

Eco-Friendly Fire Prevention

New Developments in Flame Retardants

The electrical & electronics industry is increasingly requiring eco-friendly flame retardant solutions for the plastics used in these sectors. Halogen-free and polymeric flame retardants are driving innovation here.

Flame retardants are undoubtedly the plastics additives with the highest growth rate and by far the most attractive research and development prospects. The total market for flame retardants is estimated to grow from its present consumption of more than 2 million t at annual growth rates of 5% to a value of 7.15 billion USD by 2021 [1]. This growth, which is higher than the growth rate for plastics themselves, can be attributed to stricter guidelines for certain applications, e.g. in the transport sector, as well as to statutory requirements such as WEEE (EU Waste Electrical and Electronic Equipment Directive), RoHS (EU Restrictions on Hazardous Substances Directive) and the EU REACH regulation (Registration, Evaluation, Authorization, and Restriction of Chemicals). The response of the flame retardant producers has been new products with a high safety standard, e.g. polymeric bromine compounds and especially halogen-free products. The enormous increase in patents and patent applications relating to flame-retardant polymers since 2008 clearly shows this (Fig. 1). In the case of halogen-free flame retardants, applications involving phosphorus-containing and inorganic (aluminum hydroxide and magnesium hydroxide) components are leading the way. A majority of the researched applications today are in Chinese (2013: 60.8%), followed by Japanese (17.5%) and also Korean (6.7%). Far fewer applications are in English (10.7%) and German (2.8%), although the leading flame retardant producers are based outside Asia.

Over the last few years, new products, in particular, have been creating opportunities in the market for replacing traditional products and developing new ap-



In the electrical & electronics industry, only flame-retardant plastics are used (figure: 123rf © dvarg)

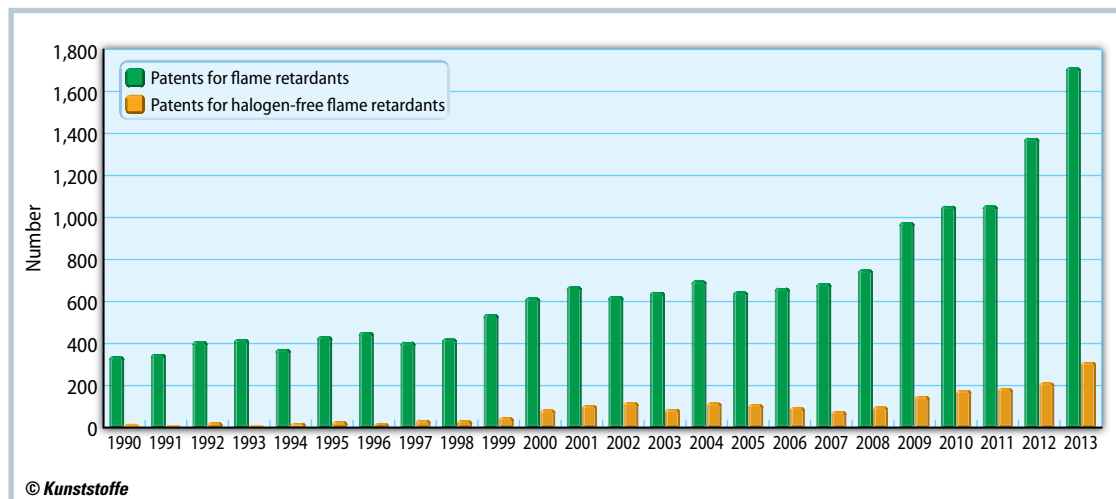


Fig. 1. Patents and patent applications for flame-retardant plastics (figure: LBF)

