The "Goods" on Fluoropolymers in Wire and Cable

James J. Henry, Dave Seiler, Richard Perrinaud

Arkema Inc.

King of Prussia, PA

+1-610-878-6023 · james.henry@arkemagroup.com

Abstract

For decades, fluoropolymer cable insulations have been considered the reference in the Wire & Cable industry for providing safety in fire situations. Fluoropolymers are inherently resistant to burning and are considered low smoke generators. As a class, fluoropolymers provide the best overall performance by reducing the severity and hazards associated with a fire. The resistance to burning prevents fires from spreading, and in contained environments, low smoke generation is paramount for human safety. Additional positive attributes of fluoropolymers include their processability, high temperature resistance, and the fact that they do not need leachable additives to perform all these functions. Unfortunately, many standards now in place limit the use of halogen-based polymers as a class. These standards group fluoropolymers in the category of "halogen" containing polymers under the presumption that all halogenated polymers are equivalent and may emit corrosive and/or toxic fumes under identical fire situations. These standards base their conclusions not on the safety performance of the materials, but simply on its chemical nature.

Over the past several years, polyolefin insulation products have been introduced as low cost, halogen free alternatives. Consequently, more and more standards have favored these new solutions over plastic materials containing halogens including fluoropolymers. These "non halogen" materials have not reached the performance of fluoropolymer materials in regards to flame retardancy and fire safety. Non halogen materials as a class introduce higher levels of smoke generation, and contribute a much higher fuel load compared to fluoropolymers. The overall performance of non halogen materials remains well below that obtained by fluoropolymer materials.

In industry, the over generalization by grouping all halogenated materials together has resulted in less use of these high performing materials where they could provide benefits. Fluoropolymers should be favored in critical building constructions, and in confined areas such as: submarine, transit and tunnel applications.

Keywords: Fluoropolymers, zero halogen, non halogen, PVC, polyvinyl chloride, PVDF, FEP, smoke, flame resistance, halogen, safety, fluorine, wire, cable,

1. Introduction

Over the past several years, Wire & Cable manufacturers have scrambled to develop a class of cables identified as Low Smoke Zero Halogen (LSOH) or simply "non-halogen" cables. As the name suggests, non-halogen cables are those produced using insulation materials that lack halogens such as chlorine, fluorine and bromine. The creation of "non-halogen" cables and compounds were originally intended as alternative cable and insulating materials to replace polyvinyl chloride (PVC) which is a chlorine containing compound (chloropolymer). PVC is used extensively in the Wire & Cable industry as a primary insulator and for cable jacketing. PVC by itself provides some flame resistance due to the presence of chlorine in its backbone. The addition of brominated plasticizers as well as a host of other fillers and additives further improves PVC's flame and smoke characteristics. Since fluoropolymers are also halogenated polymers, they have been grouped with PVC despite having vastly different performance characteristics.

Lobbyists against proliferation of PVC cables have defined corrosion and environmental concerns as two primary reasons for using non-halogenated technologies in wire and cable. It is understood that hydrogen chloride (HCl) vapors produced from burning PVC can cause corrosion type failures or loss of insulation resistance properties if allowed to condense on surrounding electronics [1]. The use of acidity and/or toxicity testing has been advocated as a means of eliminating PVC's use in Wire & Cable applications where acidity of effluent gases from a fire have been raised as issues. This broad and unscientific definition has succeeded in influencing specifications in the shipbuilding industry, automotive and truck manufacturing, aircraft, military equipment, nuclear power plants, chemical facilities, underground transit authorities, railways, and construction industries.

In the European Community (EC), the primary argument against PVC has been the evolution of acid gases "acidity" in the event of a fire can "compromise the ability of the persons exposed to them to take effective action to escape" and that "the incapacitation hazard from smoke, irritant and asphyxiant toxic gases is therefore a primary determinant of the survival or otherwise" [2]. The reasons for limiting the release of hazard gases sited by the EC, although proposed with good intentions, is based on an inaccurate premise that the presence of these acid gases interfere with a persons ability to escape a fire. There is much evidence to the contrary that indicates the presence of acid gases in a fire have little overall impact on a persons ability to egress a building. It has been argued that "All gases formed in a fire are deadly toxic irrespective of the products burning." and that "The acute toxicity of fire gases is controlled by carbon monoxide (CO), a highly toxic, non irritating gas, present in significant amounts in virtually all fires and responsible for over 90% of fire deaths [3].

