Novel polymeric, non-halogenated flame retardants

Dr Jan-Pleun Lens, VP of research & applications at **FRX Polymers**, highlights the advantages of polymeric flame retardants

Flame retardancy is a legal requirement for many plastics used in electrical equipment, consumer electronics, building and construction, textile and transportation applications. Flame retardants (FRs) inhibit ignition, slow the spread of fire or protect critical infrastructure during a fire event and reduce smoke or toxic fume production.

Over 60% of all FR plastic formulations are still based on halogen-containing FR additives, even though these materials have some severe, undesirable side effects, such as persistence in the environment, bio-accumulation in animal and human tissues, and cytotoxicity.[1,2] Furthermore, under conditions where fire or incineration occurs, a halogenated substance may contribute to the formation of highly toxic halogenated dibenzodioxins and dibenzofurans, increase the generation of polycyclic aromatic hydrocarbons and impact fire parameters, such as smoke and carbon monoxide.[3]

The combination of these issues has placed strong pressure for the global elimination of halogen-containing FRs. Driven by EU legislation that bans the use of certain families of brominated FRs, such as polybromodiphenylethers (PBDEs) and prohibit the recycling of bromine FR-containing plastics in other plastics, many companies and researchers are looking for alternatives. This is further supported by initiatives like the US EPA's Design for the Environment Alternatives assessment for decabromodiphenylether (decaBDE) and hexabromocyclododecane (HBCD).

Furthermore, it is highly desirable that FR agents do not migrate out of their host plastic, exposing humans to these often toxic chemicals and diminishing the application's FR function over time. The migration of low molecular weight (MW) halogenated FRs from households and the exposure of humans and animals to these chemicals have featured in recent studies that show high levels of PBDEs in the blood of dogs that live primarily indoors.[4]

This study also detected newer FRs that have come onto the market as PBDEs have been removed, including HBCD, Dechlorane Plus and decaBDE. These are largely unregulated but pose concerns because they are structurally similar to organic pollutants that have been linked to environmental and human health effects.

Many non-halogenated FR alternatives are based on phosphorus. However, these are typically small molecules and, like most halogenated FRs, tend to migrate out of the host plastic over time.

Some, like resorcinol diphosphate and bisphenol A diphosphate, are liquids that are inherently difficult to compound into molten plastic and, once incorporated, decrease the heat and mechanical properties of the composite. When plastic parts end up in landfill, migration may bring these diphosphates into the environment, which is undesirable, because of the concerns over their aquatic toxicity expressed in Risk Phrases under Directive 67/548/EEC, like R50/53.

In order to prevent migration of FR agents, one can use reactive type or polymeric FRs. Reactive FRs can be copolymerised in the main chain or as pendant side groups of polymers. However, this approach generally requires the polymer manufacturing processes to be modified, which is generally associated with high costs.

A better approach is to blend polymers that need to be flame retarded with polymeric FRs. As in any polymer blend, the polymeric FR will be entangled with the host polymer into a physical network, thereby imparting permanent flame retardancy while maintaining most of the original mechanical and thermal properties of the host polymer.

To address the issues of the persistence, bioaccumulation and toxicity of halogenated FRs, a polymeric halogenated FR to replace HBCD has been introduced to the market. Developed by Dow and made commercially available via three major suppliers of halogenated FRs, the advantage of this polymeric material is that it will not migrate out of the host plastic.

Nonetheless, some applications where these polymeric brominated FRs are used require the use of antimony trioxide (ATO) as a synergist. ATO is a heavy metal oxide and is a suspected carcinogen. The effects of antimony poisoning are similar to those of arsenic poisoning. Finally, materials that contain brominated polystyrene still need to be recycled separately and, during incomplete incineration, furans and dioxins can still be released.

Table 1 – Polyphosphonates compared to halogenated & other phosphor-based FRs

	Halogenated FRs	Phosphor-based FRs
Small molecules	*PBEs, PBDEs, TBBPA, decaBDE, HBCD* – Persistent, bioaccumulative & toxic – Use ATO as synergist – Migrate from host plastic – Formations of dioxins & furans at incomplete incineration	*Organic phosphates, phosphinate salts, DOPO* + Halogen-free – Migrate from host plastic – Can negatively affect thermal and mechanical properties of host plastic – Aquatic toxicity concerns (diphosphates)
Polymeric	*Brominated polystyrene* + Do not migrate from host plastic – Use ATO as synergist – Formation of dioxins & furans possible at incomplete incineration	*Polyphosphonates* + Halogen-free + Do not migrate from host plastic + Favourable human & aquatic toxicity profile. Do not bioaccumulate + Supplied as pellets (no liquid handling or dust formation) + Improves properties other than flame retardancy

Polyphosphonates

FRX Polymers is the first company to supply non-halogenated, non-migrating FR materials of low concern to human health and the environment commercially, under the brand name Nofia*. This technology is based on chemistry that allows the polymerisation of a phosphonate monomer into unique oligomeric and polymeric FRs. Compared to halogenated FRs, recently introduced polymeric brominated FRs and other phosphorus-based FRs, these polyphosphonates have clear advantages (Table 1).

