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Effect of DOP-based compounds on fire retardancy, thermal stability, and mechanical properties of DGEBA cured with 4,4′-DDS

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The structure-property-relationships, thermal stability and flame retardancy of a DGEBA-DDS system containing various organo-phosphorus compounds as flame retardants is investigated. Three non-reactive (DOP-ethyl, DOP-ethylhexyl and DOP-cyanur) and one reactive (DOP-glycidyl) phosphorous compounds are added separately to the epoxy resin and the mixtures are cured with 4,4′-DDS in a substoichiometric ratio. The addition of such DOPO-compounds leads to improved flame retardancy at low phosphorus contents of about 2 wt.% (about 20 wt.% of additive) without significantly affecting other important properties such as fracture toughness (K_{Ic}) and glass transition temperature (T_g) of the matrix. Neither the type nor the amount of additive affects the fracture toughness of cured epoxies up to additive concentrations of between 18 and 24 wt.%. Furthermore, the loss in glass transition temperature of the cured resin can be correlated with the amount and chemical reactivity of the organo-phosphorus additive. The reactive DOP-glycidyl and the non-reactive DOP-cyanur additive are observed to maintain the highest glass transition temperature of the epoxy system mainly due to a higher extent of the cross-linking reaction. The results presented in this study highlight the potential of optimising the flame retardancy and the resulting physical and mechanical properties of epoxy systems for liquid composite moulding applications by varying the chemical structure of the organo-phosphorus compounds. *© 2006 Springer Science + Business Media, Inc.*

1. Introduction

Owing to their ease of processing, low cost, good mechanical properties, and environmental advantages, epoxy resins are commonly used for applications including adhesives, insulating materials for electrical devices as well as fibre-reinforced composites in the transportation sector. As a result of the increasing usage of such polymers, varying qualification requirements as well as the current trend towards the sustainable conservation of resources, the flame resistance and thermal stability as well as the toxicological consequences of combustion of flame-retardant epoxy resins have recently become a subject of considerable attention [1]. Many approaches have been made to improve the thermal stability and flame retardancy of epoxy resins using either non-reactive or reactive flame retardants [1–8]. Non-reactive flame retardants are widely used because of the comparative ease of promoting flame retardancy to polymeric materials. However, there are several disadvantages such as poor compatibility, migration, and a reduction of

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the mechanical properties of the final product [9, 10]. Today, the trend of the newly emerging chemistry is to develop and employ halogen-free flame retardants to meet the new environmental regulations, standards, and test methods. An overview of the recent developments of halogen-free flame retardants is given in the literature [1].

Some of the most widely used flame retardants are phosphorus-containing compounds. Many studies [2, 4–7, 11–20] have shown that a high degree of flame retardancy and thermal stability can be imparted to an epoxy resin through the use of phosphorous compounds. The limiting oxygen index (LOI) can be as high as 51 with an accompanying char yield of 45 wt.% when the phosphorus content in the epoxy resin exceeds 10 wt.% [19]. A common strategy to increase the flame retardancy of epoxy resins is to blend reactive or non-reactive organo-phosphorus compounds with an epoxy resin or to use an organo-phosphorus compound as a curing agent [11, 14, 16]. One of the compounds that has attracted attention is the 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). Several researchers [12–16] have used this compound, or a modification of it, and have obtained a significant improvement in the flame retardancy of epoxy resins. However, there still exists a lack of knowledge about how the mechanical properties and water uptake of the cured products are affected when DOPO-based compounds are used as a flame retardant at different phosphorus concentrations.

In the present study, the influence of four different types of DOPO-based flame retardants on the thermal stability (TG analysis), flame retardancy (LOI & UL94-V) and water uptake of an epoxy resin were investigated, with special emphasis on the curing behaviour (DSC), dynamic mechanical properties (DMA), and fracture toughness (K_{Ic}) of the final product. The aim was to evaluate whether there is an optimum additive type and concentration which significantly improve the combustion behaviour without sacrificing other important properties of the cured material such as K_{Ic} and T_{g}. For this reason, one reactive and three non-reactive compounds were used at different concentrations as flame retardants and added separately to a diglycidyl ether of bisphenol A (DGEBA), cured with a substoichiometric amount of 4,4′-diamino diphenyl sulphone (4,4′-DDS). The resulting mechanical and physical properties of the epoxy system are correlated with the changes in the structure of the epoxy network for increasing additive concentrations.

2. Experimental

2.1. Materials

A difunctional epoxy resin (DGEBA, Ruetapox 0162) with an epoxy equivalent weight of 173 g/eq which is free of hydroxyl groups was supplied by Bakelite and used as-received. The DDS hardener, with an amine equivalent weight of 62 g/eq, was purchased from Merck (synthesis grade) and was also used as-received. Three non-reactive DOPO-based compounds, namely DOP-ethyl (DOP-Et), DOP-ethylhexyl (DOP-EtHex) and DOP-cyanur (DOP-Cyan), and a reactive DOP-glycidyl (DOP-Gly) flame retardant were synthesised in the laboratory [31], with a purity exceeding 97% as determined by means of NMR spectroscopy. The DOP-Et, DOP-EtHex and DOP-Cyan additives have phosphorus contents of 12.7, 9.4 and 10.9 wt.%, respectively, while the DOP-Gly has a phosphorus content of 11.4 wt.%.

The chemical structures of the materials used in this study are summarised in Table I.

