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Radiation Processing of Fluoropolymers

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Introduction

Fluoropolymers represent a group of rather specialized polymeric materials. The chemistry of the majority of fluoropolymers is derived from compounds used in the refrigeration industry.

The monomers for commercially important large-volume fluoropolymers are shown in Table 1.

Table 1: Monomers for fluoropolymers

$CF_2 = CF_2$
Tetrafluoroethylene (TFE)

$CF_2 = CF\text{-}\ CF_3$
Hexafluoropropylene (HFP)

$CF_2 = CF\text{-}\ OC_3F_7$
Perfluoropropylvinyl ether (PPVE)

$CF_2 = CF\text{-}\ OCF_3$
Perfluoromethylvinyl ether (PMVE)

$CFCl = CF_2$
Chlorotrifluoroethylene (CTFE)

$CH_2 = CF_2$
Vinylidene fluoride (VDF)

$CH_2 = CF$
Vinyl fluoride

These can be combined to yield homopolymers, copolymers and terpolymers. The resulting products range from rigid resins to elastomers with unique properties not achievable by other polymeric materials. In general, they exhibit the following properties:

Chemical inertness
Nonstick or non-wetting surface (hydrophobicity, low dirt pickup)
Low coefficient of friction
Resistance to elevated temperatures

The specific properties depend on the structure of the polymer, with considerable variations with the presence of atoms other than fluorine in the backbone of the polymer.

The main factor responsible for the above-mentioned properties is the very high strength of the C-F bond (see Table 2). The polymer with the most pronounced “fluoropolymeric” properties is poly(tetrafluoroethylene), PTFE, known under the original trade-name Teflon. Because of the large size and mutual repulsion of adjacent fluorine atoms, the PTFE macromolecule is a twisting helix, comprising 13 CF_2 groups every 180-degree turn. This configuration is thermodynamically favored over a planar zigzag (typical for polyethylene) [1]. The fluorine atoms form an outer sheath, which protects the carbon backbone and provides the chemical inertness and stability. It also lowers the surface energy of the material, giving it low friction and nonstick properties. Additional characteristic of PTFE are an exceptionally high molecular weight (about 10^6) and a very high degree of crystallinity (90% or more in the virgin polymer). The extremely high viscosity (10^{10} - 10^{12} Pa.s) due to the very high molecular weight is the reason why PTFE cannot be processed as a melt and requires special processing methods, similar to those used in powder metallurgy or ceramic technology. Copolymerization of TFE with other monomers yields melt-processible materials, which have generally lower crystallinity, somewhat higher friction coefficient than the homopolymer and exhibit a markedly reduced cold flow.

Table 2: Carbon bond energies

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

Source: Iezzi, R. A. in *Modern Fluoropolymers* (Scheirs, J., Ed.), John Wiley & Sons, New York, 1997

Polymers containing fluorine can be divided into several groups. *Fluoropolymers* described above are defined by ISO as polymers made from monomers containing one or more fluorine atoms (fluoromonomers), or copolymers of such monomers with other monomers, the fluoromonomer(s) being in the greatest amount by mass [2]. Fluoropolymers can be divided into two major groups, namely *fluoroplastics* and *fluoroelastomers.* If the macromolecules are composed of only carbon and fluorine, such materials are referred to as perfluoroplastics and perfluoroelastomers. Others are *fluorinated polymers* and include fluorinated acrylates, fluorinated polyurethanes, fluorinated and perfluorinated ionomers and copolymers of CTFE and vinyl ether.

The current worldwide annual production of fluoropolymers is around 150,000 metric tons, of which polytetrafluoroethylene represents about 55% and fluoroelastomers are about 27% of that [3]. In general, overall growth in consumption of fluoropolymers during the past several years has been about 6-7 % [4].

