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Optimization of PVDF-TrFE Based Electro-Conductive Nanofibers: Morphology and In Vitro Response

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Abstract: In this study, morphology and in vitro response of electroconductive composite nanofibers were explored for biomedical use. The composite nanofibers were prepared by blending the piezoelectric polymer poly(vinylidene fluoride–trifluoroethylene) (PVDF-TrFE) and electroconductive materials with different physical and chemical properties such as copper oxide (CuO), poly(3-hexylthiophene) (P3HT), copper phthalocyanine (CuPc), and methylene blue (MB) resulting in unique combinations of electrical conductivity, biocompatibility, and other desirable properties. Morphological investigation via SEM analysis has remarked some differences in fiber size as a function of the electroconductive phase used, with a reduction of fiber diameters for the composite fibers of 12.43% for CuO, 32.87% for CuPc, 36.46% for P3HT, and 63% for MB. This effect is related to the peculiar electroconductive behavior of fibers: measurements of electrical properties showed the highest ability to transport charges of methylene blue, in accordance with the lowest fibers diameters, while P3HT poorly conducts in air but improves charge transfer during the fiber formation. In vitro assays showed a tunable response of fibers in terms of viability, underlining a preferential interaction of fibroblast cells to P3HT-loaded fibers that can be considered the most suitable for use in biomedical applications. These results provide valuable information for future studies to be addressed at optimizing the properties of composite nanofibers for potential applications in bioengineering and bioelectronics.

Keywords: electroconductive; nanofibers; composites; electrospinning



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1. Introduction

Electroconductive polymers have garnered significant attention in recent years due to their unique combination of electrical conductivity, mechanical, and chemical properties. This makes them suitable for a wide range of applications in fields such as electronics, energy storage, and sensing [1–3]. In this context, research efforts have focused on exploring the properties and potential of various electroconductive polymeric composites and developing new methods for their synthesis and characterization for biomedical use [4–7].

Despite these efforts, there are still many questions that need to be addressed, particularly with regard to the optimization of polymer properties for specific applications such as bioelectronics. Furthermore, the development of new electroconductive polymers and materials with improved performance is of ongoing importance. This is particularly true for applications in demanding environments, where high levels of performance and stability are required [8–10].

In the last years, electroactive materials such as copper oxide (CuO) [11,12], poly(3-hexylthiophene) (P3HT) [13,14], copper phthalocyanine (CuPc) [15], and methylene blue (MB) [16] have emerged as promising candidates for biological purposes including biosensors, tissue engineering, and drug delivery. CuO has been extensively investigated as

a potential material for biosensors due to its excellent electrocatalytic activity and high stability in biological environments [17,18]. For instance, P3HT, a p-type semiconducting polymer, has been used in tissue engineering applications as a neural scaffold material due to its biocompatibility, good electrical conductivity, and mechanical properties [19]. CuPc has shown promise in drug delivery due to its ability to encapsulate drugs and selectively release them in response to specific stimuli, such as light or pH [20–22]. MB, a redox-active dye, has been widely used in electrochemical biosensors due to its ability to act as an electron mediator and its excellent electrochemical activity [23–26].

The unique properties of these electroactive materials have enabled their use in a wide range of bioelectronics and biological applications. These applications include biosensors for monitoring various biomolecules and metabolites, tissue engineering for the regeneration of damaged tissues, and drug delivery for targeted and controlled release of therapeutic agents.

In this context, the use of these materials embedded into nanofibers has the potential to revolutionize the biotechnology field. It can provide a foundation for future research efforts aimed at optimizing the properties of electroconductive polymers with piezoelectric platforms and expanding their use in various fields. Herein, a comparative study on composite piezoelectric PVDF-TrFE fibers embedded with electroactive phases, i.e., namely, CuO, P3HT, CuPc, and MB, was proposed in order to investigate the correlations among electroconductive properties, morphology, and in vitro response.

2. Materials and Methods

Nanofibers were fabricated using PVDF-TrFE ($M_w = 35,000$) dissolved in tetrahydrofuran (THF) at a 13 wt% solution, as published elsewhere. [27] The active materials used to perform the composite nanofibers were copper oxide (CuO) nanoparticles of 25 nm (partially passivated, 99.8%, 25 nm; US Research Nanomaterials, Houston, TX, USA), poly(3-hexylthiophene) (P3HT) (regioregular, ca. $M_n 54,000$ – $75,000$, electronic grade, 99.995% trace metals basis; Sigma-Aldrich, St. Louis, MO, USA), copper phthalocyanine (CuPc) (sublimed grade, dye content 99%, $M_w = 576.07$; Sigma-Aldrich, St. Louis, MO, USA), and methylene blue (MB) ($M_w = 319.85$; Sigma-Aldrich, St. Louis, MO, USA). Subsequent composite fibers were formed by adding a selected amount of the active component for every 1.5 g of 13 wt% PVDF-TrFE/THF. Experimental amounts are shown in Table 1. Solutions were electrospun using 1.5 mL via a 23 G syringe, under a high voltage of 17 kV, with a pump rate of 300 $\mu\text{L}/\text{h}$, and collected on a slow-rotation mandrel (300 rpm) 13 cm apart.

Table 1. Specifications of composite solutions.

Active Component	Weight (mg)	Amount of 13 wt% PVDF-TrFE/THF (g)	Composite Solution (wt%)
P3HT ¹	1.4	1.45	0.09
Cu Phthalocyanine	10.9	1.5	0.721
Methylene Blue	10.2	1.5	0.675
CuO	8.9	1.5	0.589

¹ 0.14 g of 1 wt% P3HT/THF was added to 1.3 g of 13 wt% PVDF-TrFE/THF.

The morphology of the nanofibers was investigated by using scanning electron microscopy, SEM (JEOL JSM-IT-100). Briefly, a properly sized nanofiber sample was mounted on a sample holder by carbon double adhesive tape. Selected images were used for quantitative analyses. In detail, fiber diameters were measured from 100 nanofibers randomly using the SEM built-in measurement system. Meanwhile, energy dispersive spectroscopy (JEOL JSM-IT-100: EDS) analysis was used for a qualitative estimation of the elemental composition of the nanofibers.

Electrical properties of the composites were evaluated by drop casting the composite solutions over interdigitated gold electrodes to reveal the bulk electrical conductivity in air, at laboratory conditions. The electrical characterization was performed by three

sweeps: from 0 V to 5 V, 5 V to −5 V, and −5 V to 0. This sweep shows possible charge traps and redox properties in the drop-casted films promoted by the characteristic properties of the conductive phase and the randomness of the electroactive molecules in the piezoelectric polymer.

For in vitro assays, L929 cell line (fibroblasts derived from mouse, Sigma-Aldrich, St. Louis, MO, USA) were used. The L929 cells were cultured in a 75 cm² cell culture flask in Dulbecco's Modified Eagle Medium (DMEM, Sigma-Aldrich, Milan, Italy) supplemented with 10% of fetal bovine serum (FBS, Sigma-Aldrich, St. Louis, MO, USA), antibiotic solution (streptomycin 100 µg/mL and penicillin 100 U/mL, Sigma-Aldrich, Milan, Italy), and 2 mM of L-glutamine (Sigma-Aldrich, Milan, Italy). The cells were incubated at 37 °C in a humidified atmosphere with 5% of CO₂ and 95% air. Before the assays, samples were cut and placed into 96-well cell culture and sterilized with UV light for 30 min.

The cytotoxicity of fibers was evaluated by using the XTT assay protocol (XTT, Roche Diagnostics Deutschland GmbH, Mannheim, Germany, purchased by Sigma-Aldrich) at 24 and 72 h. The L929 cells were seeded at a density of 1×10^5 cells per well onto PVDF, P3HT, MB, CuO, and CuPc fibers. The cell culture plate (TCP) was used as a control. At each scheduled time, the culture medium was replaced with 100 µL of fresh medium and 50 mL XTT solution was added, followed by 4 h of incubation. After the incubation time, the supernatant was measured using a plate reader (Wallac Victor 1420, PerkinElmer, Boston, MA, USA) at 450 nm of absorbance. The XTT assays were based on the reduction of tetrazolium salt XTT by mitochondrial enzymes into soluble formazan dye by living cells. In order to evaluate morphology and cell spreading, L929 were investigated by confocal laser scanning microscopy (LSM 510, Carl Zeiss, Berlin, Germany). Cell Tracker™ Green CMFDA (Invitrogen, Life Technologies Corporation, Eugene, OR, USA) in phenol red-free medium at standard conditions. Then, samples were washed with PBS (phosphate-buffered saline) solution and incubated for 1 h in complete medium. After the incubation, samples were washed three times and cells were fixed with 4% of PFA. Before imaging, samples were stained with 1 µg/mL DAPI (4',6-diamidino-2-phenylindole) for 5 min, and then washed. For proliferation tests, 6×10^3 cells per well were seeded onto P3HT, MB, and CuPc electrospun fibers to then perform cell proliferation at 1, 3, and 7 days by using XTT assay. The resulting amount of formazan dye was directly proportional to the number of viable cells for each electroactive culture.

3. Results

The combination of electroactive components with piezoelectric matrices represents an interesting strategy to fabricate innovative devices. These devices have customizable electroconductive properties as a function of the peculiar properties of the dispersing phases. In this context, electrospinning offers the opportunity to emphasize this effect by creating electrostatic interactions among polar groups at the surface interface.

