Blends and Composites Based on Fluoropolymers

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Summary: Fluoropolymers represent a rather unique group of polymeric materials. Essentially, current most widely used commercial fluoropolymers are derivatives of ethylene and propylene, also known as fluorocarbon polymers. Other, more complex fluorinated polymers are also important technically, but these are used in considerably smaller amounts. Because of the unique chemistry and properties, fluorocarbon polymers rarely form good blends. The only exceptions are homopolymers and copolymers of vinylidene fluoride, which form blends based on thermodynamic compatibility with certain polymers, such as acrylates and methacrylates. However, most known fluoropolymers can be used to produce fiber and fabric reinforced composites as well as composite films and coatings.

Introduction

Fluoropolymers in their simplest form are polymers or copolymers of saturated hydrocarbons in which all or some hydrogen atoms have been replaced by fluorine atoms or combination of fluorine and chlorine. Theoretically, there are many possible combinations but most commercially significant are derivatives of ethylene and propylene, sometimes referred to as fluorocarbon polymers. Other, more complex polymers are fluorinated acrylates, polyurethanes, polyimides and other.

Fluorocarbon polymers can be divided into two distinct groups:

1. Perfluorinated fluorocarbon polymers, which have a main chain consisting of carbon and fluorine only: PTFE, FEP, PFA
2. Partially fluorinated fluorocarbon polymers, which have a main chain consisting of fluorine and other atoms, such as chlorine or hydrogen: ETFE, PCTFE, PVDF, PVF, ECTFE

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General properties of thermoplastic fluoropolymers are listed below:

- Good to outstanding resistance to aggressive chemicals
- Good to outstanding resistance to most common solvents
- Excellent and sometimes unique dielectric properties
- Good to outstanding release properties
- Good to outstanding resistance to UV radiation and weather
- Low coefficient of friction

Selected properties of common commercial fluorocarbon polymers are summarized in Table 1 and their weaknesses are listed in Table 2.

Factors contributing to the characteristics of fluoropolymers are mainly:

- Strong C-F bond exists in the main chain (see Table 3)
- Shielding of the carbon chain by bulky fluorine atoms
- Low interchain forces exist in most of them
- Some are nonpolar
- Some are crystalline

Table 1: Selected properties of commercial fluoroplastics [2]

Polymer	Property					
	Melting point, / °C	Specific gravity / $g.cm^{-3}$	Tensile modulus, / MPa	Tensile strength, / MPa	Friction coefficient	Dielectric constant
PTFE	327	2.18	476	26.2	0.1	2.1
FEP	260	2.15	345	23.1	0.2	2.1
PFA	306	2.15	655	27.7	0.3	2.1
ETFE	271	1.72	826	44.0	0.25	2.6
PVDF	168	1.77	1724	40.7	-	8.8
PVF	200	1.48	-	96.6	-	7.7
PCTFE	211	2.10	1552	35.4	0.4	2.5
ECTFE	240	1.68	1655	49.6	-	2.5

Table 2: Weaknesses of common fluoropolymers

Fluoropolymer	Weakness
PTFE	Creep, low resistance to ionizing radiation, microporous, highly permeable
PVDF	Low resistance to ketones and strong alkali
PCTFE	High processing temperatures
FEP	Low fatigue resistance, poor high temperature properties
ETFE	Low resistance to elevated temperatures and oxygen
PFA	Low heat deflection temperature

Table 3: Carbon bond energies [1]

Bond	Bond energy, kcal/mol
C – F	116
C – H	99
C – O	84
C – C	83
C – Cl	78
C – Br	66
C – I	57

The most common commercial fluorocarbon homopolymers are:

PTFE	poly(tetrafluoroethylene)	$- CF_2 - CF_2 -$
PVDF	poly(vinylidene chloride)	$- CH_2 - CF_2 -$
PVF	poly(vinyl fluoride)	$- CH_2 - CHF -$
PCTFE	poly(chlorotrifluoro ethylene)	$- CF_2 - CFCl -$

The most common commercial fluorocarbon copolymers are:

FEP	Fluorinated ethylene propylene	$- CF_2 - CF_2 - CF_2 (CF_3) -$
PFA	Copolymer of TFE and PPVE*	$- CF_2 - CF_2 - CF_2 (O\text{-}C_3F_7) -$
MFA	Copolymer of TFE and PMVE**	$- CF_2 - CF_2 - CF_2 (O\text{-}CF_3) -$
ECTFE	Copolymer of ethylene and CTFE	$- CH_2 - CH_2 - CF_2 CFCl) -$
ETFE	Copolymer of ethylene and TFE	$- CH_2 - CH_2 - CF_2 - CF_2 -$

