Polymeric, Non-Halogenated Flame Retardants with Broad Applicability in Multiple Industries

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FRX POLYMERS® Inc. (FRXP) is commercializing a unique series of non-halogenated, inherently flame retardant (FR) plastics. After founding the company in 2007, a monomer and polymer pilot facility were built and operated in Chelmsford, MA. Since then, FRXP won Frost and Sullivan's 2008 Innovation of the Year Award for Flame Retardant Additive Materials, won the 2009 Society of Plastics Engineers business plan competition for sustainable new materials, and was featured on the Economic Report, which aired on CNN Business Segments in April 2009. In the last two years, FRXP made substantial progress towards becoming a global supplier of a unique flame retardant additive solution for a wide range of plastics. The number of employees doubled to 15; the number of granted patents tripled to 14 and over 60 patent applications have been filed; all toxicological tests have been successfully completed to support global product registration; and a 50 metric tons per year semi-commercial polymer plant was built and was sold out in 2011 to support 6 commercial customers and more than 100 qualifying customers.

This technology is nominated for the small business award.

The major focus area of this technology is the design of greener chemicals. Additionally, this is accomplished through the use of greener reaction conditions.

All the development work for making phosphonate monomer and polymers has been performed in our laboratories in Chelmsford, MA. In 2010, a 100 metric tons per year monomer production facility, a small scale wet lab, and a new applications lab were added to the Chelmsford operations. In 2011, the labs were further expanded by adding multiple analytical instruments.

Abstract

Traditional, halogenated, small-molecule flame retardant (FR) additives readily migrate out of their applications, exposing humans to these often toxic chemicals and diminishing the application's flame retardant function. Electronic device manufacturers have instituted voluntary bans on plastic formulations with halogen-containing FR additives. Also other industries like building and construction and transportation are moving away from these halogenated FR additives. Consequently, the plastics industry is searching for cost-effective, non-migrating, non-halogenated alternatives.

FRX POLYMERS® Inc. (FRXP) is the first company to develop polymeric forms of phosphorus for use as non-migrating FR additives that are also cost-effective and halogen-free. FRXP converts diphenyl methylphosphonate (DPMP) into polymers with over 10 percent phosphorus. These unique polymers have the highest limited oxygen index (LOI) measured for thermoplastic materials, highlighting their FR functionality. The polymers can be used as standalone, inherently FR materials; they can also deliver FR performance and often additional beneficial properties to polycarbonate blends, polyesters, thermoplastic polyurethane, unsaturated polyesters, epoxies, and polyureas. Being polymeric, the FRXP materials will hardly deteriorate the physical properties of these

plastics. Replacing bromine with phosphorus in FR additives should allow greater recycling of plastics after use.

The DPMP monomer synthesis has essentially quantitative yields. The polymer synthesis is a solvent-free, melt-based process whose only major byproduct, phenol, can be recycled into the starting monomers. Less than 5 percent waste is expected from FRXP polymer and copolymer production. Because they can be processed by melt processing techniques, FRXP polymers can be used in applications such as fibers and blow-molded articles that were impossible with other FR additives.

FRXP is scaling up its additives for applications including electronic housings, industrial carpeting, textiles, electrical connectors and switches, wire and cable, printed circuit boards, and transparent laminates. The FRXP materials have completed Premanufacture Review under the Toxic Substances Control Act (TSCA) and are proceeding toward global registration. FRXP plans to expand its current polymer pilot plant from 50 to 100 metric tons per year (TPA) early 2012. Furthermore, basic engineering has started to build a 2,500 TPA commercial plant that should be operational in October 2013.

Introduction

Flame retardancy is a legal requirement for many plastics used in electrical equipment and consumer electronics, building and construction, fiber/textile, and transportation applications globally. The FR materials inhibit ignition, slow the spread of fire or protect critical infrastructure during a fire event. Fire deaths were estimated to claim the lives of ten to twenty people per million population in developed countries (Source: SRI International). Many injuries (some permanent) can result from fleeing or battling fires. Recent numbers by the National Institute of Standards and Technology showed that homeowners now have 3 minutes to get out of the house with a fire compared to 17 minutes in the 1970s because of more home synthetics, which make fires ignite and burn faster because synthetics release more toxic gases when burned. Finally, as much as 1% of a country's GDP can be lost to fire each year (Source: SRI International).

