Guide to the Safe Handling of Everflon™ Fluoropolymer Resins

EVERFLON ACADEMIC

PREFACE

The information presented in this brochure is provided free of charge and submitted in good faith and is correct to the best of Everflon™ present knowledge.

Following the Guide does not guarantee compliance with any regulation nor safe operation of any processing facilities. Users are cautioned that the information upon which this guide is based is subject to change that may invalidate any or all of the comments contained herein.

Everflon™ will be unable to accept responsibility or claims from any party, related to information presented in this brochure. Freedom under patents, copyright and registered designs cannot be assumed.

INTRODUCTION

Fluoropolymer resins are produced and sold worldwide by Everflon™. They have found application in nearly every field of modern industrial, technological, and scientific endeavour. In applications ranging from power generation to emission controls on vehicles to semiconductor manufacture to aerospace, Everflon™ fluoropolymers provide superior performance in products that contribute to increased safety in offices, homes, industries and communities.

Of the many properties that characteriseEverflon™ fluoropolymer resins, one of the most important is the resistance to heat. While few plastic materials have continuous service temperatures much above the boiling point of water, Everflon™ fluoropolymer resins can withstand the temperatures inside baking ovens and in the engine compartments of jet aircraft. The combination of resistance to a broad range of fuels, solvents and corrosive chemicals, heat resistance and excellent dielectric stability means fluoropolymer resins yield an extremely versatile family of engineering materials.

These unique properties may provide certain essential performance characteristics needed in the event of fire, in fluid containment or exclusion, electrical overload and similar emergencies.

Due to the general inertness of the Everflon™ fluoropolymer resins, they fall outside all definitions of hazardous materials within European transport regulations and Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures. As with any natural or synthetic material, overheating or combustion of these resins can produce toxic effluents. Additives used with fluoropolymers may also present certain hazards. This guide includes information on the safe handling, processing and use of the materials identified in Chapter II. Although compounded fluoropolymers or resins in the form of micro-powders or lubricant powders will not be dealt with in detail, due to the variety and number of formulations, some general comments will be included in this guide.

Everflon™ PTFE

PTFE is a polymer consisting of recurring tetrafluoroethylene monomer units whose formula is [CF2-CF2]n. PTFE does not melt to form a liquid and cannot be melt extruded. On heating, the virgin resin forms a clear coalescable gel at 330°C+/-15°C. Once processed, the gel point (often referred to as the melting point) is 10°C lower than that of the virgin resin. Everflon™ PTFE is sold as a granular powder, a coagulated dispersion/fine powder, or an aqueous dispersion. Each is processed in a different manner.

Everflon™ FEP

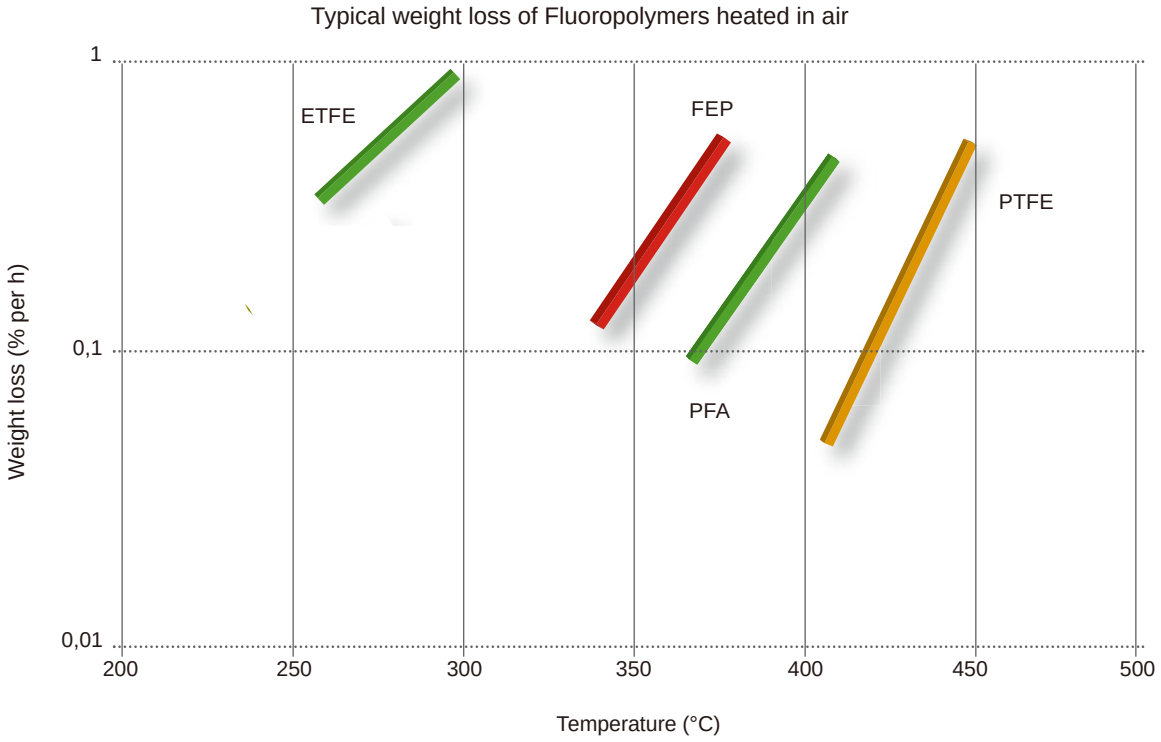
FEP fluorocarbon resin is a copolymer of tetrafluoroethy lene and hexafluoropropylene with the formula [(CF(CF3)-CF2)x(CF2-CF2)y]n. It has a melting point range of 260°-270°C and is melt processible. It is supplied in the form of translucent pellets, powder or as an aqueous dis persion.