Both the monomer process and the polymerisation process honour some of the 12 Principles of Green Chemistry. The key economic enabler for this new technology lies in the ability to produce a low-cost, high-purity, phosphor-containing monomer safely. With advances in reaction conditions and catalyst usage, it is possible to make a very high-purity monomer with a very high yield. The process does not use any solvents and its atom economy expressed as MW product/ ΣMW reactants x 100 is 100%.

Table 2 - Performance of polyphosphonates in different systems

Polymer	Phosphonate	Loading (wt%)	Additional FR additive	FR test	Rating
-	Copolymer	100	-	UL94	VTM0/0.1mm V0/0.2mm
PET	Homopolymer	5-20	-	ASTM D6413-99 NFP92-507 UL94	Flame out time <1s M1 V0/0.8mm
PC	Copolymer	15-50	Sulfonate salts	UL94	V0/0.4mm
PC/ABS	Copolymer	85	Teflon	UL94	V0/1.6mm
GF PBT	Homopolymer Copolymer	15-25	Melamine cyanurate (MC) Teflon	UL94	V0/0.8mm
TPU	Homopolymer Oligomer	2-20	RDP Phosphinate salts	E84, E162 UL94	Class A V0/0.1 -1.6mm
TPEE	Copolymer	5	Exolit, MC, ATH	UL94	V0/1.6mm
Epoxies	Oligomer	10-30	ATH		
UPET	Oligomer	10-30	ATH / RDP	E162	Class A

The polymers from the phosphor-containing monomer are made through a melt-based process. The chemistry offers the possibility to tailor the products to a wide range of compositions and MWs. Varying the reaction conditions (time, temperature, pressure and catalyst), either oligomers or polymers of high MW can be produced.

By using different co-monomers, the polymer properties of the polyphosphonates can be tailored to specific needs. In addition, by replacing some of the phosphonate monomer with diphenylcarbonate, various phosphorus-containing analogues of polycarbonate can be made with phosphorus content from very low levels to >10%.

The by-product of the polymerisation reaction is captured and reused to produce any of the starting monomers, so little or no waste is generated. Thus, the polymerisation reaction also demonstrates an atom economy of 100%. The E-factor, defined as total mass of waste/mass of desired product is nearly zero. Both monomer and polymer process are now operated in commercial plants and the polyphosphonates are available to the market.

Applicability

Polyphosphonates and polyphosphonate-co-carbonates can be used as stand-alone, melt processable, inherently FR materials but they are also compatible with and deliver FR performance plus a number of unique properties to polyesters, polycarbonate (PC) blends, polyurethanes, epoxies, unsaturated polyesters and polyureas. Being polymeric, they typically do not affect the properties of the host plastics and in some cases improve them. Eliminating bromine in the FR package further allows greater recovery and recycling of plastics after their intended use.

Nofia HM1100 polyphosphonates are produced as transparent pellets with a phosphor content of about 10.5 wt% and a similar transparency to PC. The glass transition temperature is relatively high (~105°C) and the melt stability is such that it can be processed via melt spinning, blow moulding, blown film, cast extrusion and injection moulding.

Nofia CO3000 and CO6000 polyphosphonates are mainly used as a blend component in a wide range of thermoplastics. Polyphosphonate-co-carbonates have properties ranging between those of a pure polyphosphonate (high FR) and a pure polycarbonate (very good impact). Finally, the Nofia OL series of phosphonate oligomers contain varying amounts of reactive end groups for use in a wide range of thermosets.

Depending on the polymer system, the application, and the specific FR requirements there is a preferred material and usage level (Table 2). Much research is focused on identifying optimised formulations where polyphosphonates are further combined with other FR agents for an even more improved – and sometimes synergistic - FR performance. In some applications the polyphosphonates can be the main FR agent; in others, they are used as a booster in systems where other FR agents are used as the main component.

Fibre applications

One major example of the unique application possibilities is the ability to spin polyester fibres directly from blends of the host resin (e.g. PET) and the polyphosphonates. Thus, secondary processes, like dip coating fibres with (often halogenated) FR additives, are no longer required. In this way, inherently FR staple, mono-filament and multi-filament fibres can be produced. Fibre applications where polyphosphonates have been already applied include flame retarded technical textiles, carpets, wire and cable braidings and wigs and hair extensions.

Due to the polymeric nature of the polyphosphonates, they do not negatively affect the spinning process. The melt strength of the polymer blends is not compromised and spinning can be done in the same processing conditions as for the neat polyester materials.

Because the polyphosphonates are melt-processable and do not have a discrete particle size, even the smallest diameter fibres can be produce with a tenacity similar to the neat polyester.

