

Flame-retardant Epoxy Resins

Flame Retardants. While phosphorus-based flame retardants in epoxy resins often showed inadequate processing and material properties, recent work has succeeded in developing phosphorus-containing resins, curing agents and additives with significantly improved properties. Based on an organophosphorus compound, halogen-free, flame resistant epoxy resin systems can now be produced with good mechanical properties.

There is no let up in the trend towards using high-performance glass, carbon and aramid fibre-based composites for structural and function purposes. The range extends from structural elements in aeronautical and automotive engineering, through interior trim, to circuit boards for the electronics industry.

To meet the variety of mechanical, thermal and electrical requirements, epoxy resins (EP), because of their versatility, are used in a range of different applications. The products manufactured are usually subject to specific fire safety regulations, making it necessary to use flame retardants. At the same time, the toxicological properties of the flame retardants and the recycling of products containing flame retardants are subject to

ever close scrutiny. Depending on the application of the final product, application-specific fire-protection standards must be met.

Flame Retardants for Epoxy Resins

Selection of the flame retardants for fibre composites must take into account not only the FST (Fire Smoke Toxicity) requirements, but also the processing properties of the matrix system and the required mechanical properties of the part. On one hand, there are specific flame protection requirements for different applications (e. g. aeronautical engineering for structural elements or interior parts). (The most important test standard for interior materials in aeroplanes is the FAA standard FAR 25.853). On the other hand the starting material and the final com-

posite part must be appropriate for the subsequent mechanical requirements. The difficulty in producing flame-retardant fibre composites with the wet-resin technology that are widely used (resin infusion and resin transfer moulding) lies in the fact that the resin systems require a low viscosity (<100 mPas) for infiltration, so that they do not displace the fibre layers. In the case of insoluble additives, particle sizes less than 5 µm are required to avoid filtering out of the particles. That means that all flame retardants that cause a viscosity increase or have particle sizes greater than 5 µm cannot be used. In this case, flame retardants that can be homogeneously mixed with epoxy resins offer clear advantages.

Until now, reactive halogenated products were mainly used for EP systems, which hardly affect the other material properties, but are not approved in civil

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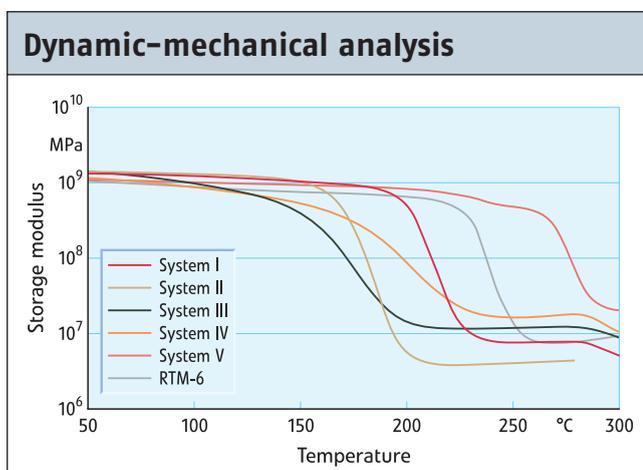


Fig. 1. Measurement of the shear modulus as a function of temperature gives good values for epoxy resin systems with reactive phosphorus-containing flame retardants

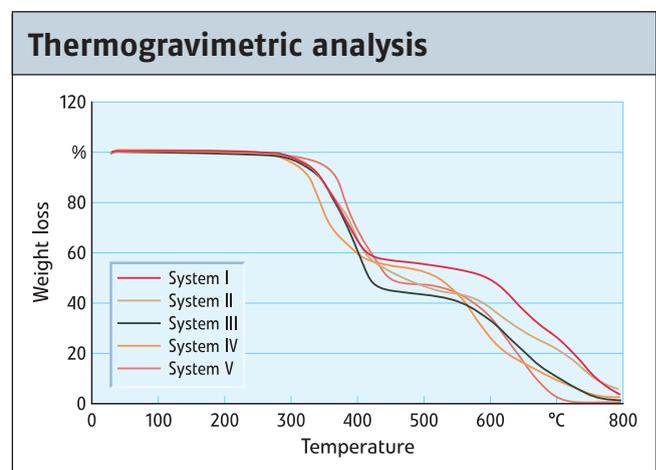


Fig. 2. Epoxy resins with the reactive phosphorus-containing flame retardants Polydis PD3710 (DOPD) are stable against migration

aviation because they liberate large quantities of toxic fumes in the event of a fire. Therefore either epoxy resins with intrinsic flame protection, e. g. phenolic resins and cyanate esters, or flame retardant systems that meet the high material specifications should be used [1]. A particularly interesting class in this regard are organophosphorus-based flame retardants.