Flame retardant plastics and additives comprise a worldwide materials market of over $15 Billion with growth rates of 5 to 6% per year. Over 60% of all FR plastic formulations in use today are based on halogen containing FR additives like brominated and chlorinated hydrocarbons. However, this popular class of flame retardant additives is being shown to have severe, undesirable side effects such as persistence in the environment and bio-accumulation in animal tissues, human blood, breast milk, and food products. A National Oceanic and Atmospheric Administration study found polybrominated diphenyl ethers (PBDEs), a class of FRs used in household furniture and electronic equipment, in sample sites from the Pacific, Gulf and Atlantic Coasts as well as in the Great Lakes. Places with higher population showed greater presence of PBDE in mussels, oysters and zebra mussels. Additionally, researchers detected dechlorane plus, another widely used chlorinated FR that has been suggested as replacement for decabromodiphenylether (decaBDE), one type of the PBDEs, in every one of 20 air samples they collected during two cruises on the Atlantic Ocean between the Arctic and Antarctica (Environ. Sci. Technol., DOI: 10.1021/es103047n). Studies with rats have shown negative effects of PBDEs in liver, thyroid and neural development functions. Tetrabromine bisphenol A, the most popular brominated FR in current use, which is also used as a substitute for the PBDEs has significant cytotoxicity (*Biochem J.*, 2007, 408(Pt 3): 407–415). Finally, halogenated FR additives can form highly toxic dioxins and furans during burning and thermal disposal.

These issues combine to place great pressure on a global elimination of halogen containing FR agents. Driven by EU legislation such as the Reduction of Hazardous Substances and Waste Electrical and Electronic Equipment directives, which ban the use of certain families of halogen containing FRs in plastics and ban the recycling of non-banned bromine containing plastics amongst non-halogen containing plastics, respectively, many companies and researchers are looking for better alternatives. This is further supported by initiatives like the U.S. Environmental Protection Agency's Design for the Environment Alternatives Assessment Programs for decaBDE and hexabromocyclododecane (HBCD).

Furthermore, it is desired that FR agents (like any additive) do not migrate out of their applications, exposing humans to these often toxic chemicals and diminishing the application's flame retardant function. Exemplary for the migration of low molecular weight halogenated FR additives from households and the exposure to these chemicals by adults, children, and their pets are the results of a recent study that show high levels of PBDEs in the blood of dogs that live primarily indoors (*Environ. Sci. Technol.*, 2011, 45 (10), pp 4602–4608). This study also detected newer flame retardants that have come onto the market as PBDEs have been removed, including HBCD, Dechlorane Plus, and decabromodiphenylethane. The chemicals are largely unregulated but pose concerns because they are structurally similar to organic pollutants that have been linked to environmental and human health effects.

FRXP is the first company to deliver a non-halogenated, non-migrating FR retardant solution with a broad applicability in different industries. The technology is based on chemistry that allows the polymerization of a phosphonate monomer into unique oligomeric or polymeric FRs with phosphorus content greater than 10%. Yields from the monomer process are essentially quantitative. The polymer is made through a solvent-free, melt based process in which the major by-product, phenol, is being recycled into the starting monomers. Thus, less than five percent waste is expected from the production of FRXP polymers and copolymers. Based on economic studies and quotations from suppliers, the products will be extremely cost-competitive with other, existing FR solutions and will approach the cost price of large volume engineering resins at scale.

The real challenge in flame retarding any material is to achieve an acceptable performance in a fire situation while still maintaining the useful properties of the material in the application (e.g. physical properties, stability, appearance). Being a high molecular weight material, FRXP polymers will hardly deteriorate the physical properties of the polymeric systems in which they are used. Furthermore, FRXP polymers are melt processable, which allows use in applications like fibers for textiles and carpeting and blow molded articles that has never before been possible with any FR additive.

DPMP Monomer Process

The key economic enabler for this new technology lies in the ability to safely produce a low-cost, high purity DPMP starting material. FRXP has developed several novel pathways to producing DPMP (US07,569,717; US07,888,534; US07,928,259). Starting materials can be either phosphorous trichloride, phenol, and methanol or triphenyl phosphite and trimethyl phosphite. Supplies of such starting materials with the required purity are available in the market today.