Figure 1 shows PVDF-based fibers collected onto the aluminum foil for ca. 10 min. Qualitatively, different colors of composite were recognized as a function of the active phase embedded; by comparing SEM images of deposited fibers, it is possible to recognize a homogeneous spatial distribution of fibers onto the collector that are characterized by a slight preferential alignment, in all the cases, qualitatively ascribable to the interaction of PVDF polar groups with applied electric forces. A limited number of beads—in the case of CuO, P3HT, and CuPc—until to none—in the case of PVDF-TrFE and MB—was recognized, thus confirming the optimization of the process conditions shown in Figure 2. EDS analysis was used to identify the elemental composition of the nanofibers with each peak corresponding to the elements present in the composite. For CuO, it shows peaks corresponding to copper and oxygen, while CuPc shows corresponding peaks to copper and carbon with smaller amounts on nitrogen and oxygen. For P3HT and MB, peaks corresponding to the elements carbon and hydrogen were present, while sulfur and nitrogen were not detected. This might be due to the detector not being sensitive enough to detect the low concentrations of those elements in the collector. The aluminum peak at 1.5 keV

came from the foil collector and could also mask the small signal from those elements at such low concentrations. A decrease in diameter was observed in the case of fibers embedded with electroconductive phases. In particular, PVDF-TrFE fibers showed an average fiber diameter of ca. $3.75\ \mu\text{m}$, while those of the composite fibers decreased by 12.43% for CuO ($\sim 3.28\ \mu\text{m}$), 32.87% for Cu Phthalocyanine ($\sim 2.52\ \mu\text{m}$), 36.46% for P3HT (~ 2.38), and a remarkable 63% for MB ($\sim 1.39\ \mu\text{m}$), as shown in Figure 3. Notably, the deposition of fibers without the use of rotating collectors led to a reduced evaporation rate, thus promoting a longer electrostatically stretch before landing over the collector, and, therefore, a smaller diameter at the sub-micrometric scale. In the case of composite fibers, the presence of electroactive components concurs to amplify the effect of electrostatic forces on fiber diameters, thus favoring the deposition of thinner fibers, with respect to pure ones.

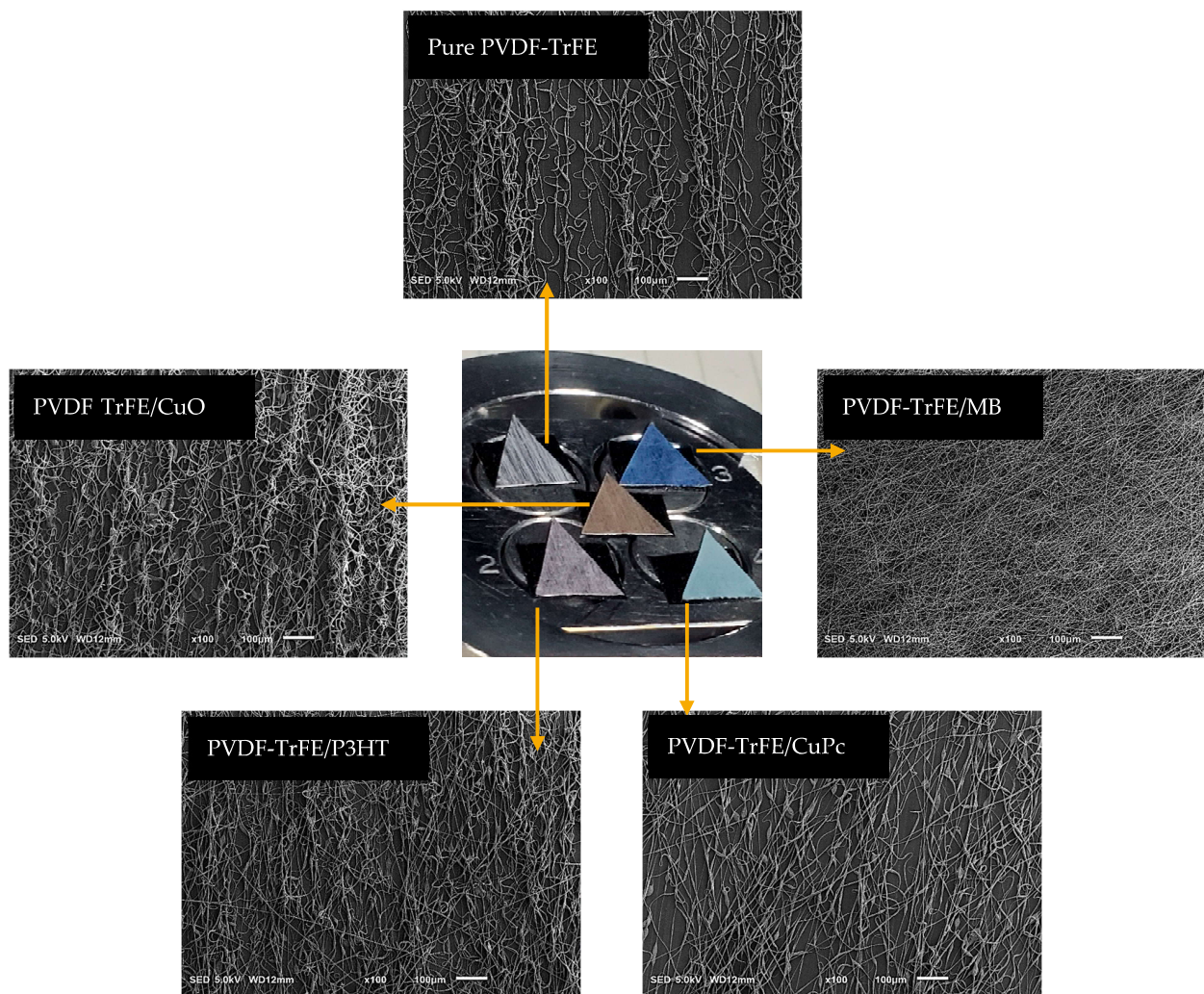


Figure 1. Different PVDF-TrFE electrospun fibrous membranes with electroconductive phases: qualitative evaluations.

Current–voltage (I–V) curves shown in Figure 4 were recorded on pure and composite PVDF-TrFE nanofibers embedded with different active components. This result is strictly related to the intrinsic electrical properties of different active components used and their interaction with the PVDF-TrFE matrix. In particular, the I–V measurements showed that PVDF-TrFE composites of MB and CuPc had moderate conductivity, with MB exhibiting a redox electron transfer mechanism and CuPc with a charge carrier hopping mechanism. Composites with CuO and P3HT had poor conductivity in air, with an electron and hole hopping mechanism, respectively.

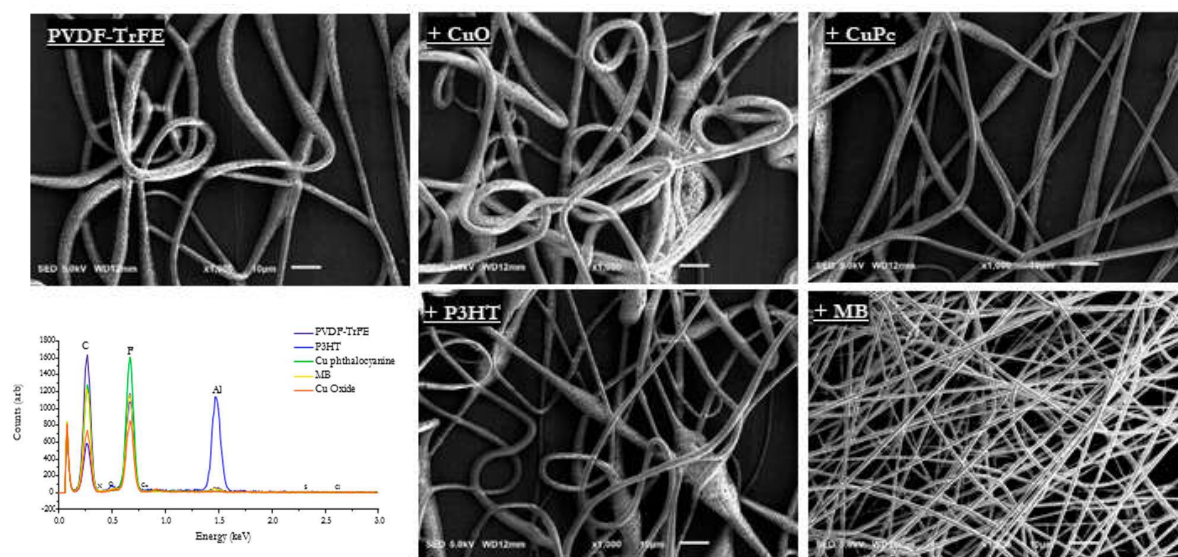


Figure 2. Comparison of pure and composite PVDF-TrFE nanofibers: SEM and EDS analysis.

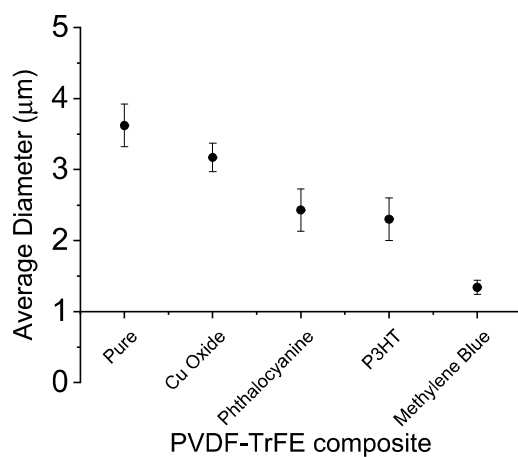


Figure 3. Quantitative evaluation of pure and composite PVDF-TrFE nanofibers' fiber diameters via image analysis.

