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LETTER

Effective halogen-free flame retardancy for a monocomponent polyfunctional epoxy using an oligomeric organophosphorus compound

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Epoxy-based resins are commonly used for applications including adhesives, insulating materials for electrical devices as well as for fibre-reinforced composites in the transportation sector. The growing importance of modern epoxy resins for the manufacture of high-performance fibre-reinforced composites is partly reflecting the potential to be tailored for the use in liquid composite moulding (LCM) approaches such as resin transfer moulding (RTM) that are rapidly gaining a widespread acceptance in the aerospace or automotive industry. However, applications in mass transport systems especially are sensitive to fire, smoke and toxicity (FST) aspects in a fire scenario owing to the inherently confined operating conditions. Therefore, the use of matrix materials that delay ignition or rapidly self-extinguish after ignition and show a low toxicity upon burning are highly desired for such modern-day composite applications.

Despite intense world-wide scientific and commercial activities towards developing suitable halogen-free flame retardants for epoxies, surprisingly little effort has been spent so far on evaluating the potential of either non-reactive or reactive additives as modifiers of commercially accepted monocomponent polyfunctional epoxy systems suitable for advanced LCM technologies. In general, non-soluble modifiers (apart from nanoparticles) cannot be used as the fibrous reinforcement filters out the additive during infiltration, eventually leading to an inhomogeneous composite material. In addition, the system viscosity and fabrication process parameters limit the amount of modifier used. Thus, rather practical processing imperatives must also be considered when formulating new systems or modifying already available ones.

With regard to flame retardancy of epoxies, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)-based compounds especially have attracted much attention. In several studies [1–6], the use of such compounds has been shown to induce a significant improvement in the flame retardancy of epoxy resins while, at the same time, avoiding many disadvantages such as poor compatibility, migration of the compound, and release of toxic gases upon burning as compared to other commonly used flame retardants. Using DOPO-based compounds, the flame retardancy of neat epoxies can be improved at phosphorus contents as low as 3 wt% [3, 6], thereby limiting processing difficulties and the often severe degradation of the resulting physical and mechanical properties of the base resin [7].

It has recently been shown that the use of either non-reactive or reactive DOPO-based compounds with tailored chemical structures especially led to an

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optimised overall performance level of a neat bi-functional epoxy resin as well as of the corresponding carbon-fibre-reinforced composites at low phosphorus contents of around 2 wt% [6, 8–10] while maintaining the ease of processing generally associated with such systems. However, the maximum operating temperature of this matrix material was rather low, owing in part to the low functionality of the resin and, more importantly, to the commonly encountered reduction in glass transition temperature of the base resin following the addition of non-reactive flame retardants [6, 8].

Here, the effectiveness of a novel oligomeric organo-phosphorus compound (DOPO-Cyan-O) as an efficient, non-reactive flame retardant for modern epoxy systems is demonstrated. The compound was synthesised according to Ref. [11]. The chemical structure of the additive is shown in Fig. 1. In an extension of previous approaches, the additive is not only used to modify a standard bi-functional, amine-cured bisphenol-A (DGEBA) resin but is also evaluated with regard to its potential to improve the flame retardancy of a monocomponent polyfunctional epoxy-based resin established for high-performance composite applications (RTM6, Hexcel Composites). The total additive content was fixed at 20 wt%, leading to a phosphorus content of approximately 2 wt%. The present study highlights the potential of such oligomeric additives to impart a convincing flame retardancy to either epoxy while maintaining a sufficient level of processability and properties.

Modified resin mixtures were prepared by adding the DOPO-based compound to the RTM6 (Hexcel Composites) resin preheated to 120 °C, stirred at 1,500 rpm for 40 min. Following this initial dispersion step, part of the mixture was stored at –18 °C for further tests. The remaining sample volume was poured in aluminium moulds and was cured at 180 °C in a convection oven for 120 min. A similar procedure was followed to prepare the DGEBA-based system. Following dispersion of the additive in the DGEBA (Bakelite), 4,4′-DDS (Merck) was incorporated at 130 °C in a substoichiometric ratio into the epoxy resin (epoxy to amine equivalent ~1:0.8). In this case, stirring was continued for a further 25 min until the mixture was clear again. Again, curing was carried out for 2 h at 180 °C. In either case, cured sheets of 160 × 110 × 3 mm^3 were obtained.

