

Environmental Aspects of PTFE Based Laminates in Relation to “Halogen-Free”

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Abstract

This paper describes the regulations introduced in Europe that are driving electrical and electronic original equipment manufacturers to move towards non-bromine containing base materials and prepregs (pre-impregnated) to produce printed circuit boards, although the regulations do not actually ban the FR-4 materials, only bromine content. A review of the regulation is presented to illustrate that they do not constitute a ban of all materials that can be chemically classified as containing a “halogen” in its broadest sense, but a move towards “bromine-free”. Polytetrafluoroethylene (PTFE) based materials are not included in any current or future regulatory guidelines or bans. Data presented prove that the outstanding characteristics of PTFE including thermal stability, flame resistance, electrical properties and durability of electrical properties render this plastic as the top choice for the fabrication of printed circuit boards.

What is a halogen?

The term *halogen* is used to describe the elements of the column 17 (Group 7) of the Periodic Table of Elements. Technically speaking, the term halogen provides little descriptive value in scientific and technological discussions. *Precious metal* is a common term to refer to column 11 (Group 1b) of the Periodic Table of Elements (Figure 1). Atop this column sits copper (Cu), followed below by silver (Ag) and gold (Au). It is clear that the diversity in the value and chemical properties of these three elements is not captured by the phrase “precious metal”. Similarly, fluorine (F) sits atop column 17 of the Periodic Table of Elements, followed below by chlorine (Cl), bromine (Br), Iodine (I) and Astatine (At). The last element is unknown to an overwhelming majority of the public as well as the technical community.

A major common characteristic of halogens (Group 7) is that they all have seven electrons in the outer shell of their atomic structure. They all have a valence of -1 in their reactions with hydrogen and metals. The reactivity of halogens decreases from top (fluorine) to bottom of the column. *McGraw-Hill Encyclopaedia of Chemistry*¹ has described the differences among

halogens. “Although halogens generally undergo the same types of reactions, the extent and ease with which these reactions occur vary markedly. Fluorine in particular has the usual tendency of the lightest member of a family of elements to exhibit reactions not comparable to the other members.” Elsewhere the *Encyclopaedia* emphasises the difference between fluorine and other halogens. Fluorine is the most electronegative of elements and forms an extremely strong bond with carbon. The carbon-fluorine bond (C-F) is the fundamental reason that polytetrafluoroethylene (PTFE) is one of the most stable and inert plastics known to man. Finally, a key point is made in the *McGraw-Hill Encyclopaedia of Chemistry* about the stability of halogenated compounds. “Organic halogen compounds generally show progressively increased stability in the order iodine, bromine, chlorine and fluorine.”

				9	10	11	12	13	14	15	16	17	18
								B	C	N	O	F	He
								Al	Si	P	S	Cl	Ar
	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr			
	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe			
	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn			
	Mt	Uun	Uuu	Uub									

Figure 1. A Portion of the Periodic Table of Elements

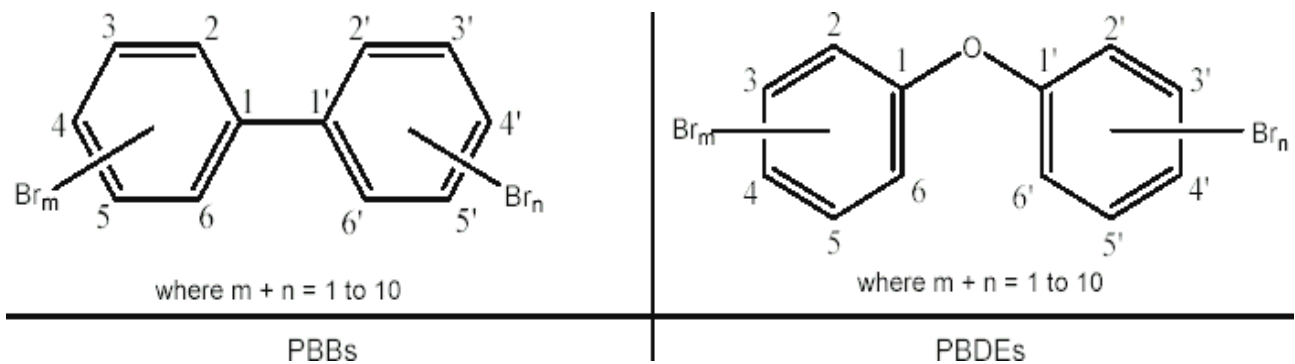
Fluorine, chlorine and bromine are vastly different from one another as will be illustrated by the data presented. Another interesting example of the fallacy of lumping together elements of a column of the Periodic Table is evident in column 12 (Group 2b). The top element *zinc* (Figure 1) is safe and is a popular material for the fabrication of cookware. Zinc oxide is an ingredient in cosmetics. Yet the two elements below zinc are cadmium (Cd) and mercury (Hg), known to be poisonous in minute quantities and both scheduled to be banned as of July 1, 2006 in the European Union.