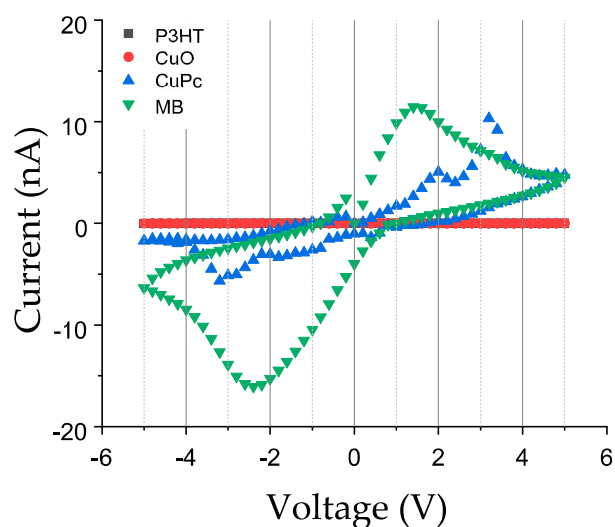


Figure 4. Electrical characterization of pure and composite PVDF-TrFE nanofibers: Current–voltage (I–V) curves as a function of different active components used.

Methylene blue shows the highest ability to transport charges, following CuPc, in accordance with fibers diameters being the thinnest for MB, and followed similarly by P3HT and CuPc. While P3HT poorly conducts in air, it improves charge transfer during the fiber formation, enhancing the formation and the decrease in fiber diameter [27,28].

The electrical conductivity of electroactive materials and their composites is determined by the movement of charge carriers through the material. The conductivity is affected by factors such as the material's crystal and molecular structure, doping level, percolation, and presence of impurities or defects. Copper oxide exhibits semiconducting properties, and its conductivity mechanism involves the movement of electrons through the material. Poly(3-hexylthiophene) is a conjugated polymer with semiconductive properties, and its conductivity mechanism involves the movement of holes through the polymer chains. Copper phthalocyanine is a small molecule organic semiconductor, and its conductivity mechanism involves the movement of ambipolar charge carriers through the material. Methylene blue acts as a redox-active dye, and its conductivity mechanism involves the transfer of electrons between the dye molecules and the electrodes via a hopping mechanism. The conductivity mechanisms of these materials can be enhanced by increasing their degree of crystallinity, improving the alignment and packing of the molecules, and facilitating charge carrier hopping. Additionally, the conductivity of the studied composites is influenced by the percolation of the active material into the composite and the properties of the PVDF-TrFE.

When PVDF-TrFE is added to these materials, it can have various effects on their conductivity mechanisms, depending on the nature of the interaction between them, as a function of the specific properties of active components used. In particular, the addition of PVDF-TrFE acts as a binder that mechanically facilitates the formation of the nanofibers and a well-connected network of particles or molecules in the composite, which can improve charge transport through the material. Additionally, PVDF-TrFE can also act as a dopant, introducing additional charge carriers into the material and increasing its conductivity. The presence of PVDF-TrFE can also modify the surface chemistry of the electrodes, leading to changes in the energy-level alignment at the interface and affecting the electron injection and charge transfer processes.

In the case of composite PVDF-TrFE fibers, the electrical conductivity can be influenced by the morphology and microstructure of the composite material. The presence of PVDF-TrFE can promote the formation of a more ordered crystalline structure, which can improve charge transport and enhance the overall conductivity of the composite material [29]. Additionally, the piezoelectric properties of PVDF-TrFE can enhance the stability of the embedded phases by reducing the solubility of the individual components and preventing leaching from the fiber body, in agreement with previous experimental evidence [30].

Taking into consideration the different response of composite PVDF-TrFE nanofibers in terms of morphology and electrical properties, *in vitro* studies were performed in order to validate their biocompatibility and suggest the best formulation for potential biomedical uses.

In vitro tests were performed on PVDF-TrFE and their composites embedded with CuO, P3HT, CuPc, and MB fibers firstly to investigate cell adhesion at 24 and 72 h (Figure 5). The results are presented with respect to the control (TCP) which represents the 100% of cell viability. After 24 h, the results showed significant differences when all the samples were compared with the TCP; however, more than 60%, in all cases, of cells were viable. However, after 72 h, CuO showed a cytotoxic effect on the L929 cells, with significant difference with respect to fibers without active materials (PVDF-TrFE). Therefore, this group was excluded for the next assay.

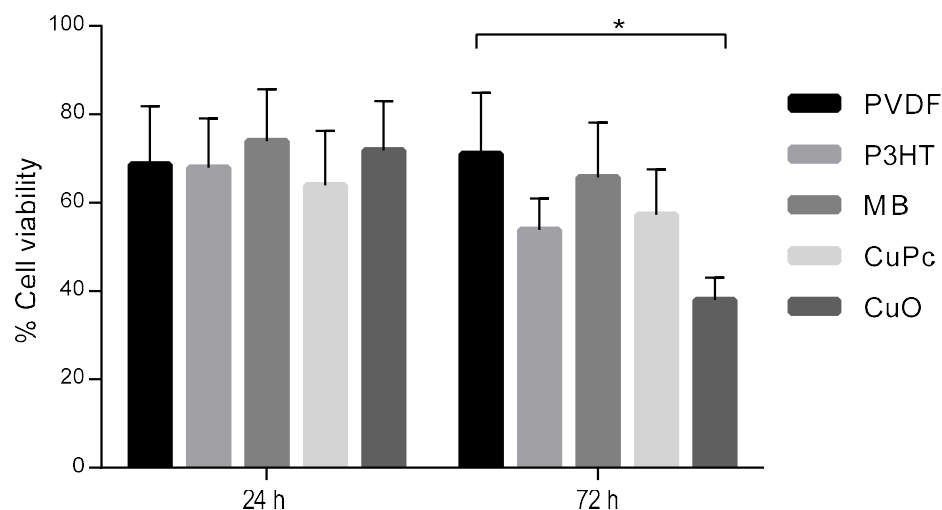


Figure 5. Comparative in vitro studies of PVDF, P3HT, MB, CuPc, and CuO electrospun fibers: cytotoxicity tests. All the results were normalized with respect to the positive control (TCP) representing the 100% of cell viability. (* $p < 0.05$).

In vitro response was also confirmed by the morphological investigation performed via confocal microscopy (Figure 6a–c). The images—showing stained cells: nuclei (blue) and bodies (green)—confirmed the ability of cells to adhere onto the PVDF TrFE fibers after 24 h, with a comparable density and similar cell morphology independently in the presence of P3HT, MB, and CuPc. However, a higher presence of cell nuclei (blue) related to the presence of live cells was recognized in the case of P3HT-loaded samples (Figure 6a), followed by MB and CuPc (Figure 6b,c), respectively.

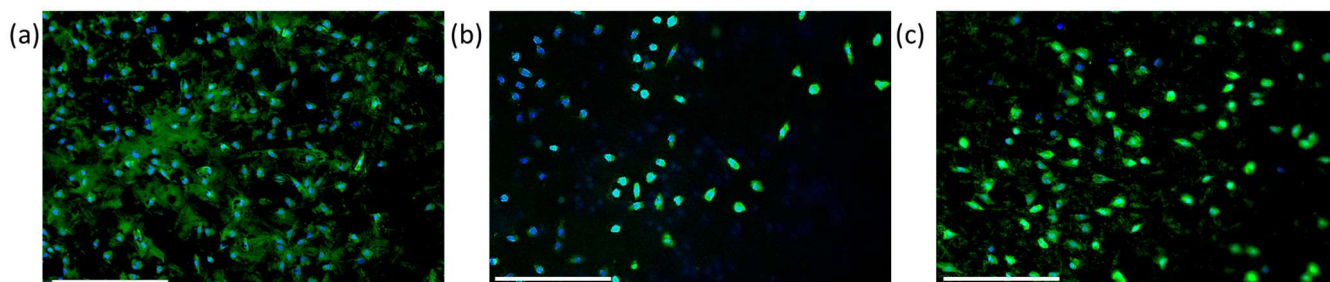


Figure 6. Confocal microscopy of L929 cells' adhesion after 24 h, onto electrospun fibers of PVDF-TrFE loaded with P3HT (a), MB (b), and CuPc (c). The images (Scale bar: 250 μm) were obtained by staining cells via Cell-Tracker Green CMFDA.

The trend was also confirmed by in vitro tests performed to evaluate cell proliferation (Figure 7). In this case, L929 cells were maintained in culture for 1, 3, and 7 days. P3HT and MB fibers showed good cell proliferation with respect to CuPc fibers. Moreover, there was an increase in cell proliferation onto P3HT and CuPc fibers after 3 days; however, there was a stop in cell proliferation after 7 days. Meanwhile, the proliferation of MB fibers remained similar from the first to the third day and increased after 7 days.