All solid plastics burn if the flammable gases formed during thermal decomposition react with atmospheric oxygen in the flame to generate sufficient heat to maintain the thermal decomposition of the plastic. The fire is extinguished when insufficient heat is developed, or when the heat feedback to the solid is inhibited [2].

A general distinction should be made between reactive and non-reactive flame retardants. Non-reactive flame retardants usually require high filler contents (≥ 50 %) in the matrix to be sufficiently active. However, this causes significant losses in mechanical properties. The trend is therefore towards flame retardants that are integrated into the thermoset network without causing any deterioration of mechanical properties.

The principle behind phosphorus-containing flame retardants is that a solid surface layer is formed, which interrupts the supply of flammable material. The degradation products of the flame retardant are transformed by heat into polyphosphoric acid, which then forms a protective layer by carbonising the polymer with the elimination of water. On the other hand, the flame retardant can additionally act in the gas phase by forming free radicals. The reasons for the high effectiveness of phosphorus-based flame retardants is that the phosphorus compound is active in the correct temperature range, can migrate to the surface of the polymer and therefore develops its activity at an early stage in the progress of the fire. The phosphorus content in the matrix should be 3 to 5 % [3, 4].

Phosphorus-based flame retardants are usually additives such as red phosphorus, ammonium polyphosphate (APP) and organo-phosphorus compounds, such as tris(chloropropyl)phosphate (TCPP), triarylphosphates and phosphinic acid derivatives [5, 6]. More rarely, reactive organophosphorus compounds, such as oxaphospholanes are used [7–9].

How Phosphorus-based Additives Work

To increase the effectiveness of phosphorus-containing flame retardants, it is nec-

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essary to produce a good leaving group in the flame retardant that can easily diffuse onto the polymer surface and become active. If the leaving group is not present, the flame-retardant effect is either poor or completely ineffective. This becomes particularly clear under intense heat (cone calorimeter). The flame retardant should also be chemically bound to the polymer matrix during the curing process so as to be stable against migration. This also applies to the reactive organophosphorus compound termed Struktol Polydis PD3710 (DOPO, manufacturer: Schill + Seilacher, Hamburg/ Germany), which, in a pre-reacted form with Novolaks as flame retardant, is already state-of-the-art for electrical laminates [10–12].

However, DOPO cannot be used directly in combination with high-performance epoxy resins, since it reacts only incompletely with them and the resin systems lose their outstanding mechanical properties. In recent developments, DOPO derivatives have been synthesised, which can meet the requirements. Although the flame-retardant properties of some DOPO grades have been known since the seventies, the mechanical properties of these systems have not been characterised, despite the fact that they are so important for the application [13–15].

Based on DOPO, a monofunctional DOPO epoxy resin, a bifunctional DOPO epoxy compound based on TGPAP (triglycidylaminophenol) and various non-reactive DOPO derivatives have been synthesised. The synthesis routes have since been optimised or newly developed in the interests of more cost effective production.

In close cooperation with the flame-retardant manufacturer Schill + Seilacher (specialty chemicals), the department of polymer materials at the University of Bayreuth/Germany, and the Institute of Industrial Chemistry at the Research Centre of Karlsruhe/Germany, it was possible to formulate flame-retardant modified single-component epoxy resin systems, which are characterised by significantly improved FST (fire smoke toxicity) characteristics. Because of the outstanding miscibility of the new flame retardant with epoxy resins, such EP systems have the advantage that they can be easily handled as single-component systems. The reactive phosphorus-containing flame retardants (EP grade) do not influence the basic viscosity of the epoxy resin systems. The flame retardants of the DOPO additive grade even reduce the viscosity of the systems. Because the flame-retardant content can be varied, the systems can be adapted to specific flame retardancy requirements. As controls, the flame retardant system V and the commercial RTM-6 were used, which are employed for primary structures in aeronautical engineering.

The studies show that the new systems (I to III) possess good to very good mechanical properties (Fig. 1, Table 1). The measured glass transition temperatures

Epoxy resins		I	II	III	IV	V	RTM-6
TGDDM		100 GT	50 GT	100 GT	100 GT	100 GT	
P-1		100 GT					
P-2			50 GT				
P-3				45 GT			
P-4					40 GT		
DDS		44 GT	44 GT	44 GT	44 GT	44 GT	
Phosphorus content	%	3	4	3	3	0	0
T _g (DMA)	°C	215	166	147	168	225	205
T _{onset} (TGA)	°C	317	315	325	311	353	–
UL 94		V0	V0	V0	V0	V1	V2
Time to ignition	s	162	236	240	–	172	130
PHRR	kW/m ²	72	65	15	–	124	168
Extinction Ds		97	45	135	–	167	370