History of Brominated and Chlorinated Flame Retardants²

Historically, the concern of the effect of halogens on the environment, and its association with the printed circuit board industry can be traced back to the use of low molecular weight chlorinated and brominated compounds in electronic and electric industries as they emerged and grew from their initial conception. One of the first classes of compounds to be highlighted as a potential for poor environmental impact was PCB's. PCB's are a class of chemicals known as polychlorinated biphenyls and were first manufactured by Monsanto in the U.S. in 1929. The primary use of these low molecular weight compounds was as a dielectric fluid in electrical equipment. However the materials were eventually found to be a possible human carcinogen and

a known animal one. Further studies revealed the materials to be bioaccumulative in the food chain, as a result PCB compounds were banned in the late 70's early 80's.

While it can be seen that the history of the use of PCB's was one of the first clear signs of the effect of halogens on the environment (in this case chlorine), it was by no means the only compound to cause issues. The use of low molecular weight brominated flame retardant materials was also generating concern.^{3,4} These compounds, PBB - polybrominated biphenyls and PBDE – polybrominated diphenylethers were used as flame-retardants in plastic components. A common application was the use of these compounds in moulded television casings. While the compounds did impart the desired flame-retardant properties, they were also capable of becoming volatile; that is, they could be measured in the gas phase. The result of this was that the compounds were capable of leaching out of the original component and entering the general environment. Studies on the toxicity of these compounds found them to be fat-soluble and bioaccumulative. The compounds are now considered toxic and are banned (or will be banned) in most industrial countries.



These low molecular weight bromine-containing compounds were not the only brominated flame-retardants that were used in the general industry. In fact the use of the properties of bromine as a flame retardant has been widespread and not restricted to the electronics industry. Bromine is unique in its efficacy as a gas phase flame retardant, (it combines with free radicals), and its compatibility with engineering thermoplastics formulations. Consequently, there are many different types of brominated flame-retardants and certainly not all are set to be banned by any future directive, or even indicated as to having any potential of negative environmental impact.

History of Oligomeric Brominated Flame Retardants

There has, however, been concern about some higher molecular weight brominated compounds. These materials having a molecular weight between monomers and polymers, typically brominated polystyrene/polycarbonate, oligomers are commonly used in conjunction with antimony trioxide, which combine to give a synergistic effect and impart flame retardant effect in the polymer compounds.⁵ These brominated materials differ from the low molecular weight PBB's and PBDE's in that they are not volatile and remain within the formulated component. The problem arises from the risk of brominated dioxin formation during uncontrolled burning, either during a fire situation or incineration. These dioxin compounds are extremely

hazardous to the environment and have, thus, further heightened the concern about the use of bromine. It must be said that these types of flame retardant materials have not been used extensively in the Printed Circuit Board industry but they add to the growing fear of the use of halogens.⁶