In other terms, cell viability and proliferation assays showed that L929 cultured on P3HT and MB composites had higher viability and proliferation rates compared with those cultured on CuO and CuPc composites. These results are consistent with previous studies that have shown that P3HT and MB can promote cell adhesion and proliferation due to their surface properties and charge transfer mechanisms [31,32]. In contrast, CuO and CuPc, partially, have been shown to exhibit cytotoxicity and negative effects on cell viability due to their oxidative stress and reactive oxygen species generation [33]. The addition of PVDF-TrFE to each composite did not significantly affect cell viability or proliferation rates.

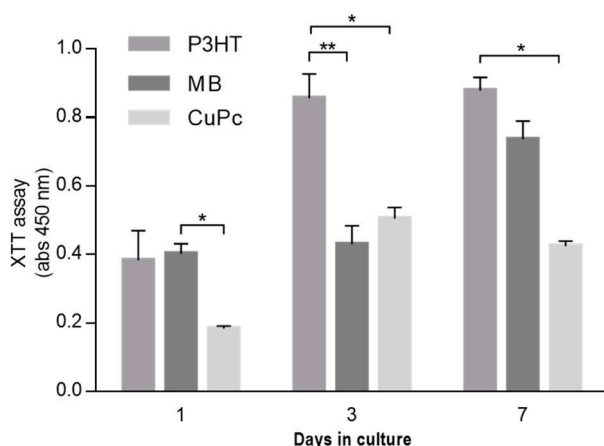


Figure 7. Cell proliferation of L929 cells seeded onto PVDF composites of P3HT, MB, and CuPc electrospun fibers. (* $p < 0.05$; ** $p < 0.01$). All the results were normalized with respect to PVDF fibers used as positive control.

These promising results demonstrated a good biocompatibility of composite meshes, able to successfully support adhesion and proliferation of fibroblasts. Accordingly, further investigations could be performed in order to evaluate also the antibacterial response for a potential application of PVDF-TrFE composite nanofibers for physical filtration and/or static entrapment of bacteria.

4. Discussion

PVDF-TrFE electrospun nanofibers are recently emerging as interesting substrates with piezo/electroconductive properties suitable for a wide range of applications in the biomedical area. Indeed, the use of PVDF-TrFE provides the strength, flexibility, and mechanical stability needed to optimize the morphology of nanofibers for scaffolds and/or bio-functional platforms. The piezoelectric and triboelectric properties of PVDF allow for the generation of electrostatic charges, which can be used to trap particles [34,35], molecular species [36], or microorganisms enhanced with the addition of electroactive phases (i.e., virus, bacteria [37–43]). In this work, the optimization of composite nanofibers by embedding active components with electroconductive properties into PVDF-TrFE nanofibers was investigated in order to investigate the effect of different conductive properties, related to different active components, on fiber morphology and in vitro response. In vitro results suggest that the conductive mechanisms ascribable to peculiar interactions among PVDF TrFE nanofibers and selected active components such as P3HT or MB play an important role in determining fiber morphological properties and in vitro response of L929 cells, in terms of adhesion and cell proliferation, in contrast with other compounds (i.e., CuO, CuPc) that show a partial cytotoxic effect. This result is not surprising but in agreement with previous experimental evidence, indicating the preferential use of CuO or CuPc for diagnostic and/or therapeutic use for cancer applications [44,45]. At this preliminary stage of the study, P3HT-loaded fibers can be considered the most suitable for use in biomedical applications, but further studies will be needed to fully elucidate the mechanisms underlying these effects, in order to finely optimize the design of fibers for specific applicative targets.

5. Conclusions

In conclusion, the present study explored the morphology and in vitro response of electroconductive composite nanofibers for biomedical applications. Blending PVDF-TrFE with different electroconductive materials such as CuO, P3HT, CuPc, and MB resulted in unique combinations of electrical conductivity, biocompatibility, and other desirable properties. Morphological analysis revealed that the fiber size was affected by the type of electroconductive phase used. The in vitro assays demonstrated a tunable response of the fibers in terms of cell viability and proliferation, with P3HT-loaded fibers showing the

most suitable interaction with fibroblast cells. These findings provide valuable information for researchers and engineers in the field of biomedical engineering and electronics, which can help optimize the properties of composite nanofibers and expand their use in bioelectronics. Additionally, further investigations could be performed to evaluate the antibacterial response of PVDF-TrFE composite nanofibers for physical filtration and/or the static entrapment of bacteria. Overall, the study highlights the potential of electroconductive composite nanofibers as a promising material for a broad application in the biomedical area, from tissue engineering to biosensors, to biofiltration.

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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-dioxo-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

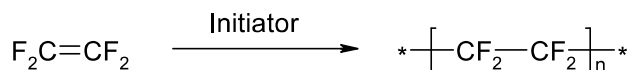
1930s

The development of the fluoropolymer industry began with the discovery of the polytetrafluoroethylene (PTFE) by Dr. Plunkett at DuPont in 1938 [9]. The white powder found by

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 planar 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/cm³. 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

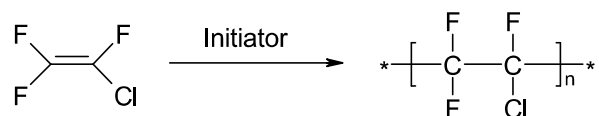
In the beginning, PTFE polymers found no use for any application due to its insolubility, high melting temperature and extremely high melt viscosity. During World War II people realized the importance of this new material. At the time, the Manhattan Project was carrying out the development of the atomic 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.

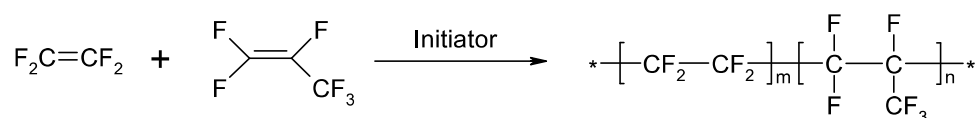
PCTFE was originally produced by M. W. Kellogg and 3M under the trade name of Kel-F [13]. After 3M discontinued the production of PCTFE (1995) [14], Daikin purchased the manufacture rights to PCTFE and produced it under the trade name Neoflon. PCTFE resin is also produced by Honeywell as Aclar and by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

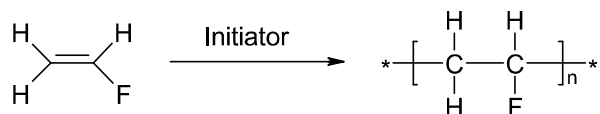
FEP can be processed by the conventional polymer processing techniques such as injection molding, extrusion and film casting. FEP has better impact strength, better wear resistance, and less permeability for organic solvents compared with PTFE. The disadvantage of FEP is the poorer resistance to thermal stress cracking. FEP exhibits similar chemical resistance, weather resistance, flame resistance, radiation resistance, and the electrical properties to PTFE. FEP is easier to surface modify to increase wettability and adhesive bonding.

FEP dispersions are generally used for coatings followed by the fuse treatment above the melting temperature of the polymer. The major applications of FEP are wire insulation, thermocouple wire insulation, chemical resistance liners for pipes and fittings, lined tanks for chemical storage, anti-stick applications, and sheet and film products for solar panels and solar collectors.

About 65% of overall worldwide consumption for FEP is for plenum cable insulation. The increasing use of local area network (LAN) cable led to a huge increase in the market of FEP. Some typical commercial FEP products are Teflon FEP from DuPont, Neoflon FEP from Daikin, and Dyneon FEP from Dyneon.

In 1961, DuPont introduced another fluoropolymer, polyvinylfluoride (PVF) (Figure 4) with the trademark Tedlar. Although only one hydrogen atom was replaced by a fluorine atom compared to the polyethylene, PVF showed more interesting properties than most fluoropolymers.

Figure 4. The polymerization of VF.



PVF is prepared by the polymerization of vinyl fluoride (VF) in an aqueous medium using a free radical initiator. A higher pressure is necessary due to the lower polymerization activity of VF compared to TFE.

The presence of the fluorine atom in PVF put it in between PE and PTFE in terms of crystallization. With a crystallinity of 40%, PVF has a melting temperature around 200 °C, and can be continuously used in the temperature range from −70 °C to 110 °C. The lower crystallinity of PVF compared to PTFE resulted in higher impact strength and better tensile strength. The relatively poor thermal stability of PVF makes PVF difficult to process traditionally. PVF film is manufactured using a plasticized melt extrusion method with plasticizers and stabilizers.

The main uses of PVF are in films and coatings applications, such as the premier surface finish for aluminum and steel home siding. The excellent resistances to weather and radiation have led to the wide application of PVF as glazing materials for solar energy collectors.

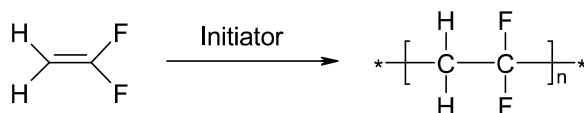
The formability of PVF is very important for lamination applications. It is critical that the laminate can stand bending during the roll forming process. PVF laminated steel finds application in industrial plants, warehouses, highway sound barriers and parking garages and provides long lasting aesthetics.

Currently, DuPont is still the main company for PVF production. With a recent expansion it plans to achieve \$1 billion in sales by 2012.

Compared to VF, vinylidene fluoride (VDF) has one more fluorine atom on the same carbon in its chemical structure. The free radical polymerization of VDF resulted in a partially fluorinated,

semi-crystalline polymer PVDF (polyvinylidene fluoride) (Figure 5), which was introduced by Pennsalt (now Arkema) with the tradename Kynar in 1961.

Figure 5. The polymerization of VDF.