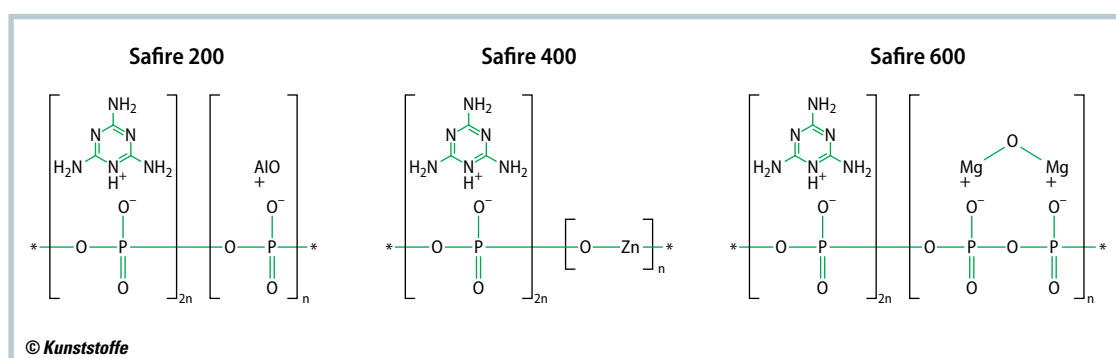


Fig. 2. Chemical structure of melamine metal phosphates in the Safire product group (figure: LBF)

applications. A main area of use for flame-retardant plastics is the electrical & electronics market (**Title figure**). In the following examples, reference is therefore made mainly to test methods in this segment, e.g. UL 94 V, Comparative Tracking Index (CTI), and Glow Wire Ignition Temperature (GWIT).

Renaissance of Polyamides

Among flame-retardant engineering plastics, polyamides are the most attractive market, with 50% of formulations expected to be halogen-free in the future [2]. Glass fiber-reinforced polyamide 66 is the main application, especially in the E&E industry. The long-established Exolit OP flame retardants (manufacturer: Clariant SE, Muttenz, Switzerland), which are based on organic phosphinates (mainly aluminum diethyl phosphinate, abbreviated to DEPAL), are frequently used in combination with melamine polyphosphate, abbreviated to MPP (e.g. Melapur200, BASF SE, Ludwigshafen, Germany, or Budit3141, Chemische Fabrik Budenheim KG, Budenheim, Germany). Alternative melamine derivatives that are

claimed to offer technical and price advantages over MPP are now also available on the market as flame retardant components.