A reasonable question is whether poly fluorobiphenyls (PFB) are produced due to the thermal degradation of PTFE. The answer is that none of the research has been able to detect the presence of PFB's in incineration residues of commercial incinerators⁷. Furthermore, fundamental investigation of the degradation of PTFE in the presence and absence of oxygen has identified the products of degradation, none of which approach or resemble the structure of PFB⁸. The major product of degradation of PTFE is carbonyl fluoride (COF_2), which hydrolyses to HF and carbon dioxide in the air by reacting with moisture. The other degradation products include perfluoroisobutylene, tetrafluoroethylene, hexafluoropropylene, HCF_3 and carbon monoxide. In the absence of oxygen, i.e., under an inert atmosphere or vacuum, polytetrafluoroethylene degrades into nearly pure monomer⁹⁻¹¹. Furthermore, generating PFB's requires careful chemical reactions under special conditions such as synthesis by diazotization-fluorination, Gomberg-Bachman arylation or Ullmann coupling reactions¹².

Brominated Comonomers

An effective way of introducing flame retardant into a polymer is to react in a bromine-containing compound into the polymeric material. This way, there is no possibility of leaching out of the compound into the general environment. The majority of printed circuit boards (PCB) produced in the world today are manufactured using base laminate materials and prepregs, which have been produced with E-glass fabrics and an epoxy based thermosetting resin. The resultant PCB's need to be flame retarded, and must conform to the UL-94 V0 requirements. As a result, the epoxy resins used are "brominated" to give the desired flame resistance. The bromine is added in the form of tetrabromobisphenol A (TBBPA), a co-monomer, which is chemically reacted with the epoxy resin to become covalently bonded in the resin matrix. This point is important because once reacted into the matrix the TBBPA is not available to leach or diffuse out of the circuit board.¹³

Once bonded covalently in the epoxy resin of the circuit board, TBBPA ceases to exist as a chemical entity and becomes part of a three-dimensional cross-linked matrix. The addition of bromine through the addition of TBBPA reduces the possibility of ignition of the material, and if ignition occurs then limits the rate of flame growth and so it is seen as a cost-effective way of preventing/impeding fire in printed circuit boards. The addition of TBBPA allows the base materials and prepregs to conform to the UL-94 V0 status required by the industry. TBBPA is the largest volume flame retardant in use today, and it is this chemical compound and its addition to the FR-4 resins, which generates the greatest interest in "bromine/halogen free" alternatives within the printed circuit industry.

Regulatory Status of FR-4 Containing Bromine

The reason for this interest is the regulatory pressure to ban the use of certain brominated substances which are clearly hazardous to people and/or the environment. In Europe an advisory group WEEE, "Waste Electrical and Electronic Equipment", has proposed a directive, which has

recently been approved by the European Union, and is concerned with the recycling and recovery of Electrical and Electronic waste. This is translated into the RoHS (Restriction of Hazardous Substances) directive in each individual country and is complimentary to the WEEE. The impact of this is that starting July 1st 2006, the following substances will be banned – lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls PBB's and polybrominated diphenylethers, PBDE's.^{14, 15,16}

Halogen Free Base Materials-Returned Waste to OEM

The term “halogen-free” for the alternative flame-retardant materials is really derived from the need to become bromine (and chlorine) free, as can be seen by the historical developments and the current legislation. It is clear that the intended reference to “halogen-free” in the PCB industry does not include iodine and fluorine.

An important feature here is that there are no other brominated materials in the process of being banned in the EU legislation. This includes TBBPA, which is incorporated in FR-4 epoxy resins so widely used in the Printed Circuit industry. However, as with the brominated oligomers mentioned earlier, there have been some suggestions that under certain incineration conditions a FR-4 resin could yield small amounts of brominated dioxins. To combat this there has been numerous studies to show that brominated dioxins are not formed during the incineration of FR-4 epoxy resins. While the “no brominated dioxins formed” reports appear to outweigh the “formation of brominated dioxins”, there is still a degree of controversy over the continued use of TBBPA and its effect on the environment. At this point though TBBPA is not a banned substance and there are no legislative actions looming in the future.