PVDF is generally prepared by two kinds of polymerization methods, the suspension method and the emulsion method. Suspension polymerization produces PVDF with high head-to-tail structure in the polymer chains, which results in higher crystallinity, higher melting temperature, and better mechanical properties at elevated temperatures [17,18].

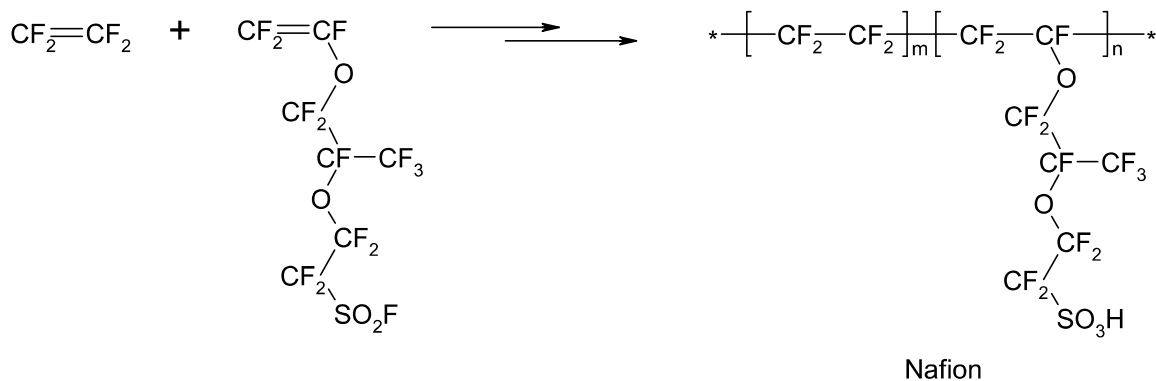
PVDF is a polymer with several crystalline forms depending on the processing conditions. It has a melting temperature (~170 °C) significantly lower than that of the other fluoropolymers. The normal processing temperatures for PVDF are in the range 200–260 °C, and the continuous service temperature for PVDF is up to 150 °C. The crystallinity of PVDF increases significantly in the first week after processing and stabilizes after 4 weeks. This phenomenon increases crystallinity up to 65% and results in the intrinsic stress and the potential stress cracking.

PVDF has very good chemical resistance to a wide range of chemicals, but it is not as good as that of other fluoropolymers. For example, PVDF can be swollen by polar solvents such as ethyl acetate and acetone. It shows medium flame resistance properties. PVDF also shares many of the characteristics of other fluoropolymers, such as thermal and oxidative stability, as well as outstanding weatherability. PVDF has substantially greater strength, wear resistance, and creep resistance than PTFE and FEP. PVDF undergoes cross-linking when exposed to ionizing radiation, which leads to a modification of its mechanical properties.

PVDF has been used in the architectural coating industry, the wire and cable industry and the chemical industry for valves, pumps and bearings. Heat-shrinkable tubing made from PVDF is used in the electronics, aerospace, and aircraft industries. The alternative arrangement of fluorine and hydrogen atoms on the polymer main chain leads to an unusual polarity with a dramatic effect on dielectric properties. PVDF has a high dielectric constant (8 ~ 9) relative to the other fluoropolymers, and it also shows strong piezoelectricity. The promising developments include actuator materials, piezoelectric ceramics, piezoelectric composites and piezomicrosensors.

The commercial PVDF products include Kynar from Arkema, Solef from Solvay, and Neoflon PVDF from Daikin. Solvay increased PVDF production capacity by 50% in 2011 to serve the strong growing demand.

In the late 1960s, Nafion was discovered by Walther Grot of DuPont. Nafion is a fluoropolymer containing sulfonate groups onto a tetrafluoroethylene backbone (Figure 6) [19–27]. It is the first of a class of synthetic polymers with ionic properties which are called ionomers.

Figure 6. The preparation of Nafion.

Nafion is synthesized firstly by the copolymerization of TFE and a perfluoro(alkyl vinyl ether) with sulfonyl acid fluoride. The resulting polymer is extruded into films and treated with hot aqueous NaOH converting the sulfonyl fluoride groups ($-\text{SO}_2\text{F}$) into sulfonate groups ($-\text{SO}_3\text{Na}$). This form of Nafion, referred to as the neutral or salt form, is finally converted to the acid form containing the sulfonic acid ($-\text{SO}_3\text{H}$) groups. Nafion can be cast into thin films by heating in aqueous alcohol at 250 °C in an autoclave. By this process, Nafion can be used to generate composite films, coat electrodes, or repair damaged membranes.

The combination of the stable Teflon backbone with the acidic sulfonic groups gives Nafion many special characteristics. It is highly conductive to cations, making it suitable for many membrane applications. The Teflon backbone interlaced with the ionic sulfonate groups gives Nafion a high operating temperature, e.g. up to 190 °C. The combination of fluorinated backbone, sulfonic acid groups, and the stabilizing effect of the polymer matrix make Nafion a very strong acid, with pK_a of -6 . Nafion's superior properties allowed for broad application. Nafion has found use in fuel cells, electrochemical devices, chlor-alkali production, metal-ion recovery, water electrolysis, plating, surface treatment of metals, batteries, sensors, Donnan dialysis cells, drug release, gas drying or humidification, and superacid catalysis for the production of fine chemicals (Gelbard, 2005). Nafion is also often cited for theoretical potential (*i.e.*, thus far untested) in a number of fields.

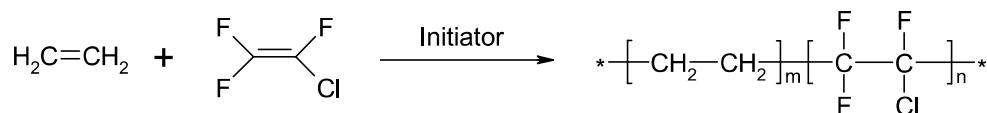
Although fuel cells have been used since the 1960s as power supplies for satellites, recently they have received renewed attention for their potential to efficiently produce clean energy from hydrogen. Nafion was found effective as a membrane for proton exchange membrane (PEM) fuel cells by permitting hydrogen ion transport while preventing electron conduction. Solid Polymer Electrolytes, which are made by connecting or depositing electrodes (usually noble metal) to both sides of the membrane, conduct the electrons through an energy requiring process and rejoin the hydrogen ions to react with oxygen and produce water. Fuel cells are expected to find strong use in the transportation industry.

Nafion is the first and still one of the most important functional fluoropolymer materials. The further development in the fuel cell industry and the automotive industry offered the prominent future for the interesting polymer systems.

1970s

After discovering that ethylene has good copolymerization properties with fluorinated monomers, many new fluoropolymers were developed to achieve more favorable application properties. The first fluoropolymer containing ethylene units was ECTFE, which was introduced to the market by the Italian company Ausimont in 1970. ECTFE is an alternating copolymer of ethylene and CTFE (Figure 7).

Figure 7. The preparation of ECTFE.



ECTFE is prepared by the copolymerization of ethylene and CTFE at relatively low temperatures (<10 °C) in an aqueous medium using a peroxide catalyst and a halogenated solvent chain transfer agent to regulate the molecular weight [28].

ECTFE polymer chains pack in an extended zigzag confirmation, which results in a crystallinity of 50%–60%. ECTFE has a melting temperature in the range of 220–245 °C depending on the polymerization methods. ECTFE can be used over a broad temperature range from –100 °C to 150°.

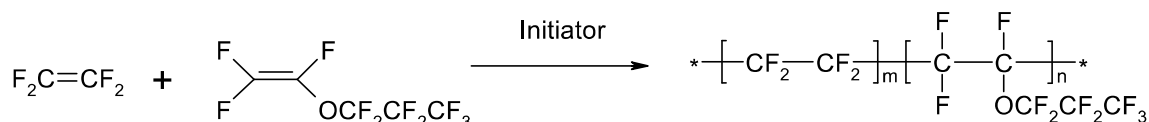
ECTFE can be processed by the standard processing methods for traditional thermoplastics in the range of 260–300 °C. It is readily converted into fibers, filaments, films, sheets, and wire and cable insulation. Noticeably, the molten ECTFE is corrosive and special corrosion-resistant steels are used for screw and barrel components.

As the copolymer with ethylene, ECTFE has moderate chemical resistance, flame resistance, and dielectric constant (2.6). While, it still has excellent radiation resistance, weathering resistance, and barrier properties, as well as good tensile, flexural and wear-related properties. The strength, wear resistance and creep resistance of ECTFE are significantly greater than that of PTFE and FEP. ECTFE film is the most abrasion resistant and highest tensile strength fluoropolymer film available.

The single largest use of ECTFE is the flame-resistant insulation for wire and cable applications, extensively used for aircraft, mass transit and automotive wiring. ECTFE also finds applications in chemical process equipments and components. ECTFE is used in aerospace applications, such as gaskets for liquid oxygen and other propellants, components for spacecraft and aircraft cabins, convoluted tubing, abrasion resistant braid and hose for expandable conduit for space suits.

At the end of 1999, Ausimont introduced a new family of ECTFE resins under the trademark Vatar, specifically designed to meet the requirements for plenum cable applications. ECTFE is currently manufactured by Solvay under the trademark Halar after acquiring Ausimont in 2002.

Figure 8. The preparation of PFA.



After the introduction of FEP, further research on TFE copolymers led to the development of PFA (Figure 8)—a copolymer of TFE and perfluoropropylvinylether (PPVE), which was introduced in 1972 by DuPont.