Everflon™ PFA

PFA fluorocarbon resin is a copolymer of tetrafluoroethy lene and a perfluorinated vinyl ether having the formula [{CF(ORf)-CF2}x(CF2-CF2)y]n where ORf represents a per fluoralkoxy group. PFA melts at 280°C minimum and is melt processible. Some grades are chemically stabilised. It is available in the form of translucent pellets, powder, and as an aqueous dispersion.

Everflon™ ETFE

ETFE is a copolymer consisting mainly of ethylene and tetrafluoroethylene, having the formula [(CF2-CF2)x(CH2-CH2)y]n often modified with a small percentage of a third monomer. Depending on the molecular structure the melting range is 210°C to 270°C. It is melt processible and is supplied in the form of pellets, powder and dispersions.



Everflon	Typical melting point (°C)	Typical maximum continuous use service temperature (°C)	Typical processing temperature (°C)
PTFE	340**	260	380
PFA	265-310	260	360-380
FEP	250-270	205	360
ETFE	210-270	150	310

POTENTIAL HEALTH EFFECTS

Everflon™ Fluoropolymer resins are known for their high chemical stability and low reactivity. These compounds are of low toxicity, demonstrating little if any toxicological activity. Where toxicological studies have been conducted on fluoropolymers, no findings of significance for human health hazard assessment have been reported.

None of the Everflon™ fluoropolymers is known to be a skin irritant or sensitiser in humans. Following grossly excessive exposure to fluoropolymer resin dust by inhalation, increases in urinary fluoride were produced. No toxic effects were observed, however. Many resins are formulated with additives such as fillers, pigments or surfactants, to provide favourable processing, or other characteristics. These additives may present other hazards in the use of the resins. Some of the additives may have regulatory occupational exposure standards.

The Safety Data Sheet should be consulted for specific health information on the additives used in their products.

During the hot processing of Everflon™ fluoropolymer resins, some fume will be generated, even at the temperatures reached during normal hot processing, and it is necessary to assume that the resulting fume will present a potential health hazard. It is essential that adequate ventilation is provided to prevent exposure to the fume in the workplace. The potential consequence of overexposure to the fumes from fluoropolymers decomposing under these conditions is “Polymer Fume Fever”. This is a temporary, influenza-like illness

with fever, chills and sometimes a cough which lasts approximately 24 to 48 hours. Onset of symptoms may not be apparent for up to 24 hours. As a precaution, any person thought to be suffering from polymer fume fever should seek medical attention.

The illness is also associated with exposure to the decomposition products produced by smoking tobacco products, such as cigarettes, which have become contaminated by fluoropolymer resins, even by trace quantities. It is essential that smoking and tobacco products be banned in work areas where fluoropolymer resins are handled.

The four main types of product formed in the decomposition of Everflon™ fluoropolymers are fluoroalkenes, hydrogen fluoride, oxidation products and low molecular weight fluoropolymer particulates.

Health hazards of the most significant decomposition products are as follows:

Hydrogen fluoride: The odour threshold of hydrogen fluoride is significantly less than the occupational exposure limits (TWA 1.8ppm – 2000/39/EC). Inhalation of hydrogen fluoride at higher concentrations will give rise to symptoms of choking, coughing and severe eye, nose and throat irritation. In severe cases, and possibly following a symptomless period, fever, chills, difficulty in breathing, cyanosis, and pulmonary oedema may develop, which may lead to death.