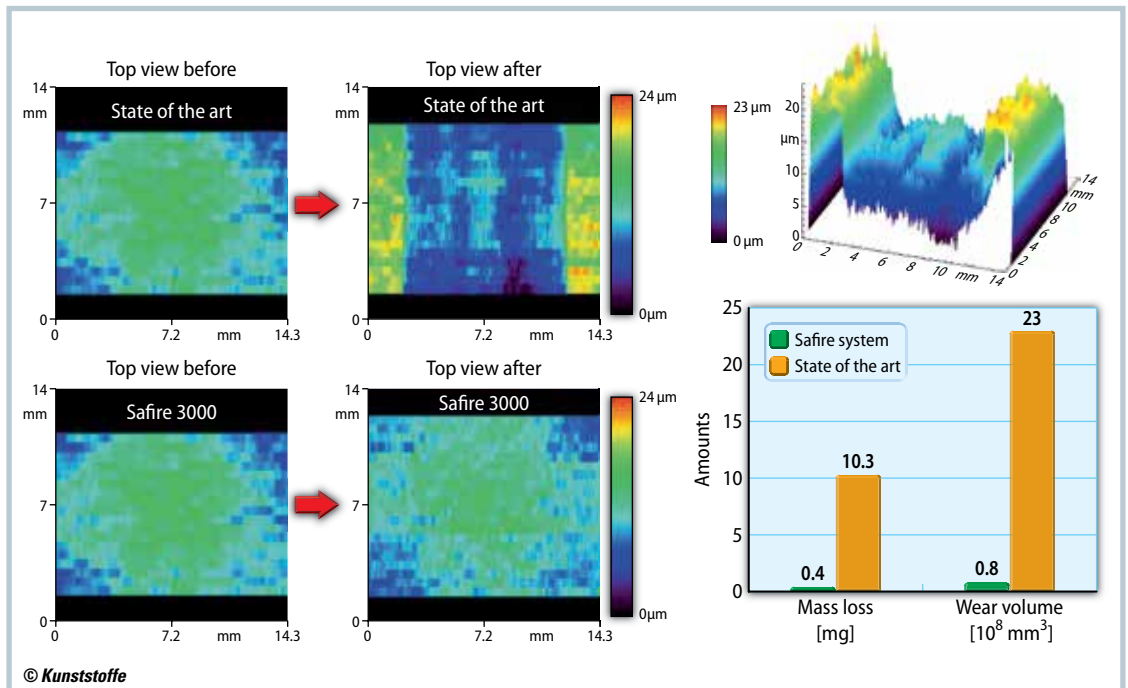
Products in the Safire range (Floridienne Chimie SA, Ath, Belgium), which represent various melamine metal phosphates (**Fig. 2**), particularly Safire 400 (in combination with small amounts of zinc borate), act synergistically with DEPAL to give an improved flame retardant effect over MPP/DEPAL. For example, at 15% total concentration, UL 94 V-0 with 0.8 mm and a CTI of 600 V are achieved. In addition, smoke density is significantly reduced, so that, for example, in the case of EN 45545-2 (transport standard) the category HL3 can be fulfilled [3, 4]. Safire 600 has very high thermal stability (> 350 °C) and is therefore suitable as a component for (semi)aromatic polyamides. Another synergistic alternative to MPP with organic phosphinates is MCA PPM Triazine HF (MCA Technologies GmbH, Biel-Benken, Switzerland). Research carried out at the Fraunhofer Institute for Structural Durability and System Reliability (Fraunhofer LBF) in Darmstadt,

Germany, showed that, in the case of glass fiber-reinforced PA6, the addition of MCA to DEPAL leads to very short burning times. The addition of zinc stannate (Flamtard S, WilliamBlythe Ltd., Lancashire, UK) to phosphinates can decrease smoke density [5] and help reduce corrosion in processing machinery [6].

Clariant, too, has launched Exolit OP1400, a new synergistic combination with DEPAL that offers increased thermal stability and so permits higher output in the injection molding process [7].

Another Safire development (Safire 3000) is one of the first solutions to provide effective flame retardancy for polyamide66 without the use of organic phosphinates. The composition of Safire3000 is a combination of the Safire products shown with a DOPO derivative (DOPO = 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide). This new flame retardant combination causes very little or no corrosion of processing machinery ([8], **Fig. 3**). A fundamental problem with other halogenated and halogen-free phosphorus-containing flame retardants has thus been solved. A dimeric DOPO derivative with equally high ther- ➤

Fig. 3. Corrosion testing of halogen-free flame-retardant-modified glass fiber-reinforced polyamide 66 (figure: LBF)



mal stability is also being developed under the name XP-7866 (Albemarle Corporation, Baton Rouge, USA).

Polyesters with Many Flame Retardant Options

For polyesters used in E&E applications, primarily PBT, organic phosphinates in combination with nitrogen compounds are also first choice. Here, users have even more varied options for effective flame retardant combinations and optimized formulations. The previous product of choice, Exolit OP1240, can be formulated more efficiently by the use of various synergists such as MPP or nano metaloxides or at lower cost with melamine cyanurate (e.g. Melapur MC, BASF) or boehmite (e.g. Apyral AOH, Nabaltec) [9]. Safire 600 has a better UL 94V-0 rating (1.6 mm after heat aging) and CTI values (575V) than MPP [4]. Another alternative is to add polyphosphonates (Nofia, manufacturer: FRX Polymers, Chelmsford, USA), which can increase the GWIT value in particular [9]. Clariant itself is also marketing a new synergistic combination (not described in detail) under the name Exolit OP 1260, which in 30% GF PBT achieves UL 94V-0 at 0.4mm and also provides very good flame retardant properties (CTI 575V, GWIT 775°C), very good flowability, and improved mechanical properties (Fig. 4)

[10]. With other nitrogen synergists used for polyamide such as MCA PPM Triazine, the total concentration of flame retardant required to attain the UL 94V-0 classification can also be reduced (Fig. 5).