If this is the case it may appear strange that the “halogen free” lobby keeps gaining momentum. The answer can be found in the WEEE directive. There is a further requirement in these regulations, which require the E&E OEM's to take back and dispose of the equipment sold at the end of its life. The WEEE has approved separation and recovery standards for electrical and electronic equipment, which require the separation of E&E equipment from unsorted waste. It also stipulates further separation of components containing brominated flame-retardants from the other E&E waste prior to disposal or recycling. These regulations will commence from July 1st 2006, and appear to be the main reason for an E&E OEM to make a decision to move away from any type of brominated flame retardants within the base materials and prepreps.

The situation is not clear and the cost balance between changing to alternative flame retardant materials and complying with the sorting regulations stipulated by the WEEE is not so easy to decipher. For the moment the non-bromine alternative materials have gained some market share, but a large amount of FR-4 type materials are still used. In the US there is no government target to introduce bans or tighter controls on brominated materials, and an IPC white paper has concluded that the bromine in FR-4 is not an environmental issue.¹⁷ However, most OEM's are now global and wish to operate freely in the world markets and so the European lead is being followed

The main focus on the use of bromine in base materials is clearly aimed at the large volume of FR-4 type materials, but they are not the only materials containing bromine which are being scrutinised. There are grades of higher performance base materials, which also contain bromine, and as such are being drawn into the “halogen-free” debate. Among these are the BT (bismalaimide-triazine) resin systems, which are usually blended with a certain proportion of

epoxy material (BT-epoxy) to aid processing. These epoxy resins normally contain a certain percentage of TBBPA based bromine content, and so these base materials are being highlighted. The BT pure resin could be used to produce a UL-94 V0 type resin system and where this is the case then halogen (bromine) issue is not applicable.

A similar picture emerges with the cyanate ester resin systems. While they are “halogen-free” when used in their pure form, it is known that some laminators blend with epoxy (FR-4) resins to impart some desired finished laminate properties. A relatively new type of base-resin system, cross-linked aliphatic rubber materials filled with organic fillers, has also gained influence in the higher performance base material sector. Here too, the use of a brominated additive is needed to achieve the UL-94 V0 flame retardant requirement, although it is not TBBPA based. As with the FR-4 type resins these other bromine-containing materials are not banned by any legislation, but they are burdened with the same momentum for the reduction in bromine in E&E equipment. By comparison PTFE base materials do not contain bromine and should not be included in the “halogen-free” debate.

Comparison of F, Cl and Br Properties

Fluorine is the most electronegative of elements and forms an extremely strong bond with carbon. The carbon-fluorine bond (C-F) is the fundamental reason that polytetrafluoroethylene (PTFE) is one of the most stable plastics known to man. Carbon-chlorine and carbon-bromine have significantly lower bond strength than the carbon-fluorine bond, as seen in Table 1. This simply means that it is much easier to break a C-Br bond because it takes about half the energy required for breaking a C-F bond. This is the reason behind the formation of small toxic compounds from brominated FR or epoxy compounds.

Table 1. Chemical Bond Strength of Carbon bond with Various Halogens at 25°C¹⁸

Chemical Bond	Bond Strength, kcal/mole	Bond Strength, %
C-F	132	100
C-Cl	95	72
C-Br	67	51
C-I	50	38

Polytetrafluoroethylene (PTFE)-based Boards

Base materials manufactured with PTFE (polytetrafluoroethylene) thermoplastic polymers have been available for many years and are used where the excellent electrical properties of the PTFE are required. PTFE has the lowest dielectric constant (2.1) and loss characteristics of any polymer. These electrical properties remain very stable over frequency and temperature and so PTFE based laminates are the main choice for high frequency applications. The PTFE polymer is made of carbon and fluorine atoms of very high molecular weight only, and no additional low molecular weight, or common flame-retardants are added. **The PTFE material is naturally flame retardant and passes the UL-94 V0 requirements** and without the need to add bromine. Thermal stability of PTFE is excellent; it can remain at much higher temperatures than other base materials with no adverse effects.

In recent times PTFE based laminates have been implicated in the “halogen-free” debate even though there has been no historical or legislative reason. The fact that fluorine is a member of the halogen group in the Periodic Table of elements appears to be the only cause of the association.

