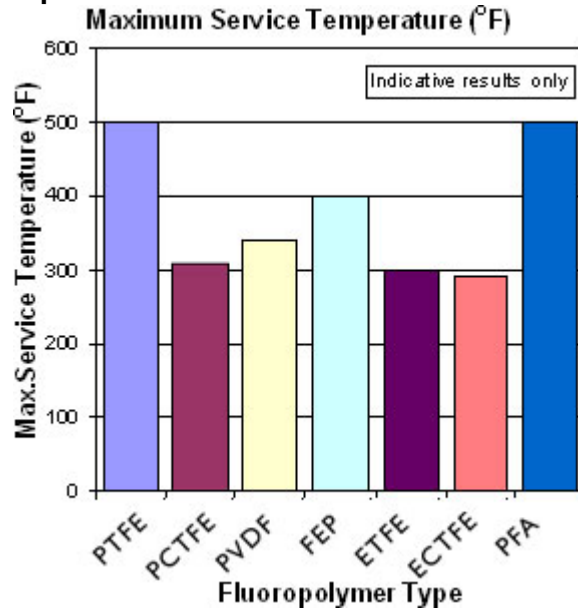
**Tensile strength:**



**Tensile Modulus:**



## Maximum Service Temperature:



While it is often easy to see that a specific application requires the special properties of the fluoropolymers, it is often less easy to determine which of the materials is best for the application. Potential users should contact experienced processors, such as Zeus, for detailed guidance on specific applications.

### Summary

Fluoropolymers are a group of plastics that are still being explored and developed by the polymer industry for growing market applications. Their unique set of properties makes them natural candidates for very demanding applications, but engineers and buyers should use the skills of the production and development specialists to select the best material for their application. For more information on fluoropolymers, see Zeus' previous Whitepapers at <http://www.zeusinc.com/whitepapers.asp>

### How Zeus Can Help

With a technical inside and outside sales force backed up with engineering and polymer experts, Zeus is prepared to assist in material selection and can provide product samples for evaluation. A dedicated R&D department staffed with PHD Polymer chemists and backed with the support of a world-class analytical lab allows Zeus an unparalleled position in polymer development and customization.

Since 1966 Zeus has been built upon the core technology of precision extrusion of high temperature plastics. Today, with a broad portfolio of engineered resins and secondary



operations, Zeus can provide turnkey solutions for development and high-volume supply requirements.

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