Good flame retardancy in glass fiber-reinforced PBT is also obtained using alternative chemistries based on inorganic phosphinates, e.g. aluminum hypophosphite, marketed under the trade-name Phoslite (Italmatch Chemicals S.p.A., Genoa, Italy) [11, 12]. In combination with a nitrogen synergist (Phoslite B65 AM) better CTI values (> 600V) are obtained than with organic phosphinates but at the expense of poorer performance in the UL 94V test.

For flame-retardant PA and PBT fibers, cocondensates with phosphorus-containing diacids have been the standard solution for many years (Trevira CS, Toyobo Heim). At the present time, development is moving in the direction of mixing PET or PA polymers directly with a phosphorus-containing polymer before the spinning process. The products being used are, for example, Ukanol FR80 (Schil+Seilacher GmbH, Hamburg, Germany) or Nofia (FRX-Polymers). This process avoids more costly cocondensation and makes the production of flame-retardant fibers far more flexible. A first example was the production of a flame-retardant polyamide fiber by Ems-Chemie Holding AG, Domat-Ems, Switzerland. Ukanol

FR80 is also an excellent flame retardant for hot melt adhesives.

Alternatives for Polycarbonate and Blends

For polycarbonate and polycarbonate blends, the aim is to replace bisphenol A-containing phosphate flame retardants. One possibility is to use a solid phosphate based on 4,4'-dihydroxybiphenyl, marketed under the name ADK Stab FP 800 (manufacturer: Adeka Corp., supplier: Adeka-Palmarole SAS, Fig. 5). Thanks to the biphenyl unit and oligomeric structure, the product has very good thermal stability and low volatility. It also enables the transparency of polycarbonate to be retained. To achieve UL 94V-0 (0.8mm), a concentration of only 3.5% (+ 0.3% PTFE) is required. In PC+ABS blends, better mechanical properties and higher heat resistance are obtained at a slightly lower concentration than with bisphenol A-based flame retardant [13].

Italmatch supplies Phoslite B85CX or, as a masterbatch, Phoslite MB9645 for polycarbonate. Phoslite B85CX achieves UL 94V-0 at a concentration of 5 to 8%; the concentration can be reduced in the presence of an antidripping agent such as PTFE [11]. An alternative flame retardant for PC and PC blends is SPB-100 (manufacturer: Otsuka Chemical Co., supplier: Hebron S.A., Barcelona, Spain), a polymeric

phenoxyphosphazene with very low water absorption and high thermal stability.

FRX Polymers markets its own transparent phosphonate copolymer, Nofia CO3000, which achieves a UL 94V-0 classification, even at 0.4 mm, and is transparent [14].

Polyolefins with Low Flame Retardant Concentration

For polypropylene applications, two flammability ratings are of interest (UL 94V-2 and UL 94V-0). In both cases, the aim is the same, i.e. to minimize the required flame retardant loading through the use of synergistic systems.

A tried and trusted halogen-free flame retardant system for polypropylene over many years has been ammonium polyphosphate (e.g. Exolit AP, manufacturer: Clariant or Buditec, manufacturer: Budenheim Chemische Fabrik), frequently used in combination with a C donor, e.g. pentaerythritol. Generally speaking, an addition of about 30% is necessary to achieve UL 94V-0. The addition of MCA PPM Triazine HF to APP (e.g. in the ratio 1:4) enables the total concentration to be reduced, while at the same time leading to shorter burning times and lower smoke densities. One reason for the improved action is the presence of the morpholine group, which increases the intumescence effect and char formation. Other products that permit a lower concentration based on APP are e.g. Exolit AP 766 or Buditec 3167.