Discussion of PTFE Properties

The simplest way to describe the properties of PTFE would be to compare and contrast it with similar chlorinated and brominated polymers. There are, however, no comparable chlorine or bromine equivalent polymers to PTFE because of the weakness of the chemical bonds that Cl and

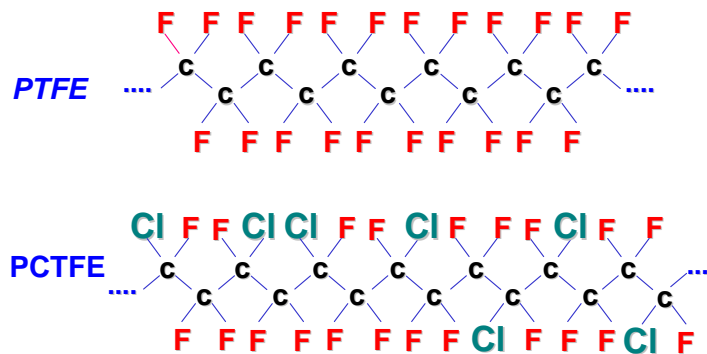


Figure 2. Chemical Structures of PTFE and some Chlorinated Polymers – *Polytetrafluoroethylene (PTFE)* and *Polychlorotrifluoroethylene (PCTFE)*

Br form with carbon. No commercial brominated polymer is known¹⁹. The absence of analogous chlorinated and brominated polymers to PTFE compels the use of a secondary option (less preferable) which is comparison of PTFE properties with that of chlorinated polymers. See Figure 2 for chemical structures of PTFE and a chlorinated polymer.

PTFE as a material is extremely inert and has a low coefficient of friction and excellent chemical, thermal and flame resistance characteristics. It is used in extremely diverse applications, some of which includes contact with food and humans. It has been extensively used in the houseware and commercial cooking and baking applications such as pan coatings, food-cooking belts, baking sheets. It is also used in the medical applications where the inert nature and low friction properties are utilized. PTFE polymer is classified as one of the safest material available to mankind. Table 2 presents the basic properties of PTFE. Table 3 shows how combinations of PTFE properties have spurred use of PTFE and other fluoropolymers in nearly all the major industries.

Table 2. Basic Properties of PTFE²⁰

- High melting point, 342°C (648°F)
- High thermal stability
- Useful mechanical properties at extremely low and high temperatures
- Insolubility
- Chemical inertness
- Low coefficient of friction
- Low dielectric constant/dissipation factor
- Low water ab/adsorptivity
- Excellent weatherability
- Flame resistance
- Purity

Thermal Stability and Flame Resistance of PTFE

A review of the applications of PTFE reveals that this polymer is used in applications where extreme heat and chemical conditions are encountered. PTFE can be continuously exposed to temperatures in the range of -260°C to 260°C. There are almost no commercial organic or inorganic chemicals that attack PTFE causing its degradation. For example, PTFE-based coatings on cookware are daily exposed to the extreme heat and temperatures applied during cooking. The safety and performance of these coatings has been proven for more than three decades.

Table 3. Major Applications and Select Uses of PTFE and Fluoropolymer²¹

INDUSTRY/ APPLICATION AREA	KEY PROPERTIES	TYPICAL USES
Chemical Processing	Chemical Resistance Good Mechanical Properties Thermal Stability Cryogenic Properties	Gaskets, Vessel Liners, Valve and Pipe Liners, Tubing, Coatings
Electrical & Communications	Low Dielectric Constant High Volume/Surface Resistivity High Dielectric Break-down Voltage Flame Resistance, Thermal stability	Wire and Cable Insulation, Connectors
Automotive & Office Equipment	Low Coefficient of Friction Good Mechanical Properties Cryogenic Properties, Chemical Resistance	Seals and Rings in Automotive Power Steering, Transmission, and Air-conditioning. Copier Roller and Food Processing Equipment Covering.
Houseware	Thermal Stability Low Surface Energy Chemical	Cookware Coatings.
Medical	Low Surface Energy Stability Excellent Mechanical Properties Chemical Resistance	Cardiovascular Grafts, Heart Patches, Ligament Replacement
Architectural Fabric	Excellent Weatherability Flame Resistance Low Surface Energy	Coated Fiberglass Fabric for Stadiums and Airport Roofs

