Avoiding Filter Effects of Flame Retardants

Completely Halogen-Free Flame Retardancy of Epoxy-Fiber Composite Components

To meet stringent flame retardancy demands of areas such as transportation and electronics, components based on thermosets increasingly require a soluble, non-powder flame retardant (FR) due to low layer thicknesses in the final product or due to liquid processing methods. Two flame-retardants developed by Clariant meet these requirements.

Due to their versatile and unique properties, plastics are now used in many areas of daily life and it is impossible to imagine life without them. In addition to packaging, construction and transport applications, they are also abundant in electrical and electronic (E & E) applications. Their use for lightweight construction materials is essential for successful fuel savings, particularly due to the increased attention paid to climate change and the associated need to reduce CO_2 emissions. Examples of such lightweight materials are interior panels for trains and aircrafts and, in recent years, applications emerging in the automotive industry as part of e-mobility.

However, due to their chemical composition, in particular their high carbon and hydrogen content, most plastics are highly flammable. Flame retardancy is a necessary prerequisite for many applications [1], although there are some plastics, such as polytetrafluoroethylene (PTFE) and phenolic resins, which are inherently flame retardant but cannot be used in every application. They are often used in the above-mentioned applications without us knowing it.

Chlorinated or mainly brominated flame retardants, which have been used for a long time, are still frequently used as flame retardants for thermosets. They are often combined with the synergist diantimony trioxide (ATO). However, these flame retardants have been the subject of criticism for some time.

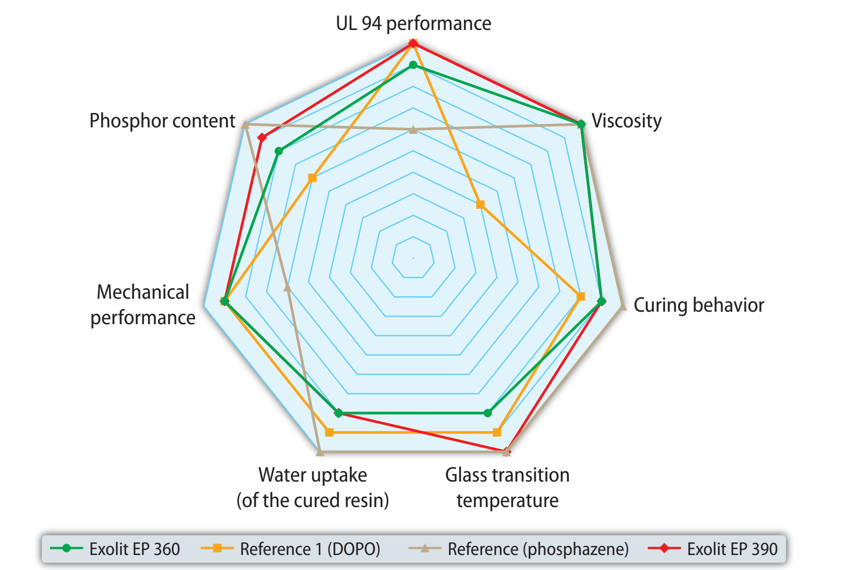

Fig. 1. Basic properties of the Exolit flame retardants compared with a DOPO- and a phosphazene-based reference in each case: the FR achieve similar or even better values than the references for all properties Source: Clariant; graphic: © Hanser

In recent decades, there has been an increasing trend to replace halogenated flame retardants with more sustainable non-halogenated products, thereby increasing their market share [2]. A successful example is phosphorus-based halogen-free flame retardants.

Halogen-Free Flame Retardants for Fiber Composites

The use of plastics based on thermoplastics or thermosets, such as epoxy resins as a matrix in combination with fibers, allows the realization of high stress-withstanding fiber composites which can be used for demanding applications. Due to their low shrinkage during curing, high resistance to chemicals and corrosion, high thermal stability, good electrical insulation properties, good adhesion, and compatibility with various materials, thermosets such as epoxy resins are used particularly frequently for electronic or high-performance applications. In addition, the possibility of combining different epoxy resins with a large number of different har- »

Component	Unit	Mixture 1	Mixture 2	Mixture 3	Mixture 4	Mixture 5 (reference system)
Exolit EP 360	g	31.7	0	62.5	0	0
Exolit EP 390	g	0	22.8	0	43.5	0
Reference (1)	g	0	0	0	0	100
DGEBA (2)	g	68.3	77.2	37.5	56.5	0
Sum of components	g	100	100	100	100	100
Phosphor content	wt. %	2.0	2.0	4.0	4.0	4.0
Viscosity (at 45 °C, 5 s^{-1})	mPa · s	1000	5800	100,000	41,000	1,000,000,000
Viscosity (at 80 °C, 5 s^{-1})	mPa · s	370	250	1900	900	100,000

Legend: (1) commercially available, multifunctional, solvent free and with DOPO modified epoxy resin, (2) DGEBA epoxy resin with 1200 mPa·s at 45 °C and 80 mPa·s at 80 °C

Table 1. Comparison of different blends of an epoxy resin made from DGEBA with different FR additions Source: Clariant

deners offers a wide range of achievable material parameters that satisfy the most diverse requirements [2].