Table 1. Properties of different epoxy resin systems containing flame retardants based on reactive phosphorus compounds

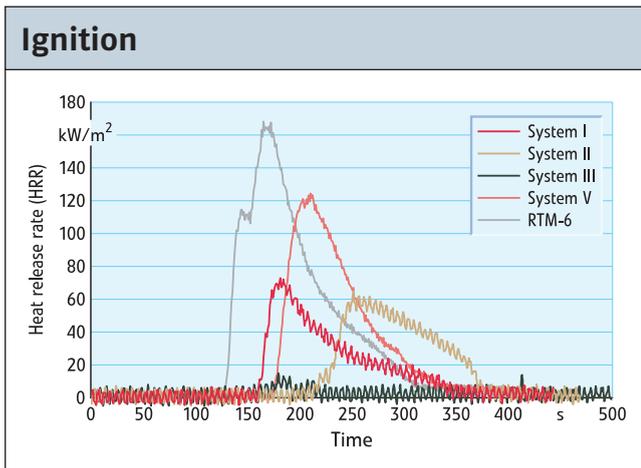


Fig. 3. Heat release rate curve as a function of time

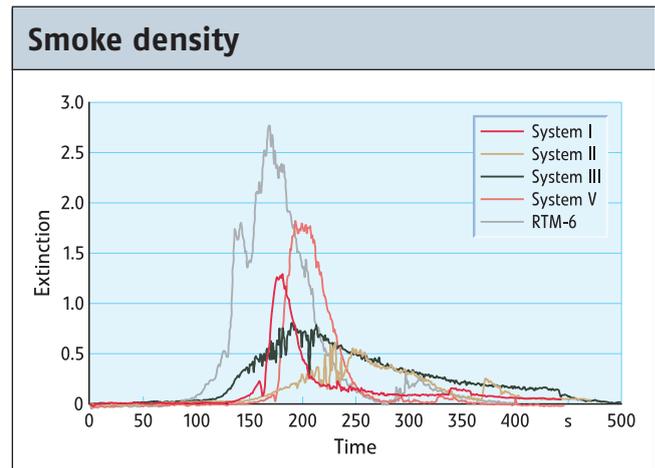


Fig. 4. Extinction/time curve

are between 147 and 215 °C. The influence of the non-reactive flame retardant on the T_g (system III and IV) can be clearly seen.

The TGA curves show that the decomposition temperatures of all flame retardant-containing systems are lower than those of the reference system V, which indicates that phosphorus-containing substances become active at an earlier stage. The non-reactive bound DOPO additive in system III remains thermally stable up to 325 °C in the matrix without outgassing, and is therefore extremely stable against migration (Fig. 2).

All the DOPO-containing systems tested according to UL 94V meet this fire protection standard and are therefore in principle suitable for use in electrical laminates (UL94 V0).

To determine the suitability of the new flame retardants even under severe heat stressing, e.g. for aeronautical applications, the three new systems were tested according to ASTM E 1345 (cone calorimeter). Under thermal stressing of 25 kW/m², two of the test laminates meet the fire safety specifications for interior trim applications according to FAR 25.583 in aircraft. Within the prescribed measurement time of 240 s, the test laminates of systems II and III do not ignite (Fig. 3). At the same time much lower smoke density than in the reference system can be observed (Fig. 4). Although the phosphorus-content of system I is adequate, much poorer fire behaviour can be observed here, since there is no effective phosphorus leaving group. The commercial system RTM-6 shows the worst fire behaviour.

All the CFRP test laminates were produced by RI technology or by pressing.

Summary

Epoxy resin systems can be rendered flame resistant by means of phosphorus-based flame retardants. Two of these systems meet both the high FST requirements and the mechanical specifications in aeronautical engineering. Further advantages of these flame retardants are the good handling during storage and processing. Storage can take place at room temperature, at which the compounds are liquid to solid, so that they can be easily dosed and stirred in. They can be easily processed by wet processes. Here, the reactive phosphorus-containing flame retardant DOPO achieve a high to very high glass transition temperature.

Because of the possible chemical variability of DOPO-based flame retardants, many promising derivatives for epoxy resin systems are conceivable. Their development will be advanced. Recent tests have shown that, in addition to an amine curing agent, a further bifunctional DOPO epoxy resin grade can be prepared. With this, a further improvement of the mechanical characteristics can be expected. The different DOPO grades open up the possibility of introducing the flame retardant into the EP system by different routes, according to requirements.

Furthermore, methods have already been found for the flame retardancy of polyurethanes, polyesters and polyolefins with phosphorus-containing flame retardants. The early field tests with a DOPO-based flame retardant in polyamide have led to very good results as regards processability and flame retardancy.

The available potential of these new DOPO-based flame retardants can also be significantly increased by further fine tuning. ■

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