The role and importance of fluorine in PTFE is best illustrated by comparing it with polychlorotrifluoroethylene (PCTFE), in which one of the four fluorine atoms in each monomer unit has been replaced by chlorine. Melting point drastically decreases from 342°C for PTFE to 220°C for PCTFE. Figure 3 illustrates actual data for the decomposition of PTFE and other fluoropolymers. At 405°C, PTFE degrades at a rate of 0.01% per hour which is minor considering that most organic material including epoxies severely/completely degrade after being held at 405°C for one hour. Table 4 shows the initial rate of degradation of PTFE and PCTFE at different temperatures. The data for degradation rate show that PTFE is over four orders of magnitude more stable than PCTFE providing evidence as to the profound differences between fluorine and chlorine.

Table 4. Initial Rate of Degradation of PTFE and PCTFE in Air^{22,23}

Temperature, °C	Initial Degradation Rate, % per hour	
	PTFE	PCTFE
365	-	12
375	0.001	25.2
385	-	50.4
400	0.006	-

Table 5. Comparison of Thermal and Combustion Properties of PTFE, PCTFE and Epoxies²⁴

Property	PTFE	PCTFE	Epoxy (bisphenol A-3000MW; 10% diethylenetriamine)
Melting Point. °C	342	220	-
Heat of Combustion, kcal/g mole	+8.01	-31.1	-1,700
Limiting Oxygen Index (LOI), %	>95	100	21-35 ¹

¹ Cycloaliphatic epoxy polymers have LOI of 18-20% and a greater tendency to burn.

It is instructive to compare the heats of combustion of PTFE, PCTFE and epoxy. A positive sign indicates heat absorbed, while a negative sign shows heat generated. PTFE actually absorbs heat to burn while PCTFE generates a small amount of heat. Limiting oxygen index (LOI) defines the percentage oxygen required in the atmosphere to achieve a self-sustaining flame using an ignition source. The difficulty of burning both PTFE and PCTFE is evident because better than 95% oxygen is required to burn these two plastics (normal ambient oxygen content is 21%). In contrast epoxies generate immense quantities of heat and can be burnt much more easily as seen in Table 4. This is precisely the reason for incorporation of brominated flame-retardants or brominated monomer in the epoxies used for printed circuit boards.