The curing behaviour of the resins was evaluated by means of isothermal differential scanning calorimetry at 180 °C. Isothermal DSC measurements were performed using a Thermal Analysis DCSQ1000 from TA Instruments with 8.0 ± 1.0 mg of uncured material; the calorimeter was preheated to the desired temperature before the unreacted sample was placed in the calorimeter cell and the heat flow was recorded

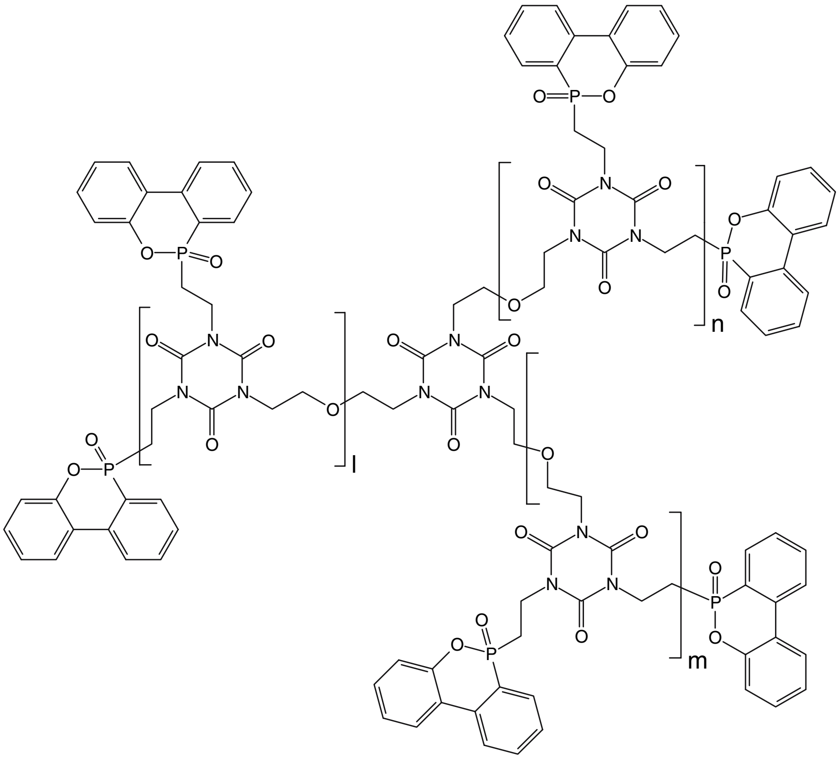

Fig. 1 Chemical structure of the oligomeric organo-phosphorus compound (DOPO-Cyan-O) employed in this study

immediately as a function of the time after the sample was inserted. The degree of cross-linking (epoxy group conversion) was calculated according to the procedure reported elsewhere [6]. Crimped aluminium pans were used for all DSC measurements. Dynamic mechanical properties of the cured neat resins as a function of the temperature were investigated on rectangular specimens of 50 × 10 × 2.8 mm^3 in the torsion mode using a Rheometrics RDAIII, operating at a frequency of 1 Hz, 0.1% of deformation, and a heating rate of 4 K/min from 25 °C to 250 °C. The glass transition temperature (T_g) of the specimens was taken as the temperature at which tan δ showed a maximum.

The critical stress intensity factor (K_{Ic}) and the fracture modulus ($E_{K_{Ic}}$) were obtained from the opening mode test according to the ISO 13586, performed on compact tension specimens (CT). The size of the specimens used in this study was 41 × 40 × 3–4 mm^3. A sharp notch was machined into the specimen and then a sharp pre-crack was generated by tapping a razor blade. Tests were carried out using a universal testing machine model Zwick Z 2.5 at room temperature and a cross-head speed of 10 mm/min. A minimum of four specimens of each epoxy formulation was tested. A flammability test (limiting oxygen index—LOI) was carried out according to the ASTM D 2863.

The DOPO-Cyan-O compound was easily dissolved in both the RTM6 and the DGEBA-based resin. No separation of the components was observed and all cured sheets were transparent and optically homogeneous. However, the isothermal DSC measurements revealed a significant acceleration of the curing reaction of the RTM6 resin, especially at low epoxy conversions. The rate of reaction of this particular epoxy is initially non-zero and proceeds through a maximum with the advancement of the reaction, reflecting the autocatalytic nature of the curing reaction [12–14]. Following this initial acceleration, the rate of reaction of the DOPO-Cyan-O-modified resin was lower than that of the unmodified reference; a behaviour that can be attributed to a combination of catalysis and dilution effects, in agreement with a recent study employing similar DOPO-based modifiers in the bi-functional epoxy [6]. The observed dilution effect of the reacting species in the mixture leads to a less developed network structure; hence, the achieved final conversion (as determined by DSC measurements) was about 12% lower than that of the unmodified resin (95% under these curing conditions). A combined catalysis-dilution effect of the DOPO-Cyan-O was also observed for the DGEBA-based system. However, the dilution effect on the curing reaction appears to be dominant in this case, in agreement with previous studies using similar additives [6].