Fluoropolymers are quite different in properties compared to chloropolymers such as PVC. Fluoropolymers provide flame resistance for the simple fact that the carbon-fluorine bond is strong and requires very high temperatures to break. This high thermal stability is one of the primary reasons why fluoropolymers as a class provide the best in flame and smoke performance. The generation of acid gases, a primary objective of introducing non-halogen cables, is greatly retarded by the inherent thermal stability of fluoropolymers. Since fluoropolymers are very resistant to thermal degradation, significantly higher temperatures are required before any fluorine species including acid gases are liberated [4]. It is this resistance to thermal degradation that separates them from other halogenated polymers such as PVC.

Experienced cable manufacturers have been frustrated by the requirement to replace some fluorinated cables with those using "non-halogenated" technologies. The cables produced using fluoropolymers most often have superior physical, mechanical and electrical properties as well as having the highest resistance to burning and the lowest smoke generation potential. These properties are inherent in most fluoropolymers and are obtained without the introduction of additives and plasticizers that may leach out over time and reduce wire performance. The replacement of some PVC applications with non-halogen cables makes sense in applications where some loss in flame and smoke properties are acceptable in comparison to a specific need to reduce the potential for corrosive gas emissions from a fire. It should be pointed out that non halogen cables, or better described as "non-chloropolymer" cables, have lower physical properties, lower flame resistance, and higher smoke generation than fluoropolymer cables [5].

2. Not all Halogens are the same

The flame retardance of bromine and chlorine can be considered different from fluorine due to the differences in the primary mechanisms responsible for providing flame resistance. Chlorinated polymers such as PVC, as well as polymers containing chlorinated and brominated additives, provide flame resistance primarily from the interaction of free chlorine and bromine radicals on the reaction intermediates produced during a fire [6]. The presence of these halogen free radicals interferes with the free radical mechanism for flame propagation to provide flame resistance. For halogens to reduce fire propagation in this manner, the release of free radicals needs to occur at a sufficiently low temperature characteristic of the early stages of burning. Bromine is considered more effective than chlorine during the early stages of flame propagation because it will dissociate into free radicals at lower temperatures. The end result is a retardation of the flame propagation process.

The mechanism of flame retardance of fluorine in contrast is not specifically related to free radical interactions, rather, it is primarily due to its ability to form strong, thermally stable bonds to carbon. In the event of a fire, significantly higher amounts of energy and higher temperatures are required to dissociate fluorine from carbon, thus improving the overall stability of the polymer. The high thermal stability of fluoropolymers is one of the primary reasons for its excellent burn resistance including low flame propagation, low smoke generation and lack of ignition.

One way to examine the relationship between fire resistance and halogen type is by reviewing their individual bonding energies to carbon. The bond energies amongst halogens differ significantly with those having higher bond energies having better fire resistance. The bond energies of bromine and chlorine to carbon are both relatively low, resulting in dissociation at lower temperatures. The energy of the carbon-fluorine bond in comparison is quite high and its dissociation does not occur until significantly higher temperatures are reached. Information on the bond energies associated between carbon and halogens can be found in Table 1.

Table 1. Bond energies of carbon to halogens [7].

Chemical Bond	Bond Energy (KCal/mole)
Carbon – Fluoride (C-F)	106
Carbon-Chlorine (C-Cl)	81.5
Carbon-Bromine (C-Br)	69

The higher thermal stability of fluoropolymers is evident when examined by thermogravametric analysis (TGA). For the purposes of this paper, TGA testing was conducted on a common low smoke PVC compound (LS-PVC) used for cable jacket applications and compared to a polyvinylidene fluoride (PVDF) fluoropolymer. The TGA results show that the PVC compound exhibited a 5% weight loss at a temperature of 264 °C (507 °F). The initial weight loss is associated with dehydrochlorination of the PVC. The TGA curve produced for LS PVC can be found in Figure 1.