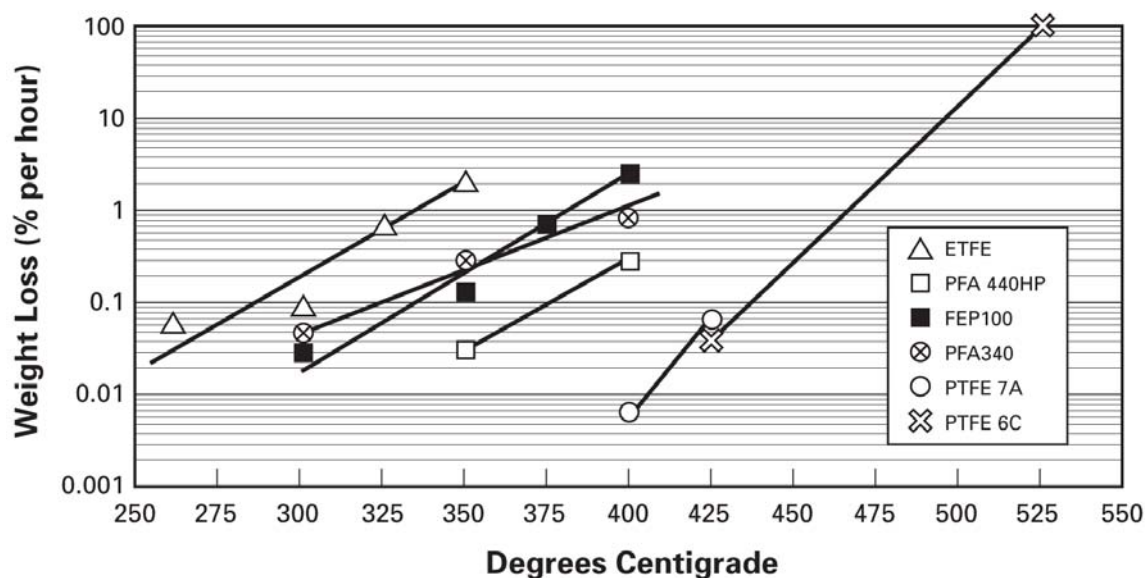


Figure 3. Weight Loss as a Result of Heating in Air²⁵ (Reprinted by permission from The Society of Plastics Industry, Inc.)

In a qualitative experiment, a small amount of different plastics was placed in a Bunsen burner under ambient conditions and the behaviour of the plastic was observed. The typical

behaviour of different plastics has been listed in Table 6. Dripping is an indication of severe degradation of the polymer. It can be seen that PTFE survives a direct Bunsen burner flame.

Table 6. Burning Behaviour of Various Plastics²⁴

Plastic	Behaviour in Burning Test
PTFE	Deforms in a flame, but does not burn. Drips are not formed.
PCTFE	Deforms in a flame, but does not burn. Drips are formed.
Epoxies	Burn slowly without dripping. A black smoke is formed with soot in air
PVC	Burns with a yellow-green flame. No drips are formed.

Electrical Properties of PTFE

A large number of properties of PTFE remain unaffected by the fabrication conditions (Table 7). Among the properties unaltered by the variable of part manufacturing process are key electrical properties such as dielectric constant and dissipation factor. The resilience of PTFE properties continues beyond fabrication and extends to a number of variables including ageing.

Table 7. Properties of PTFE Unaffected by Fabrication Processing Conditions²⁰

Mechanical	Electrical	Chemical
1. Flexibility at low temperatures	1. Low dielectric constant	1. Insolubility
2. Low coefficient of friction	2. Low dissipation factor	2. Chemical resistance
3. Stability at high temperatures	3. High arc resistance	3. Weatherability
	4. High volume resistivity	4. Low energy surface
	5. High surface resistivity	5. Nonflammability

Figure 4 presents the variation of dielectric constant as a function of temperature. Unlike a number of other material, both variables are constant at elevated temperatures especially the critical dissipation factor that controls the heat build-up in parts. Both dielectric constant and dissipation factor remain absolutely unchanged as a result of ageing in air at 300°C for 6 months. Outdoor exposure over a period of ten years had no effect on the dielectric constant and dissipation factor of PTFE, as seen in Figure 5.

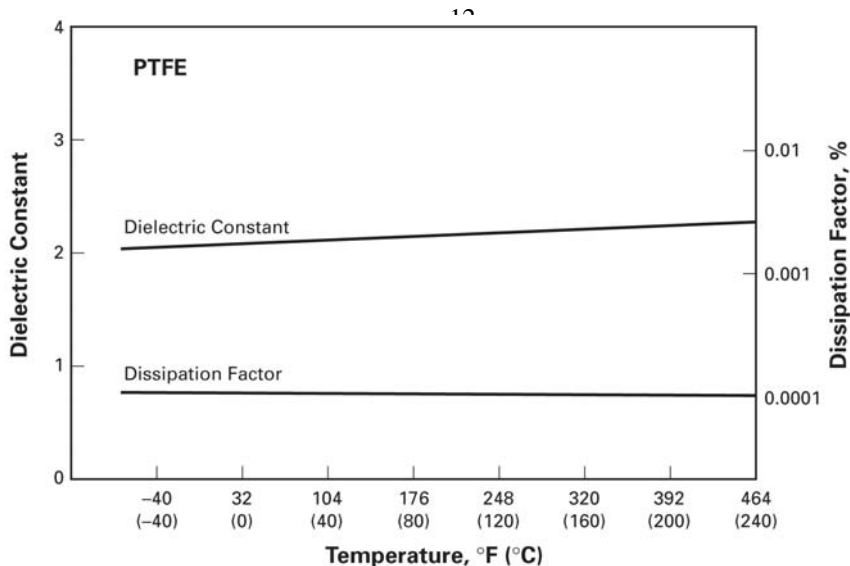


Figure 4. Dielectric Constant and Dissipation Factor as a function of Temperature²⁰