Adding the polyphosphonate separately to the polyester has further advantages. The phosphor content in the fibres can be varied from the traditional 6,000 ppm to as high as 25,000, so applications with relatively strenuous FR specifications can be targeted. A range of different polyester sources can be used, extending to recycled PET, which helps with the production of environmentally and economically favourable FR polyester fibres.

Different tests have been applied to materials made from polyester fibres containing polyphosphonates. Technical textiles made from PET staple fibre passed the ASTM D6413-99 test with an after-flame time of <1 second compared to about 50 for neat PET, without any flaming drips or edge-blackening. When tested according the NF P 92-507 test, the textiles obtained an M1 rating.

When used in carpet tiles, samples made from PET fibres containing polyphosphonates obtained a Class A rating in the radiant panel test E648. This had never before been demonstrated with polyester fibres.

Finally, an upcoming area of interest is the use of polyphosphonates in artificial wigs and hair extensions made from PET. Not only are excellent FR properties obtained but, when compared to wigs containing brominated FRs, the polyphosphonate-containing samples held the curl longer, absorbed dyes better, made a lighter weight wig and had a realistic human hair feel to the touch.

Thin & clear applications

Because polyphosphonates form miscible blends with many engineering resins, they are very suitable for applications that require thin transparent FR films or sheets. Just as polyphosphonates can be added to polyesters for spinning fibres, similar blends can also be used to extrude films from 1.6 mm to as thin as 50 μm. The resulting films are transparent, meet the VTM0 or V0 conditions at the different thicknesses and can even be biaxially oriented.

Polyphosphonate-carbonate copolymers have successfully been used as inherently flame retarded PCs. They have a unique set of properties. They are transparent and show the highest flammability rating at a thickness of 0.1 mm when tested under the Underwriters Laboratory protocol (UL VTM0 or V0). By comparison, the current state of the art for transparent PC can only achieve a UL V0 rating at 1.6 mm or thicker.

Due to miniaturisation in consumer electronics, electrical equipment and lightning applications, these copolymers are carving out a very high value niche in these thin transparent applications. More interestingly, they also show a very good performance in heat release tests like the OSU test that is being used for aviation applications.

The current commercially available transparent copolymers almost meet the '65/65' criteria. This is already much better than regular PC that does not meet these requirements but has still obtained a waiver to be used in aviation. Developments in the past year have led to a new class of transparent copolymers that actually meet all of the aviation specifications and which will be made available later this year.

Finally, polyphosphonates also form transparent blends with a broad range of polyether- and polyester-based thermoplastic polyurethanes (TPUs) with a VTM0 or V0 performance from 50 µm to 1.5 mm. When tested according to flame spread tests used in specifying materials for the building market and US rail applications, like ASTM E162 and E84, the blends meet the Class A requirements. In other areas where transparency is not needed (like wire and cable where TPUs are used alongside thermoplastic polyester elastomers in consumer electronics applications), polyphosphononates are being used to meet specific FR requirements.

Thermoset applications

Phosphonate oligomers can contain different types of reactive end groups. This allows their use in a wide range of thermosets where they can react with other monomers during the processing of the final applications. As such, they are a halogen-free alternative for epoxies used in printed circuit boards (PCBs). Most current PCBs are flame retarded with tetrabromo bisphenol A (TBBPA), a suspected carcinogen.

Phosphonate oligomers can be used, like TBBPA, as a chain extender in the manufacturing process of the epoxy resin, giving the resin its flame retardancy. However, a much more effective way is to use them in the process to make the actual copper-clad laminates (CCLs) where they can act as hardeners to the resins and give the CCLs their FR properties.

Compared to other phosphor-based FRs in this sector, phosphonate oligomers offer strong performance and higher heat resistance, which improves the capability for lead-free soldering. Very low dielectric constants and dielectric loss factors are obtained for the CCLs that contain phosphonate oligomers.

This is very important for large data applications and cloud services, where more and more speed and data storage capacity are required. Recently, phosphonate oligomers have also been qualified for use in structural panels for high speed trains and in artificial automotive leather.

Summary

Polyphosphonates are a very versatile addition to the continuously growing spectrum of FR additives. They are already being used successfully in a range of different polymer systems and applications as a permanent FR system, while simultaneously delivering a unique balance of properties.

A lot of effort is being put into expanding this area, both by FR producers and plastic compounders. Especially in combination with other FRs, the possibilities to custom design formulations that meet both FR and other non-FR requirements (mechanical, heat, stability properties) will expand greatly.

Developing optimised formulations may require a series of product development iterations, because changing one FR for another is hardly ever a simple exercise. However, a lot of ground work has been performed in evaluating polyphosphonates and phosphonate oligomers, with and without other FRs. For many different polymer systems, starting formulations are available that only need to be modified for the customer's specific resin and the specific application.

References

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