Carbonyl fluoride: Effects following inhalation, or skin or eye contact with carbonyl fluoride may initially include: skin irritation with discomfort or rash; eye corrosion with corneal or conjunctival ulceration; irritation of the upper respiratory passages; or temporary lung irritation effects with cough, discomfort, difficulty in breathing, or shortness of breath. Respiratory symptoms may be delayed for several hours. Some European Countries apply an occupational exposure standard of 2ppm (8-hour TWA).

Carbon monoxide: An odourless gas which reduces the oxygen carrying capacity of the blood, resulting in a decreased capacity for exertion, increased load on the heart and with severe exposure, unconsciousness and death.

PFIB (perfluoroisobutylene): PFIB is highly toxic by acute inhalation, and exposure to concentrations above 1ppm for any significant period of time can be fatal. The US ACGIH has ascribed a TLV – Ceiling level of 0.01ppm to PFIB.

TFE (tetrafluoroethylene): Tetrafluoroethylene is a colourless, odourless and flammable gas that is very poorly soluble in water. Tetrafluoroethylene has a very low toxicity after acute exposure and has no cardiacsensitisation potential and it has no genotoxic potential in vitro and in vivo. TFE has been found to be carcinogenic in animal studies and under the REACH regulation EC/1907/2006, industry has agreed TFE is a category 2 (GHS Cat.1b) carcinogen A multicentre epidemiology study to study the carcinogenic impact of TFE in humans, if any, involving the major producers of TFE, is ongoing. The US ACGIH has established a TLV of 2.0ppm (8-hour TWA) for TFE.

HFP (hexafluoropropylene): Hexafluoropropylene is a colourless, odourless gas that is very poorly soluble in water. Hexafluoropropylene has a low toxicity after acute exposure.HFP is generally considered to be non-gentoxic. Repeated or prolonged exposure to HFP may cause toxic effects to the kidney. The US ACGIH has established a TLV of 0.1ppm (8-hour TWA) for HFP.

Sintering operations require the use of high temperature ovens in which various amounts of decomposition products are formed. Ovens must have forced ventilation with sufficient air flow to prevent formed gases from entering the work space during oven operation and when the door is opened. Ovens must be regularly maintained and, in particular, gases from the oven must be kept from leaking into the work area.

Temperatures in excess of the normal sintering range must be avoided. To assist in this, ovens should be equipped with an independent high temperature cutoff, triggered by an increase of approximately 5% of the desired sintering temperature, in addition to the normal control system. Both systems need to be calibrated at regular intervals. It is important that an interlock is provided which cuts off the heating if the forced ventilation is interrupted. If the oven temperature exceeds the high temperature cut-off setting, the heaters must be switched off and the oven must be cooled to ambient temperature and properly vented before the door is opened.

Compounds containing fillers may be more sensitive to decomposition than PTFE alone and may require the use of lower temperatures. When opening sintering ovens after overheating, appropriate personal protection is recommended, e.g., protective clothing, a self-contained breathing apparatus, thermally insulating gloves, safety glasses, etc.

Melt processing of Everflon™ fluoropolymer resins at excessively high temperatures or exposing them for extended times at processing temperatures can cause decomposition. Such decomposition may produce gases and generate pressures in processing equipment sufficient to “blow back” through the feed port. If no vent is available for these gases, as in some compression moulding equipment, pressures can develop which may rupture metal parts and possibly cause injury to personnel near the processing equipment.

It is considered bad practice to stand in front of an extruder for this reason. The exhaust from the vacuum pump used to control the length of the melt cone during extrusion is likely to contain decomposition products from the Everflon™ fluoropolymer and should be discharged outside the workplace.

Corrosion-resistant materials must be used for processing equipment because of the corrosive properties of the melt at high temperatures.

If a Everflon™ fluoropolymer resin melt begins to darken, the colour change is an indication that thermal degradation has begun. If an operator believes that thermal degradation is occurring, zone temperatures should be lowered and the fluoropolymer resin purged from the equipment. Everflon™ Fluoropolymer resins should be processed on equipment having accurate, reproducible temperature control. Temperature cycling should be less than +/- 5°C.

Processing Everflon™ PTFE fine powder resins requires extrusion by a special process, commonly known as paste extrusion. This involves mixing the resin with a lubricant, usually volatile petroleum fraction. The use of combustible and flammable liquids of relatively low flashpoint is a significant potential fire and explosion hazard. Electrically conductive containers must be used for the solvents and equipment should be earthed to reduce ignition sources. In addition, solvents often have health hazards due to inhalation and/or skin contact associated with their use.

