BROMINATED FLAME RETARDANTS

Flame Retardants (FRs)

Incorporating a flame retardant in combustible materials and plastics is a common procedure in preventive fire safety measures and is applied to reduce the risk of fires. FRs reduce the flammability of plastics.

What do they do?

FRs are active during the starting phase of a fire wherein they prevent spread of an inner source or exterior source of ignition, hence prevent, delay or inhibit the spread of a fire. In general, FRs must achieve at least one of the following tasks during the course of a fire -

- Raise the ignition temperature
- Reduce the rate of burning
- Reduce flame spread
- Reduce, if not eliminate, smoke generation

However, once a fire has developed fully, FRs cannot prevent the further spread of a fire.

How do they act? Modes of Action

FRs act by interrupting the process of combustion in the solid and liquid phases of the substrate or in the gas phase and their effect can be of a physical or chemical nature.

Physical effect of a flame retarding agent may consist of –

- A cooling effect through which the ignition temperature is not reached
- The formation of a hard or gaseous protective layer
- A dilution effect by which the flammable material or the air is diluted by non-flammable decomposition gases

Chemical effect of flame retardants can be achieved in solid & gas phases –

- Gas phase: Prevention of forming of free radical which support the spread of fire. Halogens (chlorine, bromine) released by some FRs bind the free radicals and thus interrupting. This process in conjunction with the synergist antimony trioxide.
- Solid phase : Promoting decomposition and consequently a 'flowing-away' of the flammable material from the flame, or, formation of a charred protective layer that inserts itself between the flammable material and the oxygen/flame.

Types of Flame Retardants

Advancements of chemistry in modern times has resulted in the use of more than 175 different flame retardant chemicals, divided into following major groups –

- Halogenated FRs
- Organic phosphorous-based FRs - Halogenated & non-halogenated
- Inorganic phosphorus compounds
- Other FRs such as Inorganic metal hydroxides, Nitrogen-based compounds &mixtures, etc.

Studies reveal that halogenated systems of flame retardants dominate in the area of plastics, as against halogen-free organic phosphorus compounds and mineral flame retardants.

Halogenated Flame Retardants

Halogenated organic flame retardants are generally classified as either chlorinated or brominated flame retardants(BFRs). BFRs are further classified as either reactive (chemically bound to the polymer) or additive (mixed with the polymer). Reactive uses of FR as mostly limited to duroplastics, while additive FRs are mainly used in thermoplastics. The reactive systems, because of their chemical bond, is firmly integrated in the matrix and, in principle, cannot migrate. Whereas, the additive flame retardants can be released during or after use, more easily from the matrix and this undoubtedly is a systematic disadvantage from an environmental viewpoint.

Polybrominated Diphenyl Ethers (PBDE), a type of halogenated, FR are used as flame retardants in a wide variety of products, including plastics, furniture, upholstery, electrical equipment, electronic devices, textiles and other household products.

Concerns of BFRs

Brominated Flame Retardants, especially PBDEs, are persistent in the environment and are liable to contaminate the food chain, animals and people. PBDEs are toxic with considerable health effects on the nervous system. PBDEs bio-magnify in the food chain. The properties make PBDEs and other types of BFR chemical of very high concern. BFRs have been added to consumer products for several decades. Concern has risen over this time, because they have been found in humans, breast milk and the environment. Since the 1970s, the electronics industry has been one of the largest consumers of PBDEs, wherein about 40% of PBDEs are used in the outer casings of computers, printers and televisions.Disposal or recycling operations can release BFRs themselves or brominated dioxins. Brominated dioxins are comparable to the well-known chlorinated dioxins in toxicity.

Management of BFR plastic

Having understood the issues associated with BFRs in plastics, scientific waste management of BFR plastic is crucial. The most important step in management of BFRs in plastics is to segregate them from the non-BFR stream.

Segregation of BFR plastics

There are different ways of recognizing resins in plastics, for example, by chemical testing, sound, and smell or through burning. BFR plastics can be segregated from non-BFR plastics by using the following methods or a combination of different methods.

Salt Water Technique: Shredded plastics are poured in a saline water tank. The plastic pieces contaminated with FRs settle at the bottom of the saline water tank and are then collected separately. The ground plastic pieces are dried and packed.

Beilstein Method: A material containing bound or ionic halogens (chlorine, bromine, iodine) such as salt or polyvinyl chloride (PVC), will react with a copper wire when heated in a flame and produce a brilliant, long lasting green flame. Heated copper wire is jabbed into the sample plastic so that plastic is transferred to wire and then again held wire under lamp to give a green flame to BFR plastics

Instrument based methods: Other more accurate methods of identifying BFR and non-BFR plastics involves use of instruments which will provide exact percentage of BFR content, however, these instruments are costly to operate. Sliding spark spectroscopy, XRF / XRT technology, Raman Spectroscopy are a few instruments.

Recycling/Reuse Alternatives

There exist several disposal options for brominated flame retardant plastics once it reaches its end of life. The technology for recycling bromine from plastics waste containing brominated flame retardants exists and can be applied in a cost effective manner.

Mechanical recycling aims to recover plastic waste via mechanical processes (grinding, washing, separating, drying, re-granulating and compounding), thus producing recyclates that can be converted into new plastics products.

Feedstock or chemical recycling aims to chemically degrade the collected plastics waste into its monomers or other basic chemicals. The output may be reused for polymerisation into new plastics, for production of other chemicals or as an alternative fuel.

Incineration with energy recovery is a process wherein the energy generated during the combustion of plastic waste is recovered. This energy can be used to produce heat and/or electricity for domestic or industrial use. Incineration of plastics can also generate energy needed to extract the metals during smelting operations of e-waste recycling.

Pyrolysis decomposes BFR plastics at elevated temperature in the absence of oxygen resulting in change of chemical composition and physical phase. Pyro oil and char are generated as outputs of the pyrolysis process which can be used as a fuel.

Co-processing involves burning of plastic wastes as an alternate fuel along with primary fuel in cement kilns. Calcination takes place at 1300-1400 C. This eliminates the possibility of emissions of dioxins and furans from burning of plastics. Bromine content in BFR plastic is criticalin co-processing as the bromine is corrosive.

Above are some of the methods which are adopted to recycle/ reuse / recover BFR plastic from end of life product. Each methodology has its own advantages and limitations.

About SRI – India project

Sustainable Recycling Industries (SRI) program (www.sustainable-recycling.org) is funded by Swiss State Secretariat of Economic Affairs (SECO) and is implemented by the Institute for Material Science & Technology (EMPA) and World Resource Forum Association (WRFA). The SRI project in India aims to identify an alternative mechanism for handling BFR plastics and to develop technical standards for handling, transport and destruction of BFR plastics. The project also intends to set up a pilot take back mechanism to segregate & prevent BFR plastics from entering the secondary value chain.

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