The current major manufacturers of fluoropolymers are

DuPont (USA)
Daikin (Japan)
Dyneon (USA)
Asahi Glass (Japan)
Solvay (Europe)

Response of fluoropolymers to ionizing radiation (electron beam and gamma radiation)

As in the case of many other polymeric materials, ionizing radiation has a variety of effects on fluoropolymers and fluorinated polymers. It may cross-link them, cause chain scission or affect their surface. Quite often, these effects may occur simultaneously. The final result depends on the nature of the material, on the dosage, dosage rate and the energy of the radiation. Thus, there are many ways to exploit these processes technologically, such as cross-linking, reduction of molecular weight and surface modification alone or by grafting.

1 Fluoroplastics

In general, perfluorinated polymers undergo chain scission and those containing hydrogen atoms in their monomeric units tend to predominantly cross-link. In reality, however, the situation is not that simple. The reason for that is that the net effect is the result of two competing reactions, namely cross-linking and chain scission. The structure of the monomeric units is the important factor here.

Poly(tetrafluoroethylene) (PTFE) undergoes chain scission under normal conditions. This is exploited commercially, and that will be discussed later. However, there is an evidence [5-7] that irradiation of PTFE above its melting range (603-613 K) in a vacuum results in a significant improvement in tensile strength and elongation at 473 K and in an increase of tensile modulus at ambient (room) temperature. This clearly indicates cross-linking in the molten state, similar to effects caused by irradiation of polyethylene. At temperatures above 623 K, thermal depolymerization is increasingly accelerated by irradiation and prevails over cross-linking at yet higher temperatures [8]. A fairly detailed discussion of the process is in [9].

Fluorinated ethylene propylene (FEP) a melt-processible perfluoropolymer, when exposed to ionizing radiation at ambient temperature, it degrades in a similar way as PTFE, with the resulting reduction of its physical properties. However, if the polymer is irradiated above its glass transition temperature (80 °C) [10], cross-linking predominates and the result is an increase in viscosity. With doses above 26 kGy (2.6 Mrad), the ultimate elongation and the resistance to deformation under load at elevated temperatures are improved and the yield stress is increased. However, the improvements are offset by some loss in toughness [11].

Poly(chlorotrifluoroethylene) (PCTFE) degrades when exposed to ionizing radiation in a similar fashion as PTFE at ambient and elevated temperatures. Unlike PTFE, when irradiated above its crystalline melting point, it still exhibits chain scission [11].

Copolymer of ethylene and tetrafluoroethylene (ETFE), an alternating copolymer of the two monomers can be cross-linked by irradiation. Further improvement is achieved by the use of prorads (radiation promoters) such as triallylcyanurate (TAC) or triallylisocyanurate (TAIC) in amounts up to 10% by weight [8].

Copolymer of ethylene and trichlorofluoroethylene (ECTFE) behaves upon irradiation like ETFE, including improvement of cross-linking efficiency with the addition of prorads. Irradiation at room temperature followed by heat treatment at and above 435 K in nitrogen for 20 minutes is reported to be most effective [8].

Poly(vinylidene fluoride) (PVDF), its copolymers and poly(vinyl fluoride) (PVF), because of the presence of hydrogen atoms in their structures cross-link upon irradiation. Both PVF and PVDF are significantly thermally destabilized by radiation doses above 100 kGy, therefore for a sufficiently efficient cross-linking, polyunsaturated monomers, such as TAC, TAIC, bis(maleimido-methyl) ether and ethylene bis-maleimide are used [12].

Amorphous perfluoroplastics have been developed fairly recently by DuPont (Teflon AF®) and Asahi Glass (CYTOP®). Both contain bulky structures that are responsible for the absence of crystallinity. They are soluble in certain fluorinated solvents and can also be processed as a melt. They exhibit outstanding optical properties and are transparent to UV and visible light with a transmission well over 90%. They have very low refractive indices (Teflon AF has the lowest value of any known solid organic polymer), yet exhibit the outstanding chemical properties of PTFE. They are used for cladding of optical fibers, antireflective coatings and in electronics (e.g. photoresists) [13]. When Teflon AF was irradiated by low-energy X-rays, it was found that the inclusion of the dioxole monomer not only improves the optical properties but also increases the radiation tolerance of the homopolymer [14].