Appropriate precautions must be taken for the safe use, storage and handling of Everflon™ PTFE resins containing solvent-based lubricants. Follow the recommendations of the lubricant supplier. Removal of the lubricant after extrusion may take place in a separate batch drying oven, or in a continuous oven in-line with the extruder. Appropriate precautions need to be taken to minimise the risk of forming explosive mixtures of lubricant and air, and to prevent ignition. With inline operation, the drying oven is immediately followed by a high temperature sintering oven, and there is the possibility that incorrect operation would cause flammable vapour to be carried into the sintering zone, where it would almost certainly ignite. It is essential to have fire extinguishing equipment available. For small fires, portable carbon dioxide extinguishers are usually adequate, but a permanent installation, which can rapidly fill the complete oven with carbon dioxide in the event of a large fire is advisable. Ventilation of the drying and sintering operations requires the same precautions as described earlier in this section for operation of sintering ovens in the work place.

Coating/Impregnation

The processing of Everflon™ fluoropolymer aqueous dispersions normally requires a heating process to remove water and surfactant prior to sintering the fluoropolymer. Some surfactants and their degradation products are flammable and may have specific irritant or other adverse affects on health. The oven used to remove these products must be provided with forced ventilation to prevent a hazardous build-up of vapour. Furthermore there may be significant build up of decomposition products in the ovens. Protective equipment should be worn when removing such deposits.

Machining

Grinding, sawing, and machining fabricated shapes of fluoropolymers are performed routinely in fabricators' shops. All normal high-speed machining techniques can be used provided the tools have sharp cutting edges. Coolants are recommended to improve production rates and quality, and they will serve to control any tendency toward overheating, eliminating the need for special ventilation. Dust generated by machining products manufactured from fluoropolymer resins are generally considered a "nuisance dust".

It is commonly recommended that occupational exposure limits of 10mg/m3 total dust, 5 mg/m3 respirable dust be used. However, machining products manufactured from resins which contain fillers, pigments, or other additives may produce hazardous dusts due to the presence of fillers and other additives. Consult the additive supplier or Safety Data Sheets (SDS) for further information on additives.

Welding

Special precautions are necessary when welding fluoropolymer parts to one another. Hydrogen fluoride is generated in significant quantities by the process. Complete skin and eye protection is necessary as well as the appropriate respiratory protection which may include the use of self-contained breathing apparatus.

As with most polymers, minute quantities of residual gases may diffuse from the resins, even at room temperature. Therefore, as a matter of good occupational hygiene practice, resin containers should be opened and used only in well ventilated areas. Personnel should be instructed to minimise exposure whilst opening and closing containers. Ventilation is required in hot processing operations where fumes may be released, such as drying, extrusion or sintering.

In addition it may be required in “cold” operations such as spray coating, blending and high speed grinding or machining to remove aerosols, mists or particulates.

Appropriate exhaust ventilation should be selected dependent on the nature of the process involved and local conditions. Proprietary systems may be available for specific activities, eg., spray booths or fume cupboards and where possible these should comply with relevant standards. In other cases local extract ventilation may have to be specifically designed for the process concerned. In either case, ventilation systems should always be designed or supplied by competent extract ventilation specialists.

The design of the extraction hood, ducting system and fan should be based on a good understanding of the emissions involved. This may include environmental and process conditions which could affect the emission or cause a secondary emission. It will be necessary to specify the required capture velocity at the point of the emission sufficient to ensure adequate control. This is related to the velocity of the emission and any associated air movements or currents. Good design of the hood (e.g., slots, rim ventilation, annular extraction, booths and cabinets) is important for efficient elimination of off-gases.

It should be designed taking into account all the emission characteristics. The most effective hoods are those which enclose or contain the emission. More air is required as the level of containment decreases. The required extraction volume to give an adequate velocity at the point of emission should be determined. The ducting, fan and air cleaner can then be correctly designed to match the extraction volume requirements. Further ideas on design and information can be obtained from your resin supplier.

At processing temperatures Everflon™ fluoropolymer melt can cause severe burns; therefore, appropriate protective measures including safety glasses, gloves, and arm protection (gauntlets) are recommended during processing. Jewellery should not be worn.

If dust cannot be avoided when handling Everflon™ fluoropolymer resin powders or during machining operations, respirators or dust masks should be worn. Refer to your supplier's Material Safety Data sheet for specific guidance. While processing and handling filled compounds, in addition to the dust masks, eye protection and protective gloves may be required.