Carbon fibers or glass fibers are mainly used as reinforcement. The resulting composite materials are used instead of conventional steel or aluminum components to save weight. This makes them particularly attractive for transport applications. However, glass fiber reinforced composites are also used in the electrical industry, for example for printed circuit boards (PCB). Epoxy resin systems are often used as matrix resins and are widely used in modern electronic devices Frequent areas of application are consumer and automotive electronics, but also aerospace and defense. In view of the upcoming transition to future 5G communication systems, it is important to further optimize the performance of the composite materials. Here, too, FR play a special role.

Fiber-reinforced composites can be produced by a wide variety of processing methods. Some of the common processing methods for thermosets allow the processing of insoluble, classic powdery flame retardants such as aluminum trihydroxide (ATH), ammonium polyphosphate (APP) or aluminum diethyl phosphinate (DEPAL). Examples for these processes are the classical wet lamination (hand lamination), the prepreg process, as well as processes based on pultrusion, winding, sheet mold molding (SMC) and bulk molding (BMC).

Powdered Flame Retardants Are Unsuitable

If more complex components cannot be produced with the above processes, or if a higher number of units are to be produced in a shorter time, other processes are of interest. If components are produced using (vacuum) infusion processes, via injection techniques such as RTM (Resin Transfer Molding), by LCM (Liquid Compression Molding) or even DFCM (Dynamic Fluid Compression Molding), powdered FR are hardly or not at all processable. Since the fibers are usually placed before the resin flows or is pressed through them, the FR particles are filtered out (filter effect) and thus distributed unevenly, resulting in inconsistent, unacceptable performance.

The currently available phosphorus-based flame retardants, which in principle can be used for liquid processing, are, for example, phosphazenes or dihydro oxa phosphaphenanthrene oxide (DOPO)-based flame retardants. However, depending on the application and the processing parameters required, their use may be limited or impossible. In some cases, phosphazenes do not show sufficient solubility in the carrier resin or compatibility, and the DOPO-modified resins have a very high viscosity when used undiluted with a moderate phosphorus content.

Alternatives for DOPO and Phosphazene

Here, the halogen-free flame retardants Exolit EP 360 and Exolit EP 390 from Clariant AG, Pratteln, Switzerland, recently developed for epoxy resin applications, offer significant advantages. As can be seen in **Figure 1**, above all they offer a comparatively moderate viscosity with a high phosphorus content, little influence on the glass transition temperature (Tg) and curing behavior, and good flame-retardant performance (UL-94 test, V0 rating). Their broad epoxy resin compatibility makes the two new products readily miscible with most epoxy resins after brief prior heating, and homogeneous, particle-free systems are achieved.

Figure 2, left, shows a cured, fiber-free epoxy resin sample, which contains ATH as FR 40 phr (parts per hundred resin). The resin is clearly clouded by the FR particles. If a composite is manufactured by an infusion technique, the FR particles are filtered out by the fibers, and no uniform, fire-safe components can be produced. On the right-hand side, **Figure 2**, a comparison shows another sample where Exolit EP 360 was added in a dosage of 100 phr, more than twice as high. The cured sample is crystal clear, and no particles are present which could be filtered out.

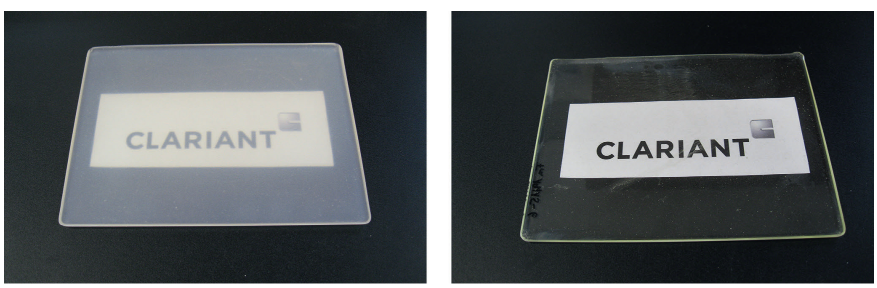

Fig. 2. The cured epoxy resin with 40 phr ATH (left) shows strong opacity due to the added FR particles. The cured epoxy resin with 100 phr Exolit EP 360 (right), on the other hand, shows no opacity © Clariant