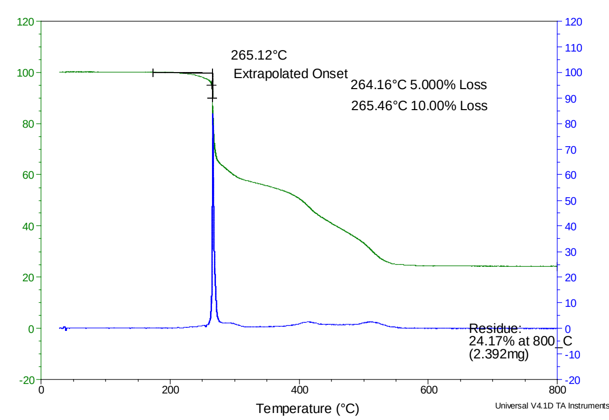


Figure 1. TGA analysis of a common LS PVC

In contrast, the 5% weight loss for a PVDF fluoropolymer was found to be about 410 °C (770 °F), which is 145 °C higher than what was found with the LS PVC product. It is this resistance to decomposition that allows fluoropolymers to resist degradation in the presence of a fire and provide excellent fire resistance properties. The TGA response for a PVDF fluoropolymer can be found in Figure 2.

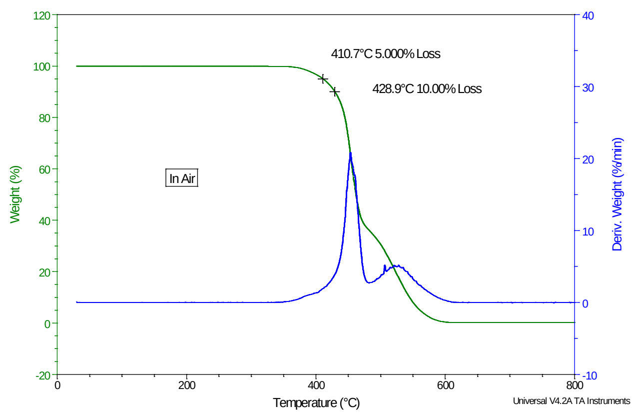


Figure 2. TGA analysis of a common PVDF

Another method of classifying the burning characteristics of polymers is by its limiting oxygen index (LOI), which is the oxygen content required to support combustion. Fluoropolymers have a wide range of LOI, from as low as 28% for ETFE up to 95% for PTFE. Certain versions of PVDF with less than 2% loading of an inorganic filler have an LOI of nearly 100%. Common chloropolymers range in LOI of 28% for PVC to as high as 44% for CPVC resins with 30% loadings of flame retardant additives. For other non halogen polymers such as polyolefin (used to produce LSOH compounds), the LOI is below 21 and can support combustion in air (air contains approximately 21% oxygen). LOI values of select polymer families can be found in Table 2.

Table 2. LOI of Polymer Families

POLYMER FAMILY	TYPICAL RANGE OF LOI	COMMENTS
Fluoropolymers	28-95	Do not maintain fire
Chloropolymers	28-44	Do not maintain fire
Polyolefins	<21	Propagates fire

As a final note, within the fluoropolymer family, there exist differences in fire behavior. Fluoropolymers such as PVDF are natural char formers [8], which provides further enhancements in flame and smoke performance. Some char formers can create a stable outer char layer in the presence of a fire that protects the underlying materials and further slows down the burning process. This characteristic is extremely important when trying to understand why such materials have superior resistance to burning, flame propagation and low smoke generation.

3. Different Halogens equals different performance

The use of the term “non halogen” is an over generalization that encompasses a wide variety of plastics having a varied range of performance characteristics. Fluoropolymers have always been classified as a separate category of materials due to their unique properties and should not be grouped with PVC, CPVC or other chlorine containing compounds Fluoropolymers in general are the most thermally stable, flame resistant, smoke resistant plastics that offer very unique properties. The use of the non-halogenated designation suggests that fluoropolymers are similar to PVC compounds, which misrepresents how each of these individual classes of materials can and should be used.

There are many reasons why fluoropolymer and chloropolymer plastics should be considered separately. Table 3 shows the smoke developed indexes and flame developed indexes for flame retarded (FR) PVC, PVDF and FEP when tested per NFPA-255 [4]. The fluoropolymers PVDF and FEP generate a very limited quantity of smoke, about an order of magnitude less than FR PVC. These results also demonstrate that FEP and PVDF fluoropolymers do not propagate the flame in the stringent NFPA-255 testing procedure while PVC does.

