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LETTER

Effective halogen-free flame retardants for carbon fibre-reinforced epoxy composites

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The flammability and fire behaviour of fibre-reinforced epoxy composites has drawn increasing attention worldwide since the fire performance of such parts for transport applications especially is critical and is facing increasingly severe environmental legislation. Much progress has been made in improving the thermostability and flame retardancy of neat epoxy resins using a variety of compounds [1]. In particular, halogen-free compounds such as the 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) successfully increase the flame retardancy of epoxy resins [2–7] while avoiding many disadvantages such as poor compatibility, migration of the compound, and release of toxic gases upon burning as compared to other common compounds. Using such DOPO-based compounds, the flame retardancy of neat epoxies can be improved at phosphorus contents as low as 3 wt% [4, 7], thereby limiting processing difficulties and the often severe degradation of the resulting physical and mechanical properties [8]. The use of either non-reactive or reactive DOPO-based compounds with tailored chemical structures especially leads to optimised overall performance levels of neat epoxy resins at low phosphorus contents [7]. However, there still exists a lack of understanding concerning the use of such compounds for the manufacture and application of fibre-reinforced epoxy composites, especially with regard to the often negatively affected delamination resistance of such composites for demanding applications.

Based on recent results [7], two promising non-reactive DOPO-based candidates were selected to modify an epoxy matrix for a woven carbon fibre-reinforced composite for high-performance applications. Here, the effectiveness of either DOP-Ethyl (DOP-Et) or DOP-Cyanur (DOP-Cyan) compounds at phosphorus contents of 2 wt% is reported, demonstrating especially that the interlaminar fracture toughness (mode I and mode II) as well as the apparent interlaminar shear strength of the composites are not degraded.

Composite plates of $40 \times 40 \times 2.8$ mm^3 containing 60 vol% of carbon fibres were manufactured using the resin transfer moulding (RTM) technique. A difunctional epoxy resin (DGEBA, Ruetapox 0162, Bakelite, commercial grade) was modified with either DOP-Ethyl or DOP-Cyanur (2 wt% of phosphorus) and cured with 4,4′-diaminodiphenylsulfone (4,4′-DDS, Merck, synthesis grade); details of the mixture preparation are reported elsewhere [7]. The fibre reinforcement consists of eight plies of woven fabric (Atlas 1/4, 5 harness satin, ECC GmbH & CO, fibre aerial weight = 370 g/m^2). A Kapton film of 13 μm thickness was introduced between the fourth and fifth carbon fabric as a sharp crack starter in the midplane of the composite. The epoxy mixtures were heated to 100 °C and driven into the closed RTM mould by vacuum, followed by curing at 180 °C for 2 h and a slow

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cooling to room temperature. A composite reference based on the non-modified epoxy system was prepared using an identical experimental procedure.

Flammability tests were carried out according to ASTM D 2863 (LOI) and UL94. The fire behaviour was additionally investigated using a cone calorimeter according to ISO 5660 (horizontal sample position using the retainer frame), applying an external heat flux of 50 kW/m^2. Dynamic mechanical properties of the composites as a function of the temperature were investigated on rectangular specimens of 40 × 10 × 2.8 mm^3 in the torsion mode using a Rheometrics RDAIII at a frequency of 1 Hz, 0.1% of deformation, and a heating rate of 4 K/min from 25 to 250 °C.

Double cantilever beam and end notched flexure specimens were used to evaluate the interlaminar fracture properties in mode I (ESIS 990603) and mode II (according to procedures established in the literature [9, 10]), respectively. The apparent interlaminar shear strength was determined using short beam shear specimens according to ASTM D 2344. For all tests at room temperature, a universal testing machine model Zwick Z 2.5 was used.

Neither of the two employed non-reactive organophosphorus compounds significantly affected the viscosity and hence the RTM processability of the matrix at this particular phosphorus concentration. All composites showed restricted flammability (see LOI values in Table 1) and revealed a self-extinguishing behaviour in the UL94 test. Yet, addition of the DOPO-based compounds increased the LOI convincingly by about 13–18%. For the DOP-Cyan modified matrix, the UL94 rating improved from a V-1 to a V-0 classification. The combustion behaviour of the composites under forced flaming conditions is representatively shown in Fig. 1. Here, the heat release rate (HRR) and total heat release (THR) are plotted for composites of identical thickness as a function of time. The ignition was hardly influenced, whereas both the HRR and the THR were significantly reduced for the modified composites. Further test results concerning the total heat evolved (THE), peak of HRR (pHRR), residue, and effective heat of combustion (total heat evolved/total mass loss) are summarised in Table 1.