Everflon™ fluoropolymer dispersions contain wetting agents which should not come in contact with the skin. It is necessary to wear protective gloves and other protective clothing to prevent skin contact when handling these products. The spray application of coatings must be performed in suitably equipped spray booths. Depending on theefficiency of this system, operators may also be required to wear safety glasses, respirators and gloves.

In regular training of personnel it is important to emphasise that tobacco products must not be carried or used in work areas. Smoking tobacco contaminated with even very small amounts of fluoropolymer resin can cause "polymer fume fever" by inhalation of the effluents.

The self-ignition temperatures (SIT) of solid PTFE products measured in accordance with ASTM D 1929 are in the range of 500°C to 560°C and hence are far above those of materials capable of sustaining combustion when the ignition source is removed. For comparison the SIT of cellulose containing materials such as wood, paper, board etc. is 240°C to 245°C. All fire and flammability tests show that fluoropolymers are amongst the most difficult plastics to set on fire. If a flame is applied to the surface of these polymers it will ignite because of the formation of gaseous decomposition products. However if the flame is removed combustion ceases. During the combustion of fluoropoly mers little or no smoke is produced. Care should be taken however to avoid the inhalation of smoke generated by all combusting materials, including fluoropolymers. The exceptionally low flammability of the fully fluorina ted fluoropolymers is also indicated by their limiting oxygen index (LOI) measured in accordance with ASTM D 2863. The oxygen index is the minimum concentration of oxygen of a mixture of oxygen and nitrogen that will just support flaming combustion of a material

The LOI for fully fluorinated polymers such as PTFE, PFA and FEP is greater than 95%. For polymers which are note fully fluorinated, the LOI is between 30 and 60% depending on the molecular structure. This compares with values of around 20% for cellulose products. PTFE does not form flammable dust clouds under normal facto ry conditions. PTFE and other fluoropolymer powders fall into dust explosion class STO.

Fluoropolymers are normally a minor component of most structures. They have a very high ignition temperature in comparison with most other organic materials and it is difficult to sustain a flame. This means that it is unlikely that fluoropolymers will be involved in a fire on their own. It is important to take account of the properties of all materials present in fires when assessing the potential health consequences of exposure to the combustion pro ducts evolved.

If fluoropolymers are involved in a fire, the hazardous gases and vapours produced include hydrogen fluoride, carbonyl fluoride, carbon monoxide, low molecular weight fluoropolymers and particulates. The toxicology of the combustion product has been investigated extensively, and it has been shown that particulates have potential, under certain laboratory conditions, to be extremely toxic. A more detailed assessment of the combustion toxicology of fluoropolymers is given in Appendix D. In a real fire situation it is not likely that any fluoropolymers present will contribute to the overall toxicity of the combustion products by virtue of the normally expected thermal degradation products (e.g. hydrogen fluoride) and will not dominate the overall toxicity due to the production of extremely toxic products.

All extinguishing agents such as water, carbon dioxide, dry powder, foam are suitable for fires involving fluoropoly mers. Extinguishing agents which are most appropriate to the surrounding materials, location of the fire and the stage of fire development should be used. For established fires water is the preferred extinguishing agent.O

FIRE AND EXPLOSION HAZARDS

Fluoropolymers are difficult to ignite and will not them selves sustain a flame so will make no contribution to the start or spread of fires. However if they are involved in a fire they can decompose and may contrib-ute to the toxicity of the fire gases formed.

It is therefore important to take normal industrial fire precautions in factories processing fluoropolymers to reduce the risk of a fire. Since the possibility of a fire starting and spreading can never be completely ruled out the relevant local authori ties should be advised of the chemical nature of the fire gases. In the event of a fire, the fire service should be warned of the possibility of the presence of toxic and cor rosive gases. Self- contained breathing apparatus must always be worn when extinguishing fires or when con ducting cleaning up operations in the presence of fire effluent. Suitable measures should be taken to prevent exposure of members of the public. If individuals are exposed, treatment may be required for inhalation of hydrogen fluoride or the other decomposition products or for skin contact with hydrogen fluoride. It is imperative that firefighters and their equipment are thoroughly decontaminated with a water wash down after fire and smoke exposure.

In the paste extrusion process flammable lubricants are normally used. The possible risk of fire or explo-sion through the formation of flammable vapour/air mixtures should also be taken into account.

Similarly with PTFE powder compounds containing carbon and metal powders, measures to prevent static charge accumulation should be taken if dust/air mixtures are likely to occur in operations such as mixing.

Thinking for You

Everflon Academic Center
Tel: +86-185-7168-9228
info@everflon.com
www.everflon.com