Table 3 NFPA-255 Data of select cables

Material	Smoke Developed Index	Flame Developed Index
Limits NFPA-255	***50 maximum***	***25 maximum***
Flame-Retarded PVC	130	50
Kynar® PVDF	14	0
FEP	17	0

As of today the best low smoke properties required by the Limited Combustible requirement in NFPA-255 can be reached only when fluoropolymers are used in the cable insulation. As previously noted, fluoropolymers can provide all these exceptional properties without the use of any migratory additives or plasticizers, which can leach out from the base polymer. Issues with long term performance due to plasticizer migration are therefore not of concern with fluoropolymers. Fluoropolymers are the plastics used to produce cables that meet the most stringent safety requirements defined by the Underwriters Laboratory (UL).

Another flame and smoke test used for construction materials is known as ASTM E84. In this severe test, some grades of PVDF have been able to achieve a 0/0 (smoke developed index/flame spread index) rating for flame and smoke; a 25/50 rating is considered excellent. Other than fluoropolymers, no class of thermoplastic polymer has ever passed a 25/50 rating in standard 25 foot long sheet (2-foot wide) ASTM E84 testing. So, by generalizing that all “halogenated” polymers are equal, fluoropolymers are being excluded from applications where they normally would be considered the top performing products. Cable manufacturers, like other industries, are therefore forced to use polymer compounds that are highly filled with additives, process poorly, and can be a very expensive option in the final construction.

The "non-halogen" or "non chloropolymer" alternatives being considered to replace PVC are commonly based on polyolefin chemistry. As can be expected, the heat of combustion of olefins is very high and the product will burn in a fire, contributing immensely to heat output and flame propagation. To offset a portion of this inherent problem, the olefin is highly loaded with fillers to reduce its overall caloric content. The fillers typically provide some endothermic response to cool the fire when burning. These products as a class do not meet the requirements for NFPA-262 Steiner Tunnel test for flame spread and smoke generation and do not offer substantial protection against fire propagation. Non halogen alternatives in general do not provide the flame resistance, low smoke generation, and chemical resistance properties that are common to all fluoropolymers used in wire and cable applications.

Heat of Combustion is a direct measure of how much heat can be released from a burning cable to help propagate the fire. Lower heats of combustion are considered inherently safer. The results in Table 4 clearly show non halogen solutions (Cables D and F) can generate more heat and smoke than PVC. The alternative solution of combining PVC and fluoropolymers was able to significantly lower the heat generated and smoke released in a fire situation. In an all fluoropolymer cable, the heat of combustion will range between 4500 and 6500 KJ/Kg, which is significantly lower than what can be achieved by any other class of polymers, and in some of these cases, zero smoke release can be obtained. Differences in heats of combustion for various cable constructions can be found in Table 4.

Table 4. Heat of Combustion Data for various cable constructions [5]

	Cable Jacketing	Cable Insulation	Heat of Combustion Jacket (KJ/kg)	Heat of Combustion Insulation (KJ/kg)	Total Smoke release rate (M2/sec)
A	FR PVC	FEP	14,977	4,856	0.17
B	FR PVC	LSPVC	14,977	15,112	0.4
C	$EVA/AL_2O_3{,}3H_2O$	$EVA/AL_2O_3{,}3H_2O$	15,284	18,814	0.5
D	$EVA/(Mg(OH)_2$	HDPE	16,033	46,493	0.24
E	$PVC/AL_2O_3{,}3H_2O$	HDPE	19,628	46,493	1.86
F	$EVA/AL_2O_3{,}3H_2O$	HDPE	16,242	46,493	0.6

4. The Hazards of Generalization

It is unfortunate that fluoropolymers have been categorized with PVC and other chloropolymers simply because they contain an element from the halogen family. The presence of a halogen is the only commonality between these two vastly different families of polymers. As previously mentioned, the thermal stability of fluoropolymers is quite distinct for this class of polymers and it is a property not shared by chloropolymers. What needs to be made clear is that elements found in a given family on the periodic chart, although having some similarities, can often be quite different, and can not be grouped together when considering final material properties.

The chemical periodic table of elements is divided into columns of elements having a similar electron outer shell. This is useful in some scientific analysis to understand potential commonalities of properties amongst elements. We cannot assume however that the final properties of materials produced with elements from a given family will be the same, or even similar. As an example, Carbon, Nitrogen, Oxygen, and Fluorine all lead the list in the periodic chart for each of there given families. In the same family as Carbon you will find Silicone and Lead. In the same family as Nitrogen you will find Phosphorus and Arsenic. Oxygen leads the family that also contains Sulfur, Selenium and Tellurium. From this simple observation, it is easy to see the problem with classifying polymers by a family of elements. It would not be logical to consider carbon and lead to be similar in properties simply because they can be found in the same family of elements. For this same reason, it is not logical to suggest that Chlorine and Fluorine will have the same characteristics if introduced into a polymer. Several other analogies can be made for Zinc and Mercury, with both elements being in the same family of the periodic table, but having very different environmental properties. There are unlimited examples of why such generalizations can not be made.