The time-dependence of the viscosity of the modified and unmodified RTM6 system at 100 °C is comparatively shown in Fig. 2. Data for the DGEBA-based systems are also included for comparison. For both modified resin systems, an initial viscosity increase as a result of the addition of the DOPO-Cyan-O can be seen. However, the viscosity of the modified RTM6 increases faster than that of the modified DGEBA resin, further verifying the more pronounced catalysis effect induced by the addition of the DOPO-Cyan-O to the RTM6 system. This particular behaviour can also be in part attributed to the higher functionality of the RTM6 system; hence, vitrification occurs faster than in the bi-functional DGEBA-based system [15].

As the impregnation resistance of the reinforcement generally increases with the viscosity of the resin, careful selection of the pressure and of the temperature for injection is required in order to fully impregnate the fibres and to fill the mould. The experimental viscosity data shown here for 100 °C serves comparative illustrative purposes only; at higher temperatures, the viscosity of all systems is lower and is within the limits for typical LCM technologies such as RTM or resin infusion (RI). Yet, depending on the particular mould geometry, the variations in system reactivity must be carefully considered.

A representative plot of the storage modulus and tan δ as a function of the temperature for the various

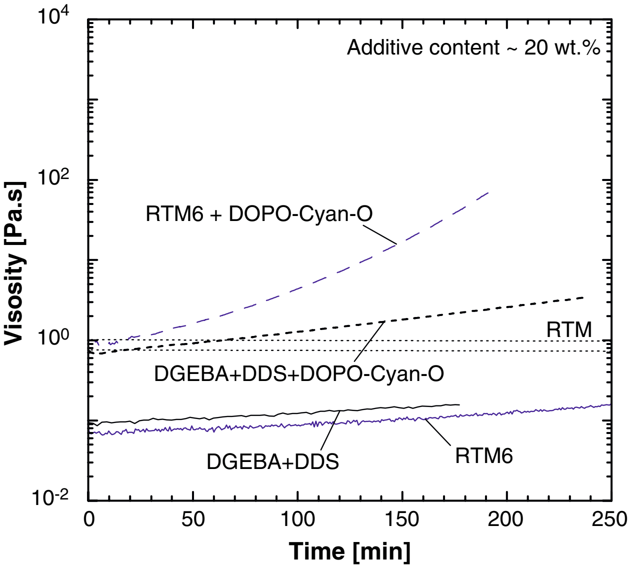

Fig. 2 Time-dependence of the viscosity of the modified and unmodified RTM6 system measured at 100 °C. The DGEBA-based system is also included for comparison

cured resin systems is shown in Fig. 3. A moderate increase of the stiffness of either DOPO-Cyan-O-modified resin in the glassy region can be seen. However, differences in the degree of cross-linking as a result of the presence of the additive molecules during curing [6] led to a decrease of the T_g, as indicated by the shift of the peak of tan δ. This observation correlates directly with the lower epoxy conversion observed in the DSC measurements. Nevertheless, owing to the higher functionality of the RTM6 system, a high glass transition temperature of about 200 °C is still maintained. A single relaxation peak was observed in the tan δ curves, verifying the complete miscibility of the oligomeric compound in either resin.

The addition of 20 wt% of DOPO-Cyan-O clearly restricted the flammability of the resulting materials as indicated by the LOI values. The LOI of the RTM6 was remarkably increased from 24.3% to 33.3% at a total phosphorus content of only about 2 wt% with a similar improvement from 21.9% to 31.2% for the DGEBA-based system. The results of the fracture mechanical experiments are summarised in Fig. 4, plotted against the LOI for both resin systems. In general, the addition of the DOPO-Cyan-O to either resin induced a minor reduction in the fracture toughness of the resulting material (Fig. 4a); an effect that is attributed to the lower cross-linking degree. Yet, the moderate decrease in fracture toughness is somewhat compensated by a gain in the stiffness at room temperature of the cured material (Fig. 4b), in agreement with the dynamic mechanical analysis results.