An alternative in PP is ADK STAB FP-2200, which is described as a phosphate ester-ZnO mixture. With an 18% addition of this product (plus 0.2% PTFE

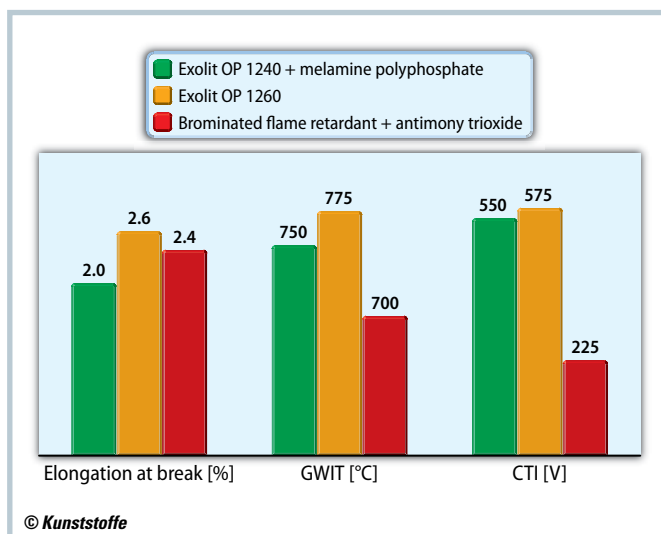


Fig. 4. Properties of halogen-free flame-retardant-modified PBT (figure: Clariant)

antidripping agent), UL 94V-0 is achieved. The reason for this is very stable char formation. This system also offers the advantages of minimal discoloration during aging and very good light stability in light-stabilized formulations (Fig. 6) [13].

Another possible alternative flame retardant for PP and other polyolefins is a pyrophosphoric acid salt available under the name Zuran 808.3 (Chitec Technologies, supplied by Raimund Müller GmbH & Co KG, Prisdorf, Germany).

In 1999, Ciba Specialty Chemicals (now BASF SE) introduced a revolutionary flame retardant known as Flamestab NOR 116 (Fig. 5) for polypropylene and polyolefins in the form of films and fibers [15]. Its effect is based on very rapid polymer degradation in a fire, as a result of which the polymer retreats from the flame. As a compound based on sterically

hindered amines (HALS) structure, Flamestab NOR 116 contributes to the light stability and long-term thermal stability of the products.

A possible alternative for fibers, non-wovens, and thin films is Aflammit PCO 900 (previously Aflammit TL 1260, manufacturer: Thor GmbH, Speyer), a cyclic phosphonate. Other flame retardants produced by Thor are based on ethylenediamine phosphate (Aflammit PCO 123, PCO 234) and other P/N combinations not described in detail (Aflammit PCO 700, PCO 800).

Another approach is to combine hypophosphites with very small amounts of halogens (Phoslite B631C). With a total concentration of 0.1% halogen, a rating of UL 94V2 (1.6 mm) is shown for an addition of 1% Phoslite. For copolymers with increasing PE content or with fillers and glass fibers, »