5. One Final Question: Why Acid and Corrosion Testing?

European standards have adopted an acidity test in order to limit the use of chloropolymers, especially PVC, which is suspected of releasing corrosive components of concern in a fire situation [2],[9]. Extensive scientific studies were carried out and presented to convince standards development organizations and end users to discard acidity testing [2],[10],[11],[12]. Government leaders and other key business segment leaders who spoke out about halogen issues and infamous "acid testing" requirements ended up voting in favor of the standards so as to not slow down the overall process [2],[12]. The concept is to ignore what could be perceived as smaller inconsistencies for the good of the overall to get a standard completed and published. Unfortunately, for the niches that are ignored in such a process, it can be a devastating business limitation. The final result is that safety, quality and performance of special wiring applications is compromised and options to wire manufacturers become limited.

Testing carried out buy the Underwriters Laboratories and Lucent Technologies in the 1990's showed that "the root cause of digital equipment failure in a fire situation is not due to metal loss or contact resistance degradation but to leakage current degradation from soot released when plastics were burning"[9]. It has been observed that cables with the highest performance rating based on large scale testing also exhibit the lowest leakage current at higher relative humidity [11]. It was shown that lower fire performance cables produced with flame retarded PVC and non halogen compounds exhibited high leakage currents. Non halogen cables that meet the IEC 745-2 criteria for pH and solution conductivity consistently failed for high leakage current, even at low relative humidity. Conversely, fluoropolymers exhibited low leakage currents even at higher humidity conditions. It was concluded that only fluoropolymers provided the effective combination of low total heat release, low peak heat release, low peak smoke release, low total smoke release low leakage current as well as low corrosion per ISO DIS 11907-3 and ASTM D5485 [11].

The acid testing proposed in IEC 754-2 has assigned an arbitrary value that cables upon burning not have an acidic value of Ph less than 4.3. There is no known confirmation as to where this designation comes from, and such a test criteria ignores the terrible effects of a cable giving off magnitudes more smoke in the form of hydrogen cyanide, carbon monoxide, and carbon dioxide. It should be noted that a pH of 4.3 is a lower acidity level than common foods that we consume regularly as part of our diet. While we would not want to dump those foods on an electronic apparatus, the point is made for non-chemists that a pH of 4.3 in itself is not some horrible environmental condition that should be avoided at any turn. A list of the Ph values of various food items can be found in Table 5 [13].

Table 5. pH range of various food items

Food item	pH range	Food item	pH range
Apples	3.34	Jellies, Fruit	3.00 – 3.50
Applesauce	3.10-3.34	Lemon Juice	2.00 – 2.60
Blueberries	3.12 – 3.33	Lime	2.00 – 2.80
Cherries	3.25 – 3.82	Mint Jelly	3.01
Chili Sauce	2.77 – 3.70	Pickles	3.20 – 3.70
Cranberries	2.30 – 2.52	Raspberry Jam	2.87 – 3.17
Gelatin	2.60	Sherry – Wine	3.37
Grapes	2.80 – 3.00	Vinegar	2.40 – 3.40

6. Conclusions

As with any engineering component design, a manufacturer has a responsibility to the customer(s) to provide a safe and reliable product at the best possible cost. Standards are developed to focus on the required performance aspects of the product and to ensure reliability and safety in its intended use. If the philosophy of the standard is restrictive or even incorrect, the manufacturer can be forced to offer either a needlessly more expensive product, or a product that may not be the most appropriate for the intended application. It is the responsibility of the standards making body to ensure that these standards allow for the best practices to be available to the manufacturer and consumer for product quality, reliability, service and price.

Classifying polymers in broad categories such as "halogenated polymers" has the effect of combining materials having varied performance characteristics. "Halogenated polymers" encompass a wide array of materials including chloropolymers, fluoropolymers and other polymers containing chlorine, fluorine and bromine as additives. The type of halogen used, as well as how it is introduced into the polymer, have a significant effect on the material behavior in a fire situation. Chlorine and bromine provide flame resistance due to their ability to dissociate early in the development of a fire. Conversely, Fluoropolymers are very thermally stable and its fire resistance is due to the extreme stability of the fluorine-carbon bonds.