Addition of the DOPO-based compounds clearly reduced the THE and the pHRR, effects which indicate an improvement in terms of flame spread and fire load. Depending on the chemical structure of phosphorus-containing flame retardants and on the base polymer, phosphorus can act both in the condensed-phase and in the gas-phase [11–14]. Considering the reduction of THE of

Table 1 Flammability and fire behaviour of the composites under investigation

Matrix	Flammability		Cone calorimeter at 50 kW/m^2			
	LOI [%] ± 0.5	UL94	THE [MJ/m^2] ± 1[b]	Peak HRR [kW/m^2] ± 10[b]	Residue [%] ± 3[b]	Heat o. Comb. [kW/m^2/g] ± 0.1[b]
EP[a]	31	V-1	25.9	376	71.9	2.2
EP + DOP-Et[c]	44	V-1	16.8	226	74.6	1.5
EP + DOP-Cyan[c]	49	V-0	16.2	252	76.8	1.6

[a] EP = DGEBA + 4, 4′-DDS 1:0.8

[b] Error based on derivation from average value of two measurements

[c] 2 wt% of phosphorus

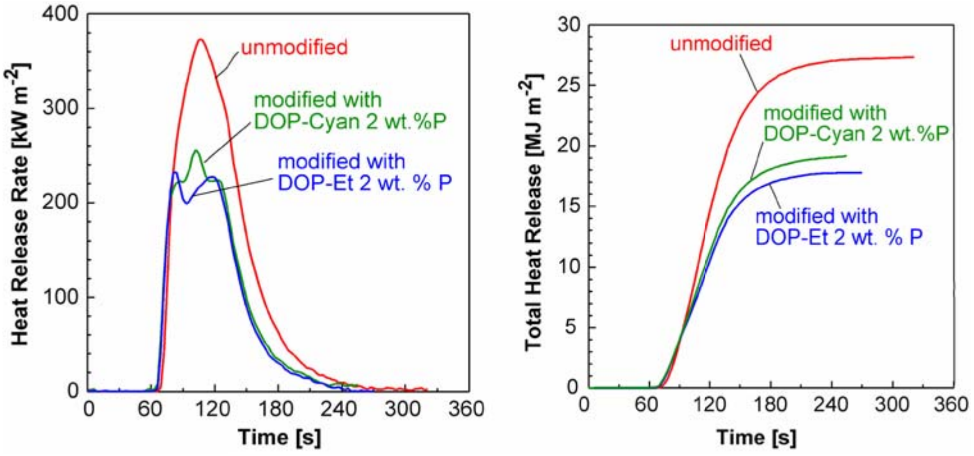

Fig. 1 Representative plots of heat release rate (HRR) and total heat release (THR) of composites with and without DOPO-based flame retardants using an irradiation of 50 kW/m^2

somewhat above one-third, the increase of residue of around 5%, and the decreasing effective heat of combustion of somewhat below one third, it becomes clear that there is a predominantly gas-phase fire retardancy mechanism and a minor contribution from a condensed-phase mechanism for these particular flame retardants in the epoxy matrix. DOPO components yield radical trapping in the gas-phase, resulting in an incomplete oxidation in the flame zone and, consequently, in a decreasing effective heat of combustion. This fire retardancy effect of DOPO for epoxy systems is sufficient in terms of flammability, flame spread, and fire load.

Representative plots of the storage modulus and tan δ as a function of the temperature for the different composites are shown in Fig. 2. Neither DOPO-additive significantly reduced the stiffness of the composites in the glassy region. However, differences in the degree of cross-linking as a result of the presence of the additive molecules during curing [7] led a pronounced decrease of the glass transition temperature and of the composite stiffness in the rubbery region. Although this typical reduction in mechanical properties of flame-retardant epoxy matrices at present still limits the use of such systems for high-performance applications, the data shown in Fig. 2 clearly highlight the potential of such tailored DOPO-based additives to achieve sufficient improvements in flame retardancy at minimised losses in the degree of cross-linking.