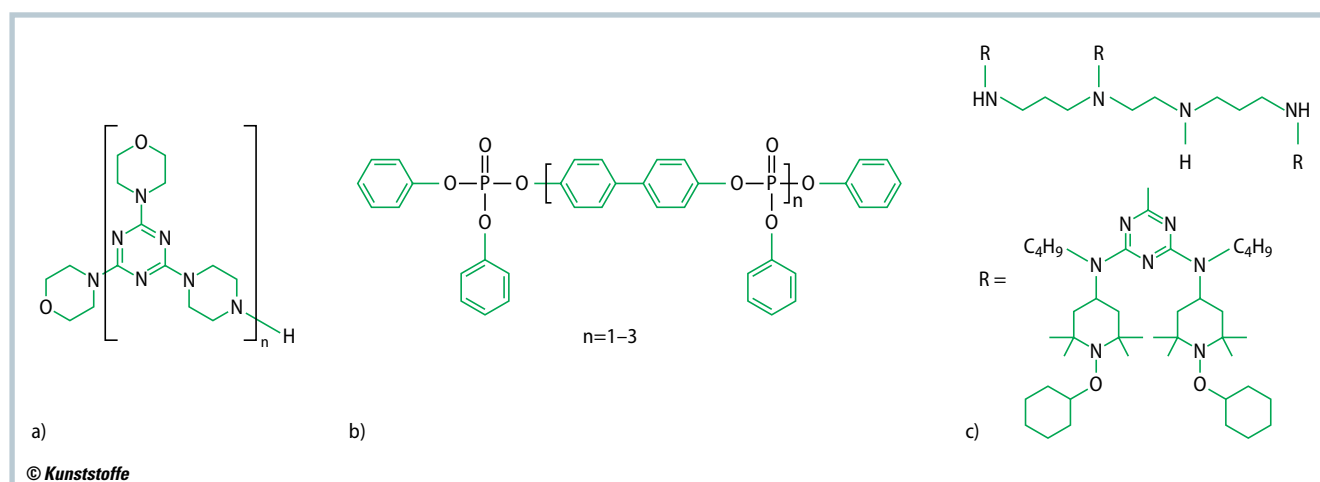


Fig. 5. Chemical structure of nitrogen-based flame retardants: MCA PPM Triazine HF (a), ADK STAB FP-800 (b) and Flamestab NOR 116 (c) (figure: LBF)

the loading has to be raised somewhat (up to 3%) [16].

Polyethylene remains the domain of inorganic flame retardants such as aluminum hydroxide. Non-inorganic flame retardants that can be used include, for example, ADK STAB FP2200 (concentration above 30%).

With EVA copolymers, it has been shown that product improvements, especially in terms of elongation value, can be obtained by using silane-modified aluminum hydroxide grades (e.g. Apyral 40HS1, manufacturer: Nabaltec AG, Schwandorf) [17]. In addition, hydrophobic modification reduces the effect of aging in a hot humid environment. The flame-retardant effect is also improved by combining ATH with small amounts of hypophosphites (Phoslite B85 AX) [13].

The challenge posed by polypropylene (and other polyolefins) of achieving a rating of UL 94V-0 (1.6mm) with further reduced flame retardant loading (<10%) may possibly be solved by a new system, developed at the Fraunhofer LBF, which is based on imides as a radical source in combination with com-

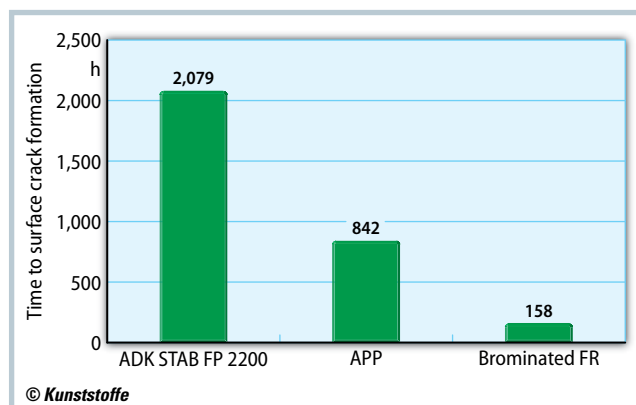


Fig. 6. Light stability of flame-retardant-modified PP formulations (figure: Adeka-Palmarole)

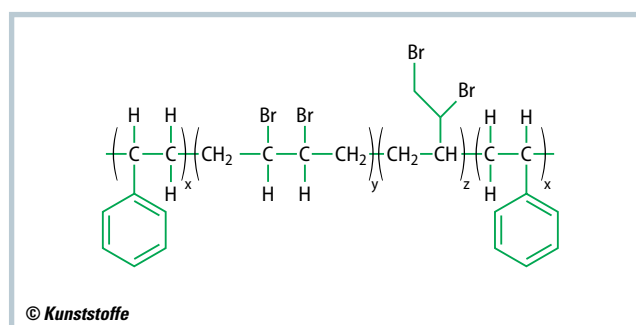


Fig. 7. Chemical structure of brominated block copolymers (figure: LBF)

mercially available phosphorus compounds [18].