Generally, PFA is prepared by an aqueous dispersion process. The copolymerization must be controlled carefully to produce a uniform copolymer with the required molecular weight and polydispersity [29,30].

Due to the PPVE units in the polymer main chain, PFA has lower crystallinity compared to PTFE. Correspondingly, PFA has a lower melting temperature (305–310 °C), lower melt viscosity and better processability. This improvement for PTFE dramatically enlarged its market by lowering the processing cost and enriched the available product categories by the flexibility of thermoplastic processing.

PFA shows comparable mechanical properties as FEP below 200 °C, and performs comparable mechanical properties as PTFE above 200 °C. The thermal stability of PFA is almost the same as that of PTFE and better than that of FEP. PFA has the same chemical resistance, flame resistance and radiation resistance as PTFE. The electrical properties of PFA and PTFE are similar. Importantly, PFA thin films have better transparency compared to PTFE.

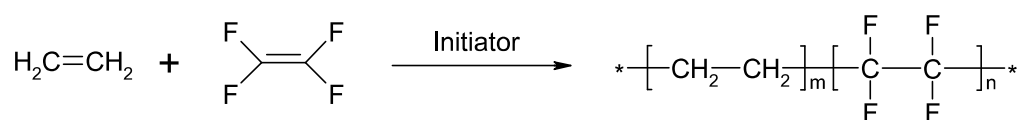
PFA can be processed by conventional melt techniques such as extrusion, injection molding and rotational molding. PFA powder can be used directly for extrusion or injection molding, and a PFA dispersion can be prepared for spray or dip-coating applications. Like PTFE, PFA can be filled with glass or carbon fibers, graphite or bronze powder to improve wear and creep properties.

The main applications of PFA are chemical resistance components for valves, pumps and pipes. PFA is also widely used in the semiconductor manufacturing industries for high purity and chemical resistant moldings.

The commercial PFA products are Teflon PFA from DuPont, Aflon PFA from Asahi Glass, Dyneon PFA from Dyneon, Neoflon PFA from Daikin, and Hyflon PFA from Solvay.

After ECTFE, the other fluoropolymer containing ethylene units—ETFE was commercialized in 1973 by DuPont. ETFE is comprised of alternating ethylene and TFE units in the polymer main chain (Figure 9).

Figure 9. The preparation of ETFE.



Due to the risk of explosive decomposition reaction, the copolymerization of ethylene and TFE must be conducted in special vessels at low pressure. Suspension polymerization is generally carried out in an inert chlorofluorocarbon solvent using fluorinated peroxides as initiator and methanol as a chain transfer agent [31,32].

The polymer chains in ETFE adopt an extended zigzag conformation and a close packing. The crystallinity of ETFE ranges from 40% to 60%, and it has a melting temperature of 225–300 °C depending on the comonomer ratio and the processing method.

ETFE possesses superior processability and improved mechanical properties compared to other TFE copolymers. ETFE can be processed by all thermoplastic processing methods such as injection molding, compression molding, blow molding, rotational molding, extrusion, and wire coating. ETFE has high tensile strength, high flexibility, excellent impact strength, moderate stiffness, good abrasion resistance and high cutting resistance. ETFE modified by glass fiber reinforcement is tougher and stiffer and has higher tensile strength than PTFE, PFA or FEP. ETFE has a broad operating temperature range from as low as $-100\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$.

As a copolymer of ethylene and TFE, ETFE has medium chemical resistance and flame resistance. Its radiation resistance is high with the advantage of being cross-linked by high-energy radiation. The radiation cross-linked ETFE wire insulation can be continuously used at $200\text{ }^{\circ}\text{C}$.

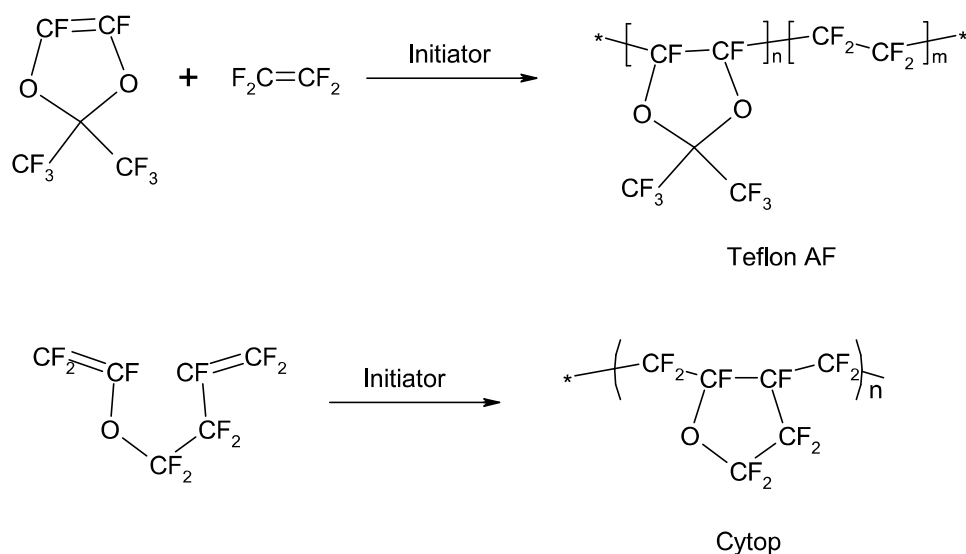
The main application for ETFE is wire and cable insulation, accounting for 60% of its market. ETFE has good resistance to petroleum and fuel permeation, which resulted in a significant growth of ETFE as fuel tubing.

The commercial ETFE products include Tefzel from DuPont, Fluon from Asahi Glass, Halon ETFE from Solvay, Neoflon ETFE from Daikin, and Dyneon ETFE from Dyneon.

1980s

Before 1980s, all the industrial fluoropolymers were semicrystalline materials. Crystalline fluoropolymers have certain shortcomings such as low optical clarity, high creep and poor solubility, which limited their processability and the type of applications. In 1985, DuPont developed an amorphous perfluoropolymer—Teflon AF. Teflon AF is a copolymer of TFE and perfluoro-2,2-dimethyl-1,3-dioxole (PDD) (Figure 10). The copolymerization of PDD and TFE is carried out in aqueous media with a fluorinated surfactant and ammonium persulfate as an initiator [33,34]. The composition of the copolymers could be adjusted by the comonomer feeding ratios. Different grades of Teflon AF products were prepared for different applications. At the same time, Asahi Glass also introduced a new amorphous perfluoropolymer—Cytop. Cytop is a homopolymer obtained via the cyclo-polymerization of perfluoro-3-butenyl-vinyl ether (PBVE) (Figure 10) [35,36].

Figure 10. The preparation of Teflon AF and Cytop.

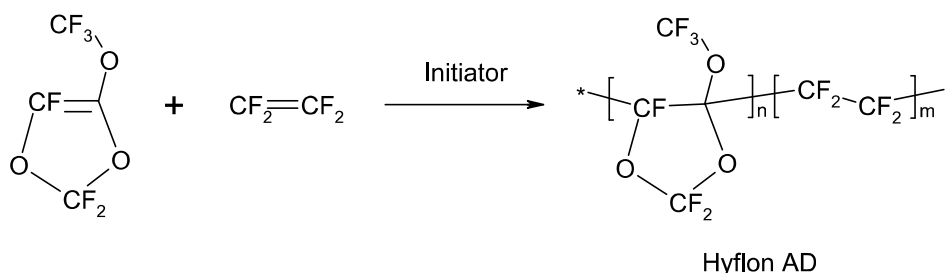


As amorphous perfluoropolymers, Teflon AF and Cytop share certain advantageous properties compared to the crystalline perfluoropolymers. Amorphous perfluoropolymers inherited the excellent chemical, thermal and electrical properties from the crystalline perfluoropolymers. At the same time, they also have high transparency, good solubility and better mechanical properties. The thin films formed from Teflon-AF and Cytop have excellent optical clarity and the lowest refractive index of all known organic materials, which makes them suitable for some special optical applications. They showed extremely high transparency over the UV, visible and near IR wavelengths. These amorphous perfluoropolymers also have the lowest dielectric constant (1.9) of all known polymers.

Amorphous perfluoropolymers can be melt-processed by all conventional processing techniques. At the same time, the good solubility in certain solvents offered them the versatile abilities in some special applications such as the ultrathin films or use with integrated circuits. For example, the spin coating of an amorphous perfluoropolymer solution is a useful processing technique for thin uniform coatings on flat substrates, and non-planar surfaces are usually coated using spraying or dip-coating methods. Amorphous fluoropolymers are used to make deep UV pellicles for electronic chip manufacturing processes. The low dielectric constant and low water absorption are great attributes for inter-layer dielectrics. The high optical transparency and very low refractive index of amorphous perfluoropolymers make them suitable for optical lenses and protective coatings. A new application for amorphous fluoropolymers is as core and cladding in optical fibers, for example the Lucina from Asahi Glass. Other interesting applications include photolithography uses for electronics, high-speed computer circuits and low dielectric constant insulators for high-performance electronic interconnects. While, the extremely high prices of amorphous perfluoropolymers restricted their use only to some special applications.