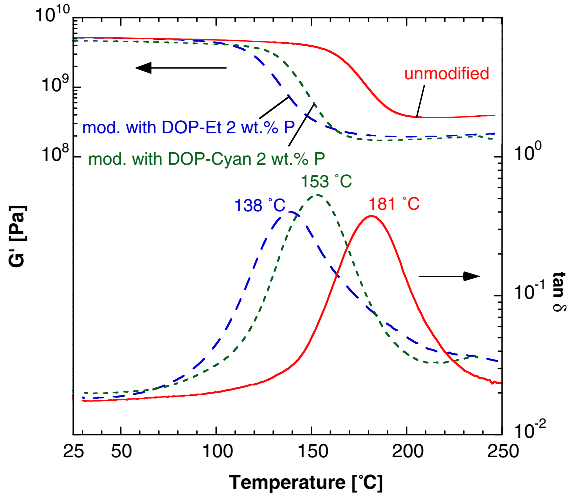

Fig. 2 Results of the dynamic mechanical analysis of the unmodified and DOPO-modified composites

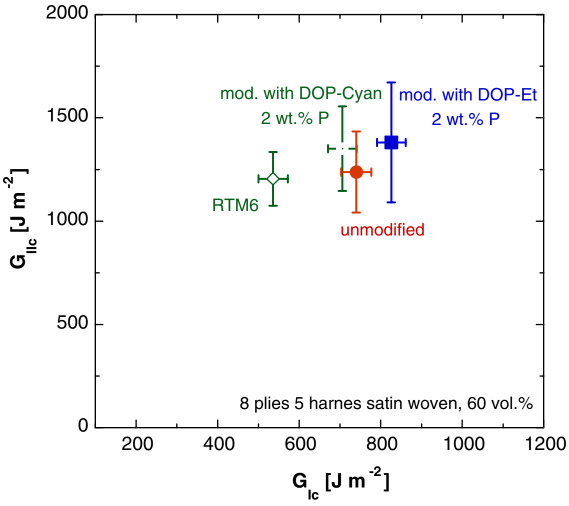

Fig. 3 G_{IIc} as a function of G_{Ic} (propagation values) for the various composites under investigation. Data for the composite based on RTM6 are included for comparison

As shown in Fig. 3, the critical strain energy release rate (G_c) of this particular composite in either mode I or mode II was not significantly affected within experimental error by the selected flame retardants. In fact, the DOP-Et additive appeared to improve the resistance to crack propagation in mode I. On the other hand, owing to the scatter of the data, the slight increase observed in mode II fracture energy for both modified composites is not convincing. For comparative purposes, data for an identical composite based on an unmodified RTM6 resin are included in Fig. 3 in order to further illustrate the relatively small differences in the fracture energies of the DOP-modified composites as compared to the reference system.

The crack growth initiation and average propagation values of the various composites fractured in mode I and mode II are summarised in Table 2. It is worth noting that the crack growth initiation values for either mode of fracture were very similar, suggesting that crack initiation is

Table 2 Interlaminar fracture toughness in mode I and mode II and apparent interlaminar shear strength of the composites

Matrix	G_{Ic} composite [J/m^2]		G_{IIc} composite [J/m^2]		ILSS [MPa]
	Initiation	Propagation	Initiation	Propagation	
EP[a]	603 ± 64	740 ± 37	588 ± 92	1238 ± 196	69 ± 5
EP + DOP-Et[b]	716 ± 118	826 ± 35	776 ± 24	1381 ± 290	69 ± 3
EP + DOP-Cyan[b]	609 ± 72	706 ± 35	667 ± 128	1351 ± 205	69 ± 6

[a] EP = DGEBA + 4, 4′-DDS 1:0.8

[b] 2 wt% of phosphorus

due to similar mechanisms in these composites, in agreement with observations from scanning electron microscopic investigations of fracture surfaces. The interlaminar shear strength of the composites was unaffected by the presence of the flame retardants in the matrix.

In summary, the experimental results presented in this study clearly highlight the potential of using non-reactive DOPO-based compounds with tailored chemical structures as a source of effective flame retardancy for carbon fibre-reinforced epoxy composites. More importantly, critical properties related to the fracture toughness of such modified composites can be maintained, effectively allowing the use of such compounds in composites for demanding applications.

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