Component	Unit	System 1	System 2	System 3	System 4
DGEBA [EEW 180 g/mol]	g	48.8	0	44.9	59.2
Epoxy Novolac [EEW 185 g/mol]	g	0	63.1	0	0
Exolit EP 360 [EEW 510 g/mol]	g	46.9	0	46.8	0
Exolit EP 390 [EEW >3000 g/mol]	g	0	32.6	0	32.6
Dicyandiamide (DICY) (1)	g	4.3	4.3	0	0
TETA	g	0	0	8.3	8.2
Total	g	100	100	100	100
Result					
Phosphor content	wt. %	3.0	3.0	3.0	3.0
UL 94 rating (at 3 mm wall thickness) (2)		V 0 (6 s)	V 0 (20 s)	V 0 (4 s)	V 0 (12 s)
Tg (max. tan δ)	°C	130	160	108	105

*Legend: *Epoxid equivalent weight; (1) dicyandiamide (DICY) was used in combination with an urea catalyst; (5) sum burning time of 5 samples in seconds*

Table 2. Comparison of different systems of epoxy resin, hardener and Exolit FR Source: Clariant

The epoxy groups (oxirane groups) present in Exolit EP 360 integrate the FR into the resin matrix, making it an integral part of it. Exolit EP 390 is not significantly reactive. However, its polymer character also means that, unlike smaller molecules such as phosphate esters or even phosphazenes (depending on the polymer), the FR does not escape from the material, as the migration behavior is minimized by the increased molar mass and a compatible chemical structure. Their versatility allows both products to be used in formulations for traditional processing (prepreg, winding) as well as for infusion and RTM processes where fire, smoke and toxicity criteria must be met.

By carefully optimizing the resin formulation and processing temperature, low viscosity systems can be achieved. **Table 1** shows five different mixtures consisting of FR (Exolit EP products and reference) and DGEBA (liquid standard epoxy resin), which is used to adjust a selected phosphorus content. A hardener, which often further reduces the viscosity, was not used.

Exolit EP 360 was used for formulation 1 and 3 and Exolit EP 390 for formulation 2 and 4. Formulation 5 contains a reference FR. The total phosphorus content of the first two samples was adjusted to 2 wt.% phosphorus, the last three samples to 4 wt.% phosphorus, which is already a very high load for many applications and smaller amounts are often sufficient to pass the UL-94 test (rating V0).

Lower Viscosity than with Other Flame Retardants

In formulations with other epoxy resins, Exolit EP 390 shows a lower viscosity than formulations with Exolit EP 360 at a comparable phosphorus content and 80 °C. This is because Exolit EP 390 itself has a higher phosphorus content and less is needed for the same phosphorus content. All formulations with the two new products have a significantly lower viscosity at 45 °C and 80 °C than the reference.

The amount of Exolit EP 360 or EP 390 required to pass a flame retardancy test depends largely on the epoxy resin and hardener (higher aliphatic content = higher flammability), the required flame retardant performance, and the overall flame retardant system used in the formulation. **Table 2** shows four different systems consisting of epoxy resin, hardener and Exolit EP-FR. The first two systems were cured with the powdered hardener dicyandiamide (DICY) and the last two with the liquid aliphatic amine triethylenetetramine (TETA).

V-0 Rating Can Be Easily Achieved

The rating UL 94, V-0 (3 mm) can be easily achieved with all systems at a dosage of 3 wt.% phosphorus. For system optimization and cost reduction, the phosphorus content can be reduced even further with the same flame retardancy rating. The sum of the afterburn times between 4 and 20 s listed in **Table 2** shows that a further reduction of the FR content is possible until the maximum UL 94, V-0 limit of 50 s is reached. The glass transition temperature (Tg) is only moderately to slightly influenced and the Tg reduction is in a range that can also be observed in DOPO based systems. The formulations were tested after complete curing, no reinforcement was used. Adjustments are necessary for fiber-reinforced composites.

The tests show, that the two new flame retardants Exolit EP 360 and Exolit EP 390 are very good for liquid, filler-free processing of epoxy resin systems for the most demanding applications. In addition to a comparatively low viscosity in the formulation, they easily pass the UL-94 test with the V0 rating. Furthermore, the products can be used in combination with other co-flame retardants to meet demanding flame retardancy criteria, as required in transport applications (EN 45545, FAR 25.853; GB/T 31467.3). These formulations are still under development. ■

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