2. Fluorocarbon elastomers

Fluorocarbon elastomers (ASTM designation FKM) are predominantly copolymers or terpolymers of different fluorinated or perfluorinated monomers with vinylidene fluoride. The presence of vinylidene fluoride in their molecules is responsible for their propensity to cross-link. Here again, the final result depends on the ratio of cross-linking to chain scission. Prorads, such as TAC, TAIC, trimethylolpropane trimethacrylate (TMPTM), trimethylolpropane triacrylate (TMPTA), N, N' -(m-phenylene) bismaleimide (MPBM) reduce the damage to the elastomeric chain by the radiation [12]. It appears that each fluorocarbon elastomer has the best cross-link yield with a specific prorad. In general, optimized compounds from fluorocarbon elastomers irradiated at optimum conditions attain considerably better thermal stability and mechanical properties than chemical curing systems [15, 16, 17]. Typical radiation dose for a sufficient cross-linking of most fluorocarbon elastomers is on the range 10 to 100 kGy.

3. Perfluoroelastomers

Perfluoroelastomers (ASTM designation FFKM) are essentially copolymers of two perfluorinated monomers, TFE and PMVE (perfluoromethyl vinyl ether) with a cure site monomer (CSM), which is essential for cross-linking. Depending on the nature of the CSM and on the curing conditions, they are capable of service temperatures up to 300 °C. Perfluoroelastomers can be cured by ionizing radiation (EB and γ-rays) without any additives. The advantage of radiation cured FFKM is the absence of any additives, so that the product is very pure. The disadvantage is the relatively low upper use temperature of the cured material, typically 150 °C, which limits the material to special sealing applications only [18].

Examples of Applications of EB Processing

1. Preparation of PTFE Micropowders

Although there are several methods to prepare PTFE micropowders (also called fluoroadditives), electron beam process is the most widely used. The feedstock may be sintered or unsintered virgin PTFE or sintered or unsintered PTFE scrap. The feedstock is placed on a conveyor belt at a specific thickness and passed under the source of electron beam to be given the desired dose. The effectiveness of the degradation process increases with the dose, see Table 5 [19] Typically multiple passes are required to achieve the desired degree of molecular weight reduction [20]. The irradiated material is then removed from the belt and transferred to grinding operation. The most widely used is grinding in fluid energy mills. The final products have particle sizes typically in the range 1 to 20 μm and molecular weight 10^4 to 10^5 [20]. The main applications are as additives to oils, greases, paints, coatings, printing inks, to thermoplastics and elastomers. The main benefits are increased lubricity, reduced wear, improved hydrophobicity and release properties, increase of chemical resistance. The amounts added are typically 5 to 15% by weight.

2. Cross-linking

Radiation cross-linked fluoropolymers are now widely used in high performance aircraft wire and cable, heat recoverable tubing and molded parts, terminators and connectors. It is estimated that commercial radiation cross-linked fluoropolymer products may be third in sales value after radiation cross-linked polyethylenes and ethylene copolymers and radiation cross-linked PVC insulated wire [21].

3. Surface modification and grafting

Modification of a polymer surface by graft copolymerization with specific functional monomers has been shown to be an effective approach to adhesion enhancement because of its simplicity in handling and control over the grafting process [22]. This is particularly useful for fluoropolymers because the inertness of their surfaces limits the range of their applications. The largest number of studies involves radiation grafting of acrylic and vinyl monomers onto fluoropolymers [23-31].

Response of fluoropolymers to UV radiation

Fluoropolymers as a group exhibit exceptional resistance to UV radiation. The strength of the C-F bond makes them resist to pure photolysis. Moreover fluoropolymers, in general, do not contain light-absorbing chromophores in their structure or as impurities. For example, PTFE did not show any deterioration after 30 years of continuous exposure in Florida.