The reaction of triphenyl phosphite and trimethyl phosphite can occur in the presence of catalytic amounts of methyl iodide and typically involves heating the components to a final temperature of about 230°C for up to one hour (**Figure 1**). A complex series of different exothermic (possibly even explosive) reactions can occur (e.g. Michaelis-Arbuzov reaction) in different temperature regions and therefore this process has been limited to small scale production. However, with advances made via reaction conditions and catalyst usage, FRXP has been able to safely scale up the production of DPMP to 100 metric tons per year with a near quantitative yield and a purity of at least 97% in the crude reaction mix, which is exceptionally high for making phosphonates. One of the features of this process is the complex formation of methyl iodide with triphenyl phosphite into a transition catalyst prior to the addition of trimethyl phosphite.

Because of the high yield and high purity, DPMP may be prepared in one-pot without the need to isolate and/or purify intermediates. Additionally, by-products are minimized or eliminated, so one or more separation steps in which by-products are removed would not be necessary. However, the polymerization process requires a very high purity DPMP and therefore additional processing is desired to guarantee monomer quality consistency. Typically, this is done through distillation, ion exchange resin columns, or other packed columns. Thus, small amounts of possible acids and iodide species are removed. Such purification techniques eliminate the use of additional solvents and contribute to the principles of FRXP to employ greener chemistry in producing our products.

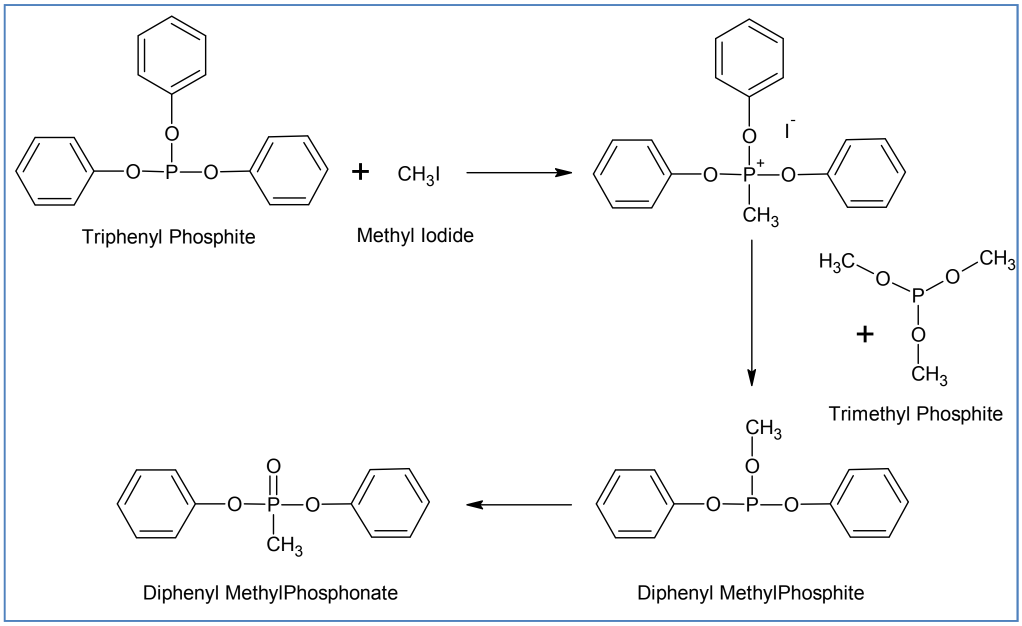

Figure 1, *Process to make diphenyl methylphosphonate (DPMP). Typically, 2 moles of triphenyl phosphite and 1 mole of trimethyl phosphite yield 3 moles of DPMP.*

FRXP Polymer Process

Though polyphosphonates were first discovered in the late 1940's and work has been done in optimizing the synthesis of these materials in the 1980's, they were never commercialized till now due to technical difficulty and high costs. FRXP recently advanced the chemistry to allow DPMP to be polymerized effectively (**Figure 2**). Instrumental in this process is the use of the tertaphenylphosphonium phenolate catalyst, which makes it possible to make polymers of high molecular weight with an improved color and higher Tg's than comparable products that were made with more traditional catalysts like sodium hydroxide. An additional advantage of the current polyphosphonates is that the hydrolytic stability, which has been one of the weaknesses of this class of materials, was greatly improved compared to the polyphosphonates that were available to date (US6,861,499, US7,560,525, US7,645,850, US7,816,486, and US7,838,604).