THV Fluoroplastic® (Terpolymer of THV, HFP and VDF)

$$- (CF_2 - CF_2)_x - (CF_2\text{-}CF(CF_3))_y - (CH_2 - CF_2)z -$$

Note: THV Fluoroplastic is a registered trademark of Dyneon LLC

* perfluoro propyl vinyl ether

** perfluoro methyl vinyl ether

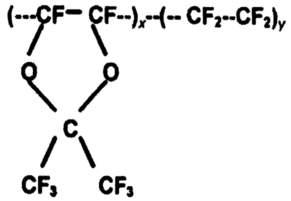
New generation of fluoropolymers developed during the past decade or so include the following:

- Modified PTFE
- Amorphous perfluoropolymers
- Novel high performance copolymers

Modified PTFE contains a small amount of a perfluorinated monomer [3]. The resulting material has a lower molecular weight, lower degree of crystallinity and consequently better weldability, lower deformation under load and higher density with fewer microvoids [3, 4]. An aqueous fine powder dispersion of modified PTFE can also be produced [5].

Amorphous perfluoropolymers are represented by Teflon® AF (DuPont) (Fig. 1.) and Cytop® (Asahi Glass) (Fig. 2). These polymers combine the advantages of conventional perfluoropolymers, such as high thermal stability, excellent chemical resistance, and low surface energy with superior physical and optical properties resulting from their structure. Moreover, they can be dissolved in selected fluorinated solvents and consequently processed in solutions mainly for specialty coatings and thin films [6]. Differences between amorphous and traditional PTFE resins are shown in Table 4.

Fig. 1: Teflon® AF



PDD TFE

Fig. 2: Cytop®

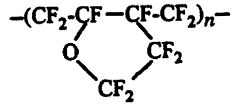


Table 4: Amorphous PTFE compared to the conventional PTFE

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

Novel high performance fluoropolymers are obtained by the incorporation of hexafluoroisopropylidene (6F) groups into certain macromolecular chains. This results in an increased solubility, thermal stability, flame and oxidation resistance, higher T_g, improved adhesion, transparency and environmental stability, while decreasing the degree of crystallinity, dielectric constant and water absorption.

The combination of these properties is a result of the disruption of crystallinity and conjugation provided by the bulky but highly thermally stable 6F group. Many heterocyclic polymers can be modified this way, but fluorinated polyimides and copolyimides appear to have the greatest potential for applications with stringent demands [7].

Blends and Composites Based on Fluoropolymers

Blends from fluoropolymers are not common because of the combination of their high melting points and their chemical nature. PTFE is added to some polymers in the form of powder to enhance lubricity and chemical resistance, but it is a physical mixture.

PVDF and is the only fluoropolymer and one of the few semicrystalline polymers capable of forming blends based on thermodynamic compatibility with other polymers [8], notably acrylates and methacrylates [9, 10]. The morphology, properties and performance of these blends depend on the structure and composition of the additive polymer and on the particular PVDF resin [11].

Composites based on fluoropolymers include fiber or textile reinforced matrix polymers or composite films and coatings.

Certain grades of PTFE, FEP and PFA are supplied in the commercial form containing typically 15-35 % of glass fibers or 10-25% of carbon fibers [12]. Such material exhibits considerably lower creep (cold flow) and is used mainly for molding. Otherwise, it is used in the form of aqueous dispersions to produce impregnated or coated composites [13]. Substrates for this technology may be woven or nonwoven fabrics. Other fluoropolymers available in the aqueous form (PFA, FEP, ETFE, PVDF, THV) are used in a similar fashion. Coated fabrics may be laminated by variety of methods, such as in hydraulic presses or between heated rolls [14].

Certain grades of ETFE, ECTFE and PVDF are also supplied with a glass fiber or carbon fiber reinforcement [12].
Composite films from melt processable fluoropolymers (PFA, FEP, ETFE, PCTFE, ECTFE, PVDF, THV) are produced by coextrusion. PTFE composite films are mainly prepared by casting from aqueous dispersions on a carrier, such as stainless steel or a polymeric belt [15, 16]. This method is suitable also for other fluoropolymers available in aqueous dispersions.

Composite coatings from PTFE, FEP, and PFA are made from aqueous dispersions and often require specialized primer, particularly, if applied to metal substrates. Coatings based on PVDF and THV can also be made from solutions in suitable solvents (ketones, acetates).

Applications

Fiber and fabric reinforced fluoropolymeric composites are used in

- Construction (roofs of stadiums, airports, malls, large buildings)
- Chemical process industry (miscellaneous molded parts, expansion joints), protective clothing
- Aircraft and aerospace industry (wiring, release sheets for composite parts)
- Food industry (belts and cooking sheets)
- Electronic and electrical industries (wiring, laminates, films)
- Automotive (molded parts, fuel hose, specialty wiring, fuel cells)
- Ceramic industries (belting)

Composite films are used in

- Electronic and electrical industry (wire wrap, batteries, computers, piezoelectric devices)
- Aircraft and aerospace industries (wire wrap, release sheets)
- Traffic signs
- Membranes
- Protective clothing

Fluoropolymer based coatings are used in

- Architectural and decorative coatings
- Cookware
- Anticorrosion coatings on chemical equipment, bridges, ships

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