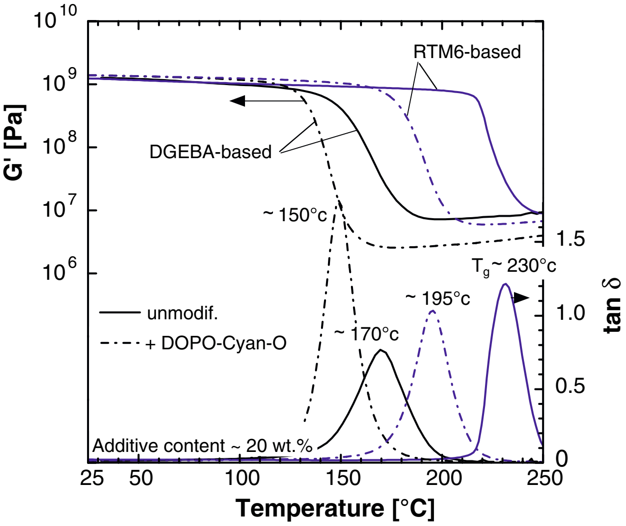

Fig. 3 Results of the dynamic mechanical analysis of the modified and unmodified thermosetting resins

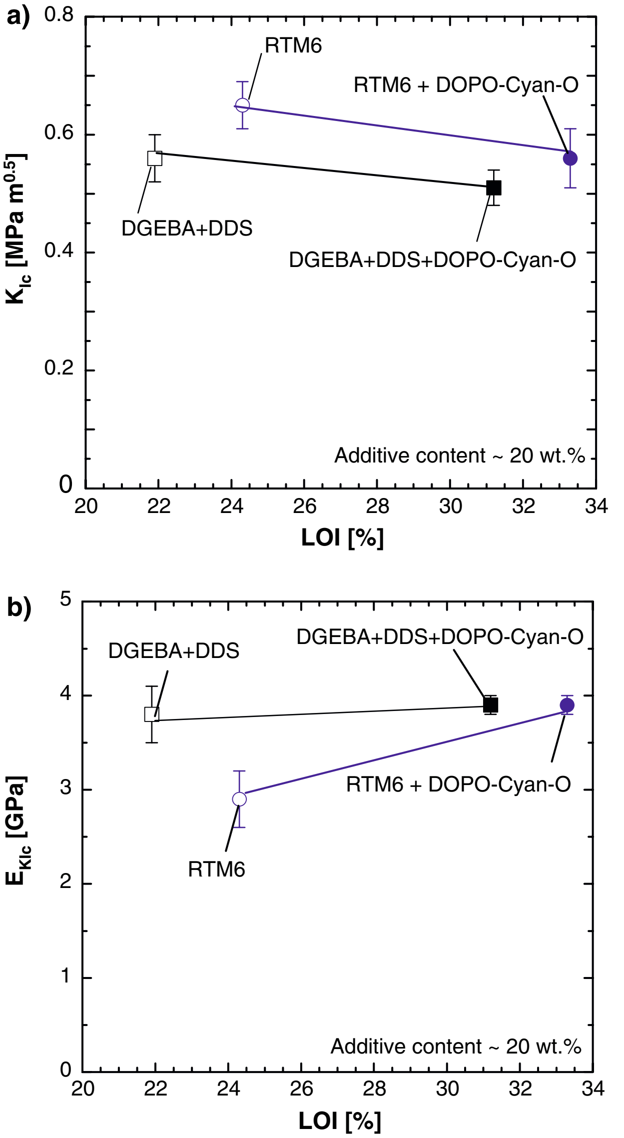

Fig. 4 Fracture mechanics tests results (K_{Ic} and E-modulus) of the modified and unmodified cured samples plotted against the LOI

In line with previous work on tailored organo-phosphorus additives for epoxies [6, 8, 9, 16], this study clearly highlights the potential of oligomeric organo-phosphorus compounds to provide a mono-component polyfunctional epoxy resin system (RTM6) with a high flame retardancy without significantly deteriorating the overall performance of the resulting material. Further optimisation and improvement can be anticipated; an analogous oligomeric DOPO-based compound with a higher molecular weight could simultaneously enhance both the fracture toughness—provided that a microstructure development occurs (as most thermoplastic modification does)—and flame retardancy of the resulting material.

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