The FRXP polyphosphonates are made through a solvent-free, melt based process. This is a thermodynamically controlled process and the chemistry offers the possibility to tailor the products to a wide range of compositions and molecular weights. Varying the reaction conditions of time, temperature, pressure and catalyst, FRXP can create oligomers or polymers of high Mw with phosphorus content from any low level to more than 10%. By changing the stoichiometry of the starting materials, different levels of reactive hydroxyl terminated end groups can be obtained. By changing the aromatic dihydroxy compound, the polymer properties of the polyphosphonates can be tailored to specific needs of customers with respect to the polymer system or the application in which the FRXP materials are being used. Finally, by replacing some of the DPMP with diphenylcarbonate (DPC), various phosphorus-containing analogs of polycarbonate can be made. The composition of these materials can be varied by simply changing the ratio of DPC to DPMP. Thus, FRXP's manufacturing plant is capable to make pure PC and pure polyphosphonate plus all polyphosphonate-co-carbonates in between. The phenol by-product of the polymerization reaction is captured and reused to either produce the aromatic dihydroxy compound or the DPMP or DPC, so little or no waste is generated.

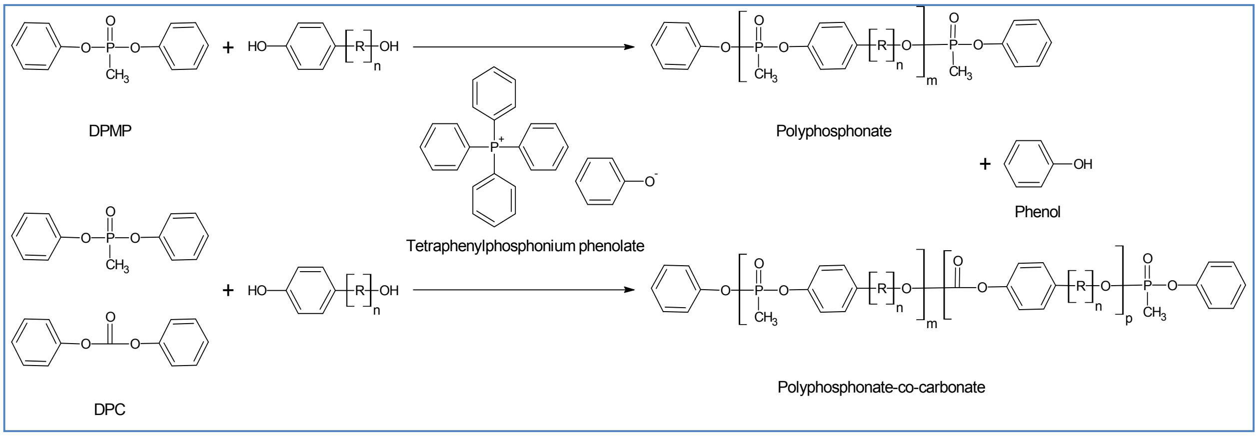

Figure 2, *Process to make polyphosphonates using diphenyl methylphosphonate (DPMP, upper reaction scheme) and polyphosphonate-co-carbonates using DPMP and diphenylcarbonate (DPC, lower reaction scheme).*

The process and chemistry to make polyphosphonates and polyphosphonate-co-carbonates are similar to industrial processes to manufacture polyesters and PC through the melt process, which is now generally applied to all newly build commercial PC plants. Further scaling up the FRXP process will therefore greatly benefit from the experience obtained in the chemical industry with the engineering and operation of these types of melt plants. This already has been demonstrated by the successful translation of the process from a 1 metric ton per year (TPA) pilot plant facility in Chelmsford, MA to a 50 TPA semi-commercial plant that was started up in July, 2010. The capacity of this plant will be expanded to 100 TPA early 2012. Furthermore, basic engineering has started to build a 2,500 TPA commercial plant that should be operational in October 2013.

Applications

There are three main FRXP product lines: homopolyphosphonates (FRX0100), polyphosphonate-co-carbonates (e.g. FRX Co35, where the amount of DPMP is about 35% of the total of (DPMP + DPC) that is used), and FRXP oligomers. The FRXP polymers have molecular weights (Mw) of up to 100,000 (polystyrene (PS) standards) whereas the FRXP oligomers have Mws <10,000 (PS standards). With a value of 65%, FRX0100 exhibits the highest Limiting Oxygen Index (LOI) of any known thermoplastic material, indicating its strong FR properties.