The outdoor durability of a fluoropolymer is directly related to its fluorine content [32]. Typically, fluoropolymers do not change after a long outdoor exposure (5-10 years) and only very sensitive analytical methods can find even the minute changes. Nevertheless, it was established that the rate and degree of deterioration depends strongly on the wavelength of the UV radiation with wavelengths shorter than 300 nm being the most damaging. Perfluoroplastics are very stable, but PCTFE tends to degrade rather rapidly under the UV light [33].

The effect of structures of several untreated and γ-irradiated fluoropolymers on their response to UV radiation is reported in [34]. The most interesting finding was that PVF, PVDF and ETFE respectively exhibit increasing UV resistance. PVF undergoes significant degradation, ETFE does not show any changes and PVDF exhibits an intermediate response.

Applications of UV Processing

1. Surface modification and grafting

Several recent studies involved UV radiation grafting of various monomers onto PTFE. UV-induced graft copolymerization of poly(ethylene glycol) monomethacrylate (PEGMA) onto an Ar plasma pretreated PTFE films. The film was shown to have greatly enhanced hydrophilicity and to be a promising new biomaterial with an excellent protein-repellent surface [35]. A considerable enhancement of adhesion of electrolessly deposited copper to H_2 plasma pretreated PTFE films was achieved by UV-induced graft copolymerization of glycidyl mehacrylate (GMA). The product has an application in the printed circuit board technology [36].

2. UV Curing of Fluorinated Coatings

Because of the exceptional inertness and stability of fluorinated polymers, they are frequently used in high performance protective coatings. Many of these are processed by radiation, most frequently by UV equipment, although some of them can be also processed by low energy electron beam. Because of the enormous number of possible formulations, it is virtually impossible to cover them here. In the following sections, there are listed some interesting applications, most of them covered by patents.

Available patent literature describes UV radiation curable coatings based on formulations containing partially fluorinated moieties. These may be combined with acrylates [37] or polyurethanes [38]. Another patent cover UV-curable fluorinated organosilane compositions for coatings and encapsulants with improved electric performance [39]. UV radiation curable fluoropolymer compositions and antireflection films made from them are subject of another patent [40]. Polyfluorooxetanes functionalized by acrylate, methacrylate or allylic groups are used as binders for radiation-curable coatings for various substrates. After curing the coating by UV light a film with low friction, low wear and antistaining properties is obtained [41]. A patent issued in 1999 covers radiation –curable siloxane group containing hexafluoropropylene copolymer compositions with good adhesion to substrates, and transparent scratch-resistant coatings and antireflection films made from them [42].

Recent Developments

1. Self-stratifying coating capable of producing a multilayer structure in one operation has been developed on the basis of partially fluorinated hydroxyl end-capped oligoester. The hydroxyl groups are then substituted by acrylic double bonds and consequently this compound can be cured by UV radiation. The fluorine level in the few nanometers of the surface of the film is significantly greater than in the bulk, thus the film has a very low energy surface [43].
2. Synthesis of photocrosslinkable fluorinated poly(dimethyl siloxanes) as UV transparent coatings for optical fiber gratings and for membranes used in VOC elimination was reported in [44].
3. Synthesis of new vinylidene fluoride-containing acrylic monomers and their use as surface modifiers in photopolymerized coatings was reported in [45].
4. Photoetching and modification of poly(tetrafluoroethylene-co-hexafluoropropylene) polymer surfaces with vacuum UV was reported in [46].
5. Plain-woven carbon fiber reinforced cross-linked PTFE composites were fabricated using electron beam. The composite exhibits a very low friction coefficient and an improved abrasion resistance when compared to cross-linked PTFE without reinforcement [47].
6. Femtosecond ultraviolet (248 nm) excimer laser was used to drill clean micrometer size vertical interconnect (microvia) in 50 µm thick PTFE film [48].

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