The differences in fire performance between fluoropolymers, chloropolymers as well as LSOH compounds is quite dramatic, and highlight the reasons why fluoropolymers need to continue to be viewed as a separate class of polymers. Combined with other performance characteristics such as insulation resistance, chemical resistance, cut through resistance, abrasion resistance, etc., it is obvious that that fluoropolymers must be considered for use when performance and safety are the primary goals. It is unfortunate that industry standards that preclude the use of PVC by using the non halogen terminology have unintentionally excluded the use of fluoropolymers from some critical Wire & cable applications. Indeed Fluoropolymers are well-known for their excellence at ensuring the safety of people in fire situation and should continue to be used when safety is paramount.

7. References

[1] Rogers, Charles E., Bennett, James G. Jr., Kessel, Stephen L. "Corrosivity Test Methods for Polymeric Materials, Part 2"

[2] Notification G/TBT/N/EEC/92: electric cables, Reply of the EC, June 2006

[3] Troitzsch, Jurgen, "Acidity as a Proposed Additional Classification Criterion in the Classes of Reaction to Fire Performance for Cables under the CPD", July 2005

[4] Henry, James J., Partridge, Ron "Low Smoke & Limited Combustible Cable Made with PVDF", Wire and Cable Technology International, March 2005.

[5] Chapin, J.T., Caudill, L.M., Hoover, J.R. "Comparison of Fire Behavior of Copper & Fiber Optic Cables in Large, and Real Scale Fire Test Facilities", IWCS 1997

[6] Gachter, R., Muller, H., Plastics Additives Handbook, Hanser, 1990

[7] Weast, Robert C., "CRD Handbook of Chemistry and Physics, 65th edition, 1984 - 1985

[8] Henry, James J., Partridge, Ron "Development of PVDF for Use in Limited Combustible Fiber Optic Cables", WAI Interwire 2005

[9] CFRA, "Emerging EC legislation on Fire Safety of Wires and Cables Represents a Major Threat to European Public Safety and the First Responders Who Are Relied Upon in Fire Emergencies", December 2005

[10] Chapin, J. Thomas, Caudill, L.M., Gandhi, P., Backstrom, R. "Leakage Current Smoke Corrosivity Testing – Comparison of Cable and Material Data", International Wire & Cable Symposium, 1996.

[11] Chapin, J. Thomas, Gandhi, P. "Comparison of LAN Cable Smoke Corrosivity by US and IEC Test Methods", Fire Risk & Hazard Research Assessment Research Application Symposium, 1997.

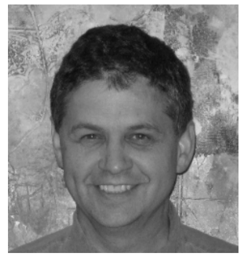
[12] SPI, Comments on EC Notification, G/TBT/N/EEC/92 (13 Oct. 2005)

[13] "Approximate pH of Food and food products", October 2003, http://www.cfsan.fds.gov/~comm/ladf-phs.html

Pictures of Authors

James Henry is a Senior Research Engineer at Arkema Inc. located at the Research Center in King of Prussia, PA. James received a Bachelors Degree in Chemical Engineering in 1986 from the University of Lowell, and his Masters Degree in Plastics Engineering in 2003 from the University of Massachusetts. Jim joined Arkema Inc. (formerly Atofina Chemicals) in January 2001 where he focuses his attentions on activities in the W&C and Chemical Processing markets.

David A. Seiler has been the Business Manager for Fluoropolymers at Arkema, Inc. since 2001. Mr. Seiler earned a B.S. degree in Chemical Engineering at the Pennsylvania State University in 1983. He is a member of NFPA, ASME-BPE, ASTM, ISPE, AICHE and ICC-ES.



Richard Perrinaud is currently a market manager for Kynar® PVDF group, mainly involved with fuel applications. Current projects included the applications related to the Automotive and Gas Stations. Prior to that assignment, he was in charge of the development of Arkema's Functional Polyolefins in North America. Present involvements included: UL971 standard committee (Flexible plastic Underground piping for gas station), Society of Plastics Industry – Fluoropolymers Section Executive Committee. Educational Background includes a Ph.D. in Polymer Science at the University of Pau, France and a post-doctorate fellowship in the Material Science department of the University of Pennsylvania in Philadelphia, PA.