New Solutions for Polystyrene Foam

In 2008, hexabromocyclododecane (HBCD) was included in the list of "Substances of Very High Concern" by the European Chemical Agency because of its persistent and bioaccumulative properties and has to be replaced on the market by the end of 2015. The capacity for this flame retardant was about 20,000t/a and its main area of application was expanded (EPS) and extruded (XPS) polystyrene foam. Following the construction of industrial capacities at Albemarle, ICL-CP und Great Lakes, the alternative currently being launched on the market is a block copolymer of polystyrene and brominated polybutadiene (BrPBPS) (Fig. 7) [19]. Because of its polymeric structure, this product has no potential for bioaccumulation. Compared with HBCD, the quantity required is only slightly higher to obtain the same flame retardancy. Because of the styrene content in the BrPBPS, it has very good compatibility with polystyrene. Virtually the same decomposition temperature and the aliphatically bonded bromide guarantee good flame retardancy performance.

Flame retardant mixtures with high efficacy in XPS have also been described

in various patents [20 to 22]. These rely on the synergistic interaction of an organophosphorus component having a defined decomposition temperature with a sulfur-containing compound acting in the gas phase via S-S groups [23].

Other Thermoplastics

Depending on the surface modification of aluminum hydroxide, secondary properties to flame retardancy can be influenced in different ways. With silicone elastomers, particularly good elongation values are obtained, interestingly enough, with an unmodified product (Apyral 40CD, manufacturer: Nabaltec), while a vinyl silane-modified ATH (Apyral 40VS1) provides improved tensile strength. In Apyral 40HS1, an organosilane without polar functionalization is used for surface modification. This enables very high elongation values to be obtained, e.g. in thermoplastic polyurethanes (TPU). The necessary flame retardant concentration to achieve UL 94V-0 (3mm) is 60% [24].

Epoxy Resins for Lightweight Composite Applications

Epoxy resins in glass fiber-reinforced composites for circuit boards or as a potting material for electrical and elec-

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Flame retardant	UL 94 [4 mm]	P-content [%]	FR-content [%]	T _g [°C]
DOPO	V0	1.6	11.2	155
DOPO + MPP (1 :1)	V0	2.1	6.5 + 6.5	157
DOPO + 30 % AlOOH	V0	0.4	2.8	168
DXM-11	V0	1.0	8.7	174
DXM-11 + MPP (1:1)	V0	0.9	5.2 + 5.2	179
DXM-11 + 30 % AlOOH	V0	0.8	7.0	171

Table 1. Synergistic flame retardant mixtures in novolac epoxy resin (DEN 438 Dow/DICY)

Flame retardant	UL 94 [4 mm]	P-content [%]	FR-content [%]	T _g [°C]
DOPO	n.c.	3.0	20.9	93
DOPO + MPP (1 :1)	V0	3.0	9.5 + 9.5	110
DOPO + 30 % AlOOH	V0	1.5	10.5	113
DXM-11	V0	2.25	28.2	137
DXM-11 + MPP (1:1)	V0	1.75	7.9 + 7.9	143
DXM-11 + 15 % MPP	V0	0.3	3.5	140
DXM-11 + 30 % AlOOH	V0	1.25	14.5	139