FRX0100 is obtained as transparent pellets and has the same transparency as regular PC (>88%). The glass transition temperature is relatively high (100-107°C) and the melt stability is such that it can be processed through fiber spinning, blow molding, and injection molding. The material can be used as standalone, inherent flame retardant thermoplastic resin but as an additive it also has great compatibility with a range of other thermoplastic materials. One major example of FRX0100 unique application possibilities is the ability to spin polyester fibers directly from blends of the host resin and FRX0100. Thus, no secondary process, like dip coating the fibers with FR additives, is required anymore. Furthermore, woven samples from these fibers obtained a class A rating in the radiant panel test which has never been demonstrated before with polyester fibers. One of FRXP major U.S. customers is currently commercializing these inherently flame retardant fibers that can be used in textiles as well as carpeting.

Another good example where FRX0100 shows added value in addition to the excellent FR properties is in glass filled polybutylene terephtalate, used in electrical connectors and switches. Compositions with FRX0100 showed much better processing behavior and improved electrical properties, such as a 2x higher Comparative Tracking Index (450V) than comparable blends with traditional FR agents and the highest Glow Wire Ignition Temperature (825°C) known for this type of materials.

The FRXP copolymers have successfully been used as inherent flame retardant polycarbonates (PC) and the first commercial application has been as a side window in hydraulic pumps that required flame retardancy. The copolymers have a unique set of properties. They are transparent and show the highest flammability rating (V0) at a thickness of 0.4mm when tested according the Underwriters Laboratory (UL) 94 protocol. The current state of the art only allows transparent PC to have a V0 rating at 1.6mm or more. However, miniaturization in consumer electronics, electrical equipment, and lightning applications calls for thinner and thinner wall thicknesses below 1.2mm and therefore new material solutions such as FRXP copolymers are required.

The copolymers can also be used in blends of PC with other polymers like acrylonitril-butadiene-styrene rubber (ABS). These blends are used in nearly all housings for consumer electronics like cell phones, computers, and televisions. To make these latter systems flame retardant, typically liquid, low molecular weight compounds like resorcinol diphosphate (RDP) and bisphenol A diphosphate (BPA-DP) are added in quantities of up to 10-20%. Liquid based additives are inherently difficult to compound into molten plastic and once incorporated, they decrease the heat properties of the composite (expressed in a decrease of Vicat and Heat Distortion Temperatures). Also, they tend to migrate out of the material during processing which requires frequent cleaning of molds resulting in down time for plastic processors. More seriously, these low Mw FR additives can migrate out off the parts during use (especially in high temperature applications), thus exposing humans to these chemicals. Finally, they can end up in the environment when the plastic parts end up in landfill. Related to this, there are concerns about the aquatic toxicity of these compounds expressed in risk sentences like R50/53. The FRXP copolymers can replace the PC portion of the PC-ABS blends and being inherently FR, there is no need to add other FR additives. Additionally, FRXP copolymers improve the heat distortion temperature and hydrolytic stability of PC/ABS alloys from 85 and 110°C to 120 and 137°C, respectively.

Finally, the FRXP oligomers, having either phenyl or hydroxyl end groups, are used as reactive FR additives in thermoset systems. The FRXP oligomers specifically are a halogen-free solution for epoxies that currently mainly use brominated FR agents. They offer strong FR performance and higher heat resistance than current FR materials, which improves the capability for lead free soldering in applications like printed circuit boards.

Conclusions

In the past years, FRXP has established a unique position in the continuously expanding market for FR plastics by offering a polymeric form of phosphorus FR material, a world first! This has been recognized by more than 100 global customers from different industries that are evaluating the material. A number of U.S. customers already have incorporated FRXP products in their formulations and are offering their products to the market. Consequently, the 50 TPA semi-commercial pilot plant that was established in 2010 already sold out and will be expanded to produce 100 TPA.

In July 2009, a series A round of financing was completed by attracting funding from two major venture capital firms who specialize in funding companies with outstanding clean technology business plans. In 2011, FRXP closed on $15.7MM in a Series B equity round of financing. These funds will be used for working capital and to partially fund FRXP's first commercial scale production facility and to further expand the company by attracting highly skilled professionals from different disciplines. This all will enable FRXP to fully commercialize a range of products that are unique, environmentally friendly, patent protected and cost effective at a most opportune time.