Table 8. Electrical Properties of PTFE as Function of Heat Ageing at 300°C²⁰

Sample	Exposure Time at 300°C	Dissipation Factor	Dielectric Constant	Dielectric Strength, kV/mm (ASTM-D-149)
125- μ m extruded PTFE film	As received	0.0001	2.1	117.1
	1 month	0.0001	2.1	
	3 months	0.0001	2.1	115.6
	6 months	0.0001	2.1	
	9 months			118

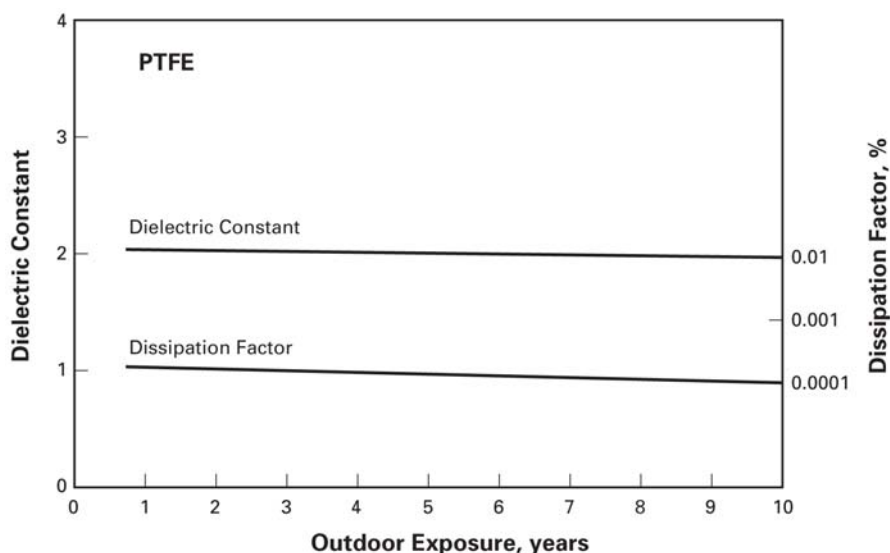


Figure 5. Dielectric Constant and Dissipation Factor as a function of Outdoor Exposure²⁰

Disposal of Waste PTFE

As PTFE is considered an inert solid it can be disposed in standard landfills. The extremely inert nature of the polymer means that there will be no risk of future environmental impact apart from taking up space in landfill areas. In practice the average amount of fluorine due to PTFE or other sources in garbage is about 100-200 g per metric ton. So the volume of space taken by PTFE is low. If incineration is performed the major part of the waste is reduced to raw gas. This raw gas contains about 5 - 10 mg/m³ part of HF that is reduced to less than 2 mg/m³ by scrubbing in basic water. This is compliant with the very severe limit of the German TA-LUFT norm. Fluoropolymers generate less CO₂ than standard urban waste. All this information is reported in a fact sheet regarding PTFE edited by the Association of Plastics Manufacturers in Europe (APME).

Conclusions

In conclusion, regulations introduced in Europe are driving E&E OEM's to move towards non-bromine containing base materials and prepregs to produce printed circuit boards, although the regulations do not actually ban the FR-4 materials. A review of the regulation indicates that they do not constitute a ban of all materials that can be chemically classified as containing a "halogen" in its broadest sense, but a move towards "bromine-free". PTFE based materials are not included in any current or future regulatory guidelines or bans. The outstanding characteristics of PTFE including thermal stability, flame resistance, electrical properties and durability of electrical properties render this plastic as the top candidate for printed circuit boards.

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