Table 2. Synergistic flame retardant mixtures in epoxy resin (DGEBA/DICY)

tronic components have always had to be flame-retardant-modified in case of possible short circuits or malfunctions. Tetrabromobisphenol A (TBBPA) has traditionally been used, and continues to be so. This is added to the epoxy resin in a so-called pre-formulation and is integrated into the thermoset network during curing. Some years ago, the Japanese company Sanko Co. Ltd, Osaka launched DOPO (6H-Dibenz[*c,e*][1,2]oxaphosphorin, 6-oxide) as a halogen-free alternative. DOPO is also bonded to the epoxy resin via a pre-formulation but, unlike with TBBPA, monofunctionally, which leads to a sharp reduction in glass transition temperature (T_g). Generally speaking, however, the flame retardant market for circuit boards is declining, since, to comply with the RoHS directive, lead-free solder must be used for circuit board manufacture in Europe. This gives rise to higher T_g requirements (from 135 °C for lead-containing solder to 170 °C for lead-free solder). These requirements are met through the use of higher-crosslinking novolak resins and sometimes also novolak curing agents. Because of the intrinsic flame retardancy of the novolaks (short-chain phenolic resins), considerably less flame retardant is needed. In addition, it has been found that DOPO or its derivatives show interesting synergistic effects with mineral flame retardants (ATH, boehmite and MPP), which offers further potential to reduce the necessary reactive flame retardant component (**Table 1**).

Besides DOPO itself, the adduct of DOPO and benzoquinone (DOPO-HQ) is also used as a bifunctional reactive

flame retardant for epoxy resin formulations, especially for encapsulation of electronic components. Besides DOPO and DOPO-HQ, other commercially available reactive phosphorus-containing flame retardants for epoxy resins are available: Fyrol PMP (ICL-CP) as a flame retardant and curing agent and phosphorus-rich Exolit EP150 and EP200 grades (Clariant). Tetrakis (DOPO-methyl) bisphenol A has been patented as a DOPO-rich reactive flame retardant with opportunities for launching on the Asian market [25].

As part of the effort to construct more lightweight, energy-saving transport vehicles, more and more fiber-reinforced composites are entering this market. For this reason, flame-retardant modification of these lightweight components is gaining increasing importance. Initial publications show flame-retardant modification of prepregs for aircraft interiors based on a synergistic flame retardant formulation of commercially available DOPO-containing novolak resins (Polydis VP products from Schill+Seilacher Struktol GmbH), and on boehmite. Highly efficient flame retardancy is attained by combining the melamine salt of DOPO acid (DXM-11, Krems Chemie Chemical Services AG) with boehmite or MPP (**Tables 1 and 2**) [26, 27].

Polyurethane Foams with Reactive Products

Polyurethane flexible foams are traditionally flame-retardant-modified with chloroalkyl phosphates, which serve as plasticizers at the same time. While

tris(2-chloroethyl) phosphate (TCEP) is classified as carcinogenic, mutagenic, and toxic, and has been listed as a “substance of very high concern” since 2010, tris(monochloropropyl) phosphate (TCPP) is today the predominant flame retardant used in PU flexible foams. However, because of its volatility, it has particular drawbacks, such as fogging. As an alternative flame retardant for PU foams, Clariant has launched a halogen-free, polymeric phosphate (Exolit OP 560) on the market. Exolit OP 560 additionally has reactive groups so that during curing it reacts into the polyurethane and forms part of the polymer network. In this way, fogging is avoided. Recently, new efficient DOPO-based flame retardants for PU foams have been described, such as the ethylene-bridged DOPO amidate, which achieves an HF-1 rating in the UL 94 HB test at a concentration of only 5 % [28, 29].

Outlook

Generally speaking, the requirements for flame-retardant-modified plastics are continuing to move in the direction of more effective flame retardants that permit lower flame retardant loading and at the same time are toxicologically safe. These can be oligomeric or polymeric flame retardant additives or, as is frequently the case with thermosets, reactive flame retardants that are integrated into the polymer network. In both cases, migration is successfully prevented and compatibility with the protected polymers can be increased. ■