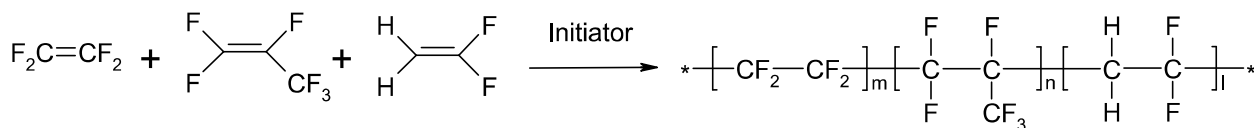
Recently, Solvay also introduced an amorphous perfluoropolymer Hyflon-AD, which is a family of copolymers from TFE and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD) (Figure 11) [37].

Figure 11. The preparation of Hyflon AD.



1990s

After the 1970s, little work was done on the traditional semicrystalline fluoropolymer materials, then in 1993 Hoechst invented THV by the copolymerization of TFE, HFP and VDF (Figure 12). Later, Hoechst granted 3M the rights for the production of THV by forming a joint venture—Dyneon in 1996. The new fluoropolymer is now known as Dyneon THV.

Figure 12. The preparation of THV.

The preparation of THV is quite similar to the traditional procedures for PTFE, FEP and PVDF [38]. THV polymer is soluble in polar organic solvents and can easily form thin films by solution casting. The film obtained is transparent through UV, visible and near IR wavelengths. THV film also exhibited excellent adhesive ability to other polymers, making them easy to utilize in a very wide range of applications.

THV fluoropolymers are processed in the range of 230–250 °C by general polymer processing equipments. THV can be processed by extrusion, blow-molding and injection.

Most applications of THV are the multilayer constructions, where a thin layer of THV provides enhanced barrier properties to other layers. THV has excellent permeation resistance and chemical resistance to be used as fuel tubings due to its flexibility and the ease of processing. Similarly, THV is used for wire and cable insulation because of its flexibility and the flame resistance. THV can also serve as a flexible liner for chemical holding tanks.

The low processing temperatures, high clarity, high flexibility and excellent adhesive properties made THV very competitive compared to other fluoropolymers.

3. The Present and the Future of the Fluoropolymer Industry

The fluoropolymer industry has not come up with any really new product since the turn of the 21st century. The existing products can satisfy most of the requirements from their industrial applications. The current efforts are focusing on reducing production costs and expanding the application markets with continued globalization development (as with most other industries).

North America is still the most dominant market for fluoropolymers especially due to the significant demand in the U.S. by the wire and cable markets. The Asia-Pacific region is expected to be the fastest growing markets for fluoropolymers, with tremendous growth driven by Japan, China and India.

Typical applications of fluoropolymers are summarized in Table 1 for different industrial segments. FEP and PVDF are the fastest growing fluoropolymer products, especially in solar cell and fiber optic applications. PVDF is expected to grow enormously due to its increasing applications in lithium-ion batteries and architectural coatings. The growths in the chemical processing, cookware, bakeware, and medical markets are also important driving forces for the fluoropolymer industry.

The general properties were summarized in Table 2 for most fluoropolymers. Additional details about each fluoropolymer can be found in the references. In order to choose a suitable material for a specific application, it is necessary to thoroughly compare all the relevant properties and the total cost of the fluoropolymer candidate [39]. There could be several choices since the application properties of the fluoropolymers overlap in most cases. Therefore, any decision should consider the requirements, the cost, the benefit, and the competitive advantage of the final product.

Table 1. Typical applications of fluoropolymers for different industry segments.

Industries	Functions	Forms
Automotive	Mechanical property, thermal property, chemical property, and friction property.	O-rings, gaskets, valve stem seals, shaft seals, linings for fuel hoses, power steering, and transmission.
Chemical industry	Chemical resistance, mechanical property, thermal property, and weather stability.	Coatings for heat exchangers, pumps, diaphragms, impellers, tanks, reaction vessels, autoclaves, containers, flue duct expansion joints, heavy-wall solid pipe and fittings.
Electrical/electronic	Dielectric constant, flame resistance, and thermal stability.	Electrical insulation, flexible printed circuits, ultra-pure components for semiconductor manufacture.
Architectural and domestic	Weatherability, flame retardancy, friction property, thermal stability.	Water-repellent fabric, architectural fabric, non-stick coatings for cookware, and fiberglass composite for constructions.
Engineering	Mechanical property, thermal stability, chemical stability, weatherability, and surface energy.	Seats and plugs, bearings, non-stick surfaces, coatings for pipes, fittings, valve and pump parts, and gears.
Medical	Surface energy, biological stability, mechanical property, chemical resistance.	Cardiovascular grafts, ligament replacement, and heart patches.

Table 2. The summary of fluoropolymers with their general properties.

Fluoropolymer	Starting Year	Melting temperature (°C)	Tensile Modulus (MPa)	Break Elongation (%)	Dielectric Strength (kV/mm)	Appl. Temp (°C)	Main Applications
PTFE	1947	317–337	550	300–550	19.7	260	Chemical processing, wire and cable
PCTFE	1953	210–215	60–100	100–250	19.7	200	Barrier film, packaging and sealing
FEP	1960	260–282	345	~300	19.7	200	Cable insulation
PVF	1961	190–200	2000	90–250	12–14	110	Lamination, film and coating
PVDF	1961	155–192	1,040–2,070	50–250	63–67	150	Coating, wire, cable, electronic
ECTFE	1970	235–245	240	250–300	80	150	Flame resistant insulation
PFA	1972	302–310	276	~300	19.7	260	Chemical resistant components
ETFE	1973	254–279	827	150–300	14.6	150	Wire and cable insulation
THV	1996	145–155	82–207	500–600	48–62	93	Barrier film and insulation

Along with the development of the fluoropolymer industry, there are more concerns about the safety and environment effects of these materials. For example, people doubt that fluoropolymers may be contributing to the buildup of the fluorinated pollutants in the environment that could threaten the whole biological system on the earth. The pollutants of most concern include trifluoroacetic acid (TFA) and perfluorooctanoic acid (PFOA). Researchers stressed that there is no evidence that the amount of TFA from fluoropolymers is dangerous to people. However, because TFA lasts so long, it could build up to levels in the environment that may pose a problem for plants [40]. Several government agencies have reviewed the safety of fluoropolymer products, including the U.S. Consumer Product Safety Commission (CPSC), the U.S. Food and Drug Administration (FDA) and the U.S. Environmental Protection Agency (EPA). As a result, U.S. and international regulatory agencies—including the U.S. Food and Drug Administration and European Food Safety Authority—affirm the safety and reliability of fluoropolymers in their various uses, as long as the materials are used according to the industry guidance [41,42].

In summary, fluoropolymers have come a long way in the past 70 years. No doubt many new fluoropolymer materials will be developed and new applications will be found for old fluoropolymers. The importance of the fluoropolymer industry will not be destabilized before the emergence of new substitute materials.

Conflict of Interest

The author declares no conflict of interest.

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March 1, 2024
Minnesota Pollution Control Agency
520 Lafayette Road N
St. Paul, MN 55155

**RE: Request for Comments-PFAS in Products Currently Unavoidable Use Rule OAH
Docket No. 71-9003-39667**

Thermo Fisher Scientific (Thermo Fisher) appreciates the opportunity to submit comments in response to the Minnesota Pollution Control Agency's (MPCA) request for comments on PFAS in Products Currently Unavoidable Use Rule.

Thermo Fisher is the world leader in serving science. Our mission is to enable our customers to make the world healthier, cleaner, and safer, whether our customers are accelerating life sciences research, solving complex analytical challenges, increasing productivity in their laboratories, improving patient health through diagnostics or the development and manufacture of life-changing therapies, we are here to support them.

Thermo Fisher appreciates the opportunity to provide the following comments and applauds MPCA's commitment to robust public engagement. We offer brief comments below in response.

MPCA Question (1): Should criteria be defined for "essential for health, safety, or the functioning of society"? If so, what should those criteria be?

Despite the apparent risks from the full lifecycle of continued uses of PFAS, its use at this time, is largely irreplaceable across products and applications within the Life Sciences, Bioproduction, and Laboratory sectors. The unique chemical properties conveyed by PFAS are essential in plastics used in every academic and clinical laboratory and in the manufacture of devices, diagnostic, and tools for research and development. The equipment used in these and other critical sectors such as mining, chip manufacturing, and in environmental monitoring and testing also uniformly and unavoidably rely on PFAS starting with basic components such as semiconductors and capacitors, displays, wiring/cabling insulations, and batteries as well as tubing and connectors where aggressive chemicals are used. In fact, every type of analytical equipment used in detecting PFAS have a critical reliance on components which themselves contain PFAS. While not every form of electrical or electronic equipment (EEE) are reliant upon PFAS, specific exclusions for PFAS used in components EEE are certainly necessary to maintain market access to critical monitoring, control and measurement equipment as well as medical devices and diagnostics instruments.

Given the complexities of a global supply chain with varying regulations impacting PFAS and other substances of concern and the unique and near existential reliance on the physical-chemical properties conveyed by PFAS substances, it is realistic to believe full elimination of PFAS throughout the global supply chain for all products will take more time that current legislation foresees. Therefore, a means to ensure the good functioning of society while invention, development, and market introduction of new chemicals advances is necessary.

In order to provide industry with clarity and certainty over new product development and market access, a means and criteria to enable a self-declaration of essentiality is needed. This is already addressed in a limited manner in SubDivision 8 of the Rule, providing for exemptions for drugs, devices, and medical applications as well as for fire-fighting foams and food packaging. We believe this list should be expanded according to essentiality for the health, safety or the functioning of society and offer 3 aligned proposals according to product use and industry sector:

Health

- i. Inclusion in any product which enables the manufacture of any drugs, medical devices, and diagnostic products (human and veterinary).
- ii. Inclusion in any product sold to support or enable research on human health or the environment.

Safety

- iii. Inclusion in any primary packaging used to ensure safety from spills/leakage of aggressive or otherwise hazardous chemicals or has functional use in primary packaging of drugs, devices, or diagnostic products.
- iv. Inclusion in any product for analysis, testing, monitoring, or measurement relating to human health and environmental pollution.

Functioning of Society

- v. Inclusion in products used for academic, governmental, or industrial research.
- vi. Any product which depends on PFAS for safe operation per established standards and building codes.

Secondarily, because the lifespan of industrial/professional monitoring, control and measurement equipment is intentionally designed for long-lasting and reliable performance with lifespans of up to 40 years, it is vital that Amara's law be amended to enable placing spare parts onto the market in keeping with commonplace objectives of a circular economy.

Where the regulation may require a case-by-case determination for Currently Unavoidable Use (CUU), the MPCA must establish criteria for:

- a) A methodology for analysis of alternatives including hazard assessment in conjunction with risk management measures for control of exposure and environmental releases – accommodating standards for best available science and adaptation as new information becomes available; and
- b) A socio-economic methodology to determine proportionate and economic feasibility for implementing alternatives which factors the broad value of use as well as cost to the citizens of Minnesota where the product is removed from the market. We also recommend that these determinations be time-bounded allowing for renewal to account for scientific and technical progress.

MPCA Question (2): *Should costs of PFAS alternatives be considered in the definition of “reasonably available”? What is a “reasonable” cost threshold?*

A “reasonable” cost threshold is not easily defined as a single value or as a cost/benefit ratio – rather it is an inexact science relating to perceived value of continued use and risk of potential harm. Moreover, we recognize the fully realized cost of any risk reduction measures relating to PFAS use must be established to determine if those measures are proportionate.

Oosterhuis et al have estimated the cost of substitution, emission control, and remediation associated with 8 persistent, bioaccumulative and toxic substances. Their data showed a high variation in the reported data ranging from approximately €50/kg to an extreme of €1.2M/kg and with PFOA and PFOS remaining the highest at €1.5K/kg and €7.7K/kg, respectively, when ranked to median estimates.¹ However, this report did not factor-in the broader socio-economic impact where an alternative is not feasible, leading to the product becoming unavailable on the market.

The market cost of implementing an alternative PFAS will include not only the development of the novel chemistry, but also the cost associated with converting that novel chemistry into an intermediate product along with validating and recertifying the alternative into an end-use product. Under a realistic scenario of no universal PFAS alternative, the socio-economic model turns to societal costs of a non-use scenario. This would include costs related to plant closures or down-sizing as well as the broader impact to the Minnesota economy if the products would become unavailable.

We ask the MPCA to require consideration of a comprehensive socio-economic analysis of the costs directly associated to implementing an alternative to PFAS as well as, alternatively, the cost associated with a non-use scenario where implementing an alternative is not possible or immediately practicable.

MPCA Question (3): *Should unique considerations be made for small businesses with regards to economic feasibility?*

No Response.

MPCA Question (4): *What criteria should be used to determine the safety of potential PFAS alternatives?*

Any component recognized as:

- Category 1A or 1B Carcinogen, Mutagen or Reproductive Toxicants
- Substances that are Persistent, Bioaccumulative and Toxic,

¹ Oosterhuis F, Brouwer R, Janssen M, Verhoeven J, Luttikhuisen C. Towards a proportionality assessment of risk reduction measures aimed at restricting the use of persistent and bioaccumulative substances. Integr Environ Assess Manag. 2017 Nov;13(6):1100-1112. doi: 10.1002/ieam.1949. Epub 2017 Jun 24. PMID: 28548694.

- Substances which are very Persistent and very Bioaccumulative,
- Substances which are Persistent, Mobile and Toxic
- Substances which are very Persistent and very Mobile
- Substances recognized as Endocrine Disruptors for human health or the environment

should be regarded as an undesirable alternative unless there are mechanisms to manage the risk of use of those substances than what is afforded with PFAS (e.g., adequate hazardous waste incineration capacity).

MPCA Question (5): *How long should PFAS currently unavoidable use determinations be good for? How should the length of the currently unavoidable use determination be decided. Should significant changes in available information about alternatives trigger a re-evaluation?*

To avoid costly and unpredictable interruptions to the market, a reasonable period must be afforded to each CUU determination. Furthermore, a reasonable transition time must be provided to allow for a petitioning for renewal or for market withdrawal following denial of an applied for CUU determination.

We recommend, particularly for professional/industrial use products which have longer design cycles than more traditional higher volume consumer products, that an initial CUU determination period of at least 12 years be granted with provisions to allow renewal applications within two years of the date of termination of the determination period. Where a renewal is not granted, there must be a further transition period of two years from renewal denial allowing for market withdrawal. A shorter CUU determination period of seven years would be appropriate after the first determination. This is particularly required given the broad scope of products potentially impacted by the market restriction and limitations in technical resources to redesign broad portfolios without compromising ongoing portfolio innovation.

The ability of industry to adopt to ‘significant changes’ in alternatives is highly dependent on factors the MCPA are unable to assess (such as a business’ ability to make critical capital investments to re-tool or to re-obtain regulatory approvals). Therefore, it is critical that the determination period be honored in full and consideration of the reasonableness of the alternatives be factored in any renewal petition.

MPCA Question (6): *How should stakeholders request to have a PFAS use be considered for currently unavoidable use determination by the MPCA? Conversely, could stakeholders request a PFAS use not be determined to be currently unavoidable? What information should be submitted in support of such requests?*

In addition to our proposal for expanding the exemption for industry sectors in SubDivision 8, we envision a process by which a party may submit an application for a CUU determination to MPCA for consideration. The application to MPCA would be constructed according to the provisions outlined in the eventual rule and submitted via a secure portal established by the

MPCA. A further provision regarding confidential business information regarding content of the application would be necessary. It would be advisable that this process be publicly transparent. Where a sectorial use exemption is not provided under subdivision 8, the CUU application should contain information on an analysis of alternatives, human and environmental exposure scenarios, as well as broader socio-economic data regarding implementation of any possible alternative and the corollary non-use implications.

MPCA Question (7): *In order to get a sense of what type of and how many products may seek a currently unavoidable uses determination, please share what uses and products you may submit a request for in the future and briefly why. There will be a future opportunity to present your full argument and supporting information for a possible currently unavoidable uses determination.*

Professional and industrial use products containing PFAS within the Life Sciences, Bioproduction, and professional/industrial monitoring, control and measurement equipment sectors as well as professional and industrial use stationary refrigeration equipment are low-volume/high-mix as compared to portfolios intended for consumer markets (e.g. domestic appliances) are high-volume/low-mix. As a result, the actual number of impacted products would be high – though containing a very small fraction of the PFAS currently emitted into the environment.

Non-inclusive list of impacted products:

- Electrical and electronic equipment used in laboratories and industrial facilities
- Environmental monitoring and test equipment
- Filtration devices used in manufacturing and bioproduction
- Laboratory apparatus (e.g., Fluorinated plastics)
- Laboratory consumables (e.g., pipette tips, fluorinated containers, semi-rigid tubing, etc.)
- Packaging of high purity chemicals, reagents and standards used in manufacture of drugs and devices as well as for sensitive laboratory applications.

MPCA Question (8): *Should MPCA make some initial currently unavoidable use determinations as part of this rulemaking using the proposed criteria?*

We believe MPCA should make an affirmative initial CUU determination for the sectorial uses described as points i-vi in response to Q1.

MPCA Question (9): *Other questions or comments relating to defining currently unavoidable use criteria and the process MPCA uses to make currently unavoidable use determination.*

- A) Please clarify definition of “Intentionally Added” as it relates to PFAS inclusion in component parts of a complex article where the end-product manufacturer did not specify inclusion of PFAS; however, an upstream supplier did intentionally may have intentionally added the PFAS unknown to the downstream user of the component?

Example Scenario: Party A (based in Minn) owns the functional specifications of a wire-harness assembly which is used as a component part of a complex article (e.g., a Mass-

Spectrometer). Party A purchases this component from Party B (based in the US) who is a distributor for a supplier (Party C). Party C (based in Asia) creates and owns the performance specifications for the insulating plastic used in co-extrusion of the wire (e.g., a specific frictional coefficient; however, they do not stipulate the performance must be enabled by PFAS Party D (based in the EU) provides the plastic resin which meets the frictional coefficient specification through formulating the PFAS into the resin. Would Party A have the obligation to file for CUU as 'intentionally adding' the PFAS into their complex article?

- B) How does MCPA envision communicating decisions on CUU Determination and renewals (if any)?
- C) What standard will MCPA make in determining if alternatives are or are not reasonably available and qualified for end applications?
- D) How does MCPA foresee enabling the circular economy by facilitating equipment repair with PFAS containing spare parts when the equipment has been placed on the market before any restriction set forth by this rulemaking?

Conclusion

Again, Thermo Fisher appreciates the chance to provide these comments in response to this proposed rulemaking. We welcome the opportunity to further engage with the MPCA to answer questions and serve as a resource.

Kind Regards,



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