2.2. Preparation and curing procedure of epoxy specimens

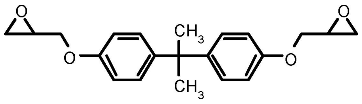
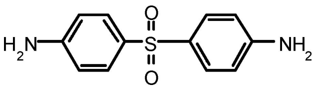
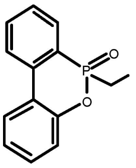
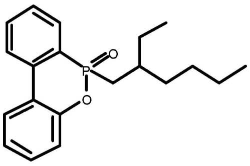
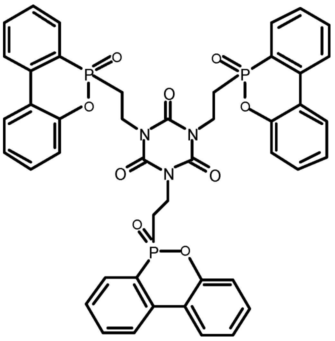
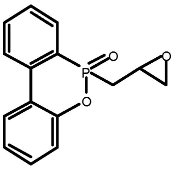
The DGEBA was placed in a glass flask and heated to 130°C in an oil bath connected to a temperature controller. The desired amount of phosphorous-containing additive was then added slowly to the resin and mixed with a mechanical stirrer for 30 min at 600 rpm, keeping the temperature constant at 130°C, until the additive was dissolved and the mixture was clear. The amount of additive introduced was designed to lead to 0.5 to 3 wt.% of phosphorus in the final resin and hardener mixture. The temperature was kept at 130°C and the DDS was incorporated in a substoichiometric ratio into the epoxy resin (DGEBA/DDS; 1:0.8). Stirring was continued for a further 25 min until the mixture was clear again. The hot mixture was then poured into a preheated aluminium mould at 130°C and placed in a vacuum oven at the same temperature for 45 to 60 min for degassing. The phosphorus containing epoxy resin was then cured as follows: the curing cycle started by a 2 K/min ramp from room temperature to 180°C. This temperature was held for 2 h and curing was completed with a –2 K/min ramp from 180°C to room temperature. For easy release of the cured epoxy resin sheets, the mould surface was coated with a thin layer of Frekote-700 NC.

Thus, a 110 × 110 × 4 mm^3 epoxy resin sheet was obtained and was subsequently machined to the desired specimen size for further testing. Control samples of DGEBA/DDS without phosphorus were prepared in the same way.

2.3. DSC, TGA and DMA measurements

Non-isothermal differential scanning calorimetry (DSC) scans were carried out on 8.0 ± 2.0 mg of premixed uncured samples with a thermal analysis DSC821 from Mettler Toledo at a heating rate of 10 K/min under nitrogen atmosphere at a flow rate of 50 ml/min. Isothermal DSC measurements were performed using the same equipment with 8.0 ± 1.0 mg of uncured material; in this case, the calorimeter was preheated to the desired temperature before the unreacted sample was placed in the calorimeter cell and the heat flow was immediately recorded as a function of time after the sample was inserted. Crimped

TABLE I Overview of the different materials used in this study

Material	Chemical structure	M_w (g/mol)	wt.% P
DGEBA		340	0
4,4′- DDS		248	0
DOP-Ethyl (non-reactive additive)		244	12.7
DOP-Ethylhexyl (non-reactive additive)		328	9.4
DOP-Cyanur (non-reactive additive)		855	10.9
DOP-Glycidyl (reactive additive)		272	11.4

aluminium pans were used for all DSC measurements. Thermogravimetric (TG) analysis of cured materials was performed using a TGA/SDTA851 from Mettler Toledo under nitrogen atmosphere (50 ml/min) from 25 to 850°C at a heating rate of 10 K/min. Chips were cut from the cured sheets and 15.0 ± 0.5 mg samples were used for the tests. All measurements were done in duplicate showing good reproducibility. The average values were obtained and the deviation between the two measurements was used to estimate the error. Dynamic mechanical analysis (DMA) was performed using a RDAIII from Rheometric Scientific at a heating rate of 4 K/min from 25 to 250°C. A cured rectangular specimen of $50 \times 10 \times 3$ mm^3 was used in the torsion rectangular geometry mode, at a frequency of 1 Hz and 0.1% of deformation. The glass transition temperature (T_g) was taken as the temperature at which tan δ showed a maximum.

2.4. LOI and UL94-V tests

The LOI was determined using an Atlas Limiting Oxygen Index Chamber according to the ASTM D2863. The minimum concentration of oxygen in a mixture of oxygen and nitrogen just needed to sustain combustion was taken as the LOI [21]. The UL94-V test was carried out according to the test method of Underwriter Laboratory Inc. [21], with test specimen bars of a length of 127 mm, a width of 12.7 mm, and a thickness of 3.5 to 4 mm. Five specimens were clamped vertically over surgical cotton and were ignited with a Bunsen burner. A flame was applied to the bottom of the specimen for 10 s twice. The duration of flaming and glowing was noted. The highest classification, 94 V-0, is achieved if the total burning time is less than 50 s, a classification 94 V-1 if the total burning time is less than 250 s. If the cotton is ignited by dripping particles, the material is classified as 94 V-2.

2.5. Water uptake

In order to measure the glass transition temperature of conditioned samples, dry rectangular specimens with the dimensions of 50 × 10 × 3 mm^3 were immersed in distilled water at a constant temperature of 70°C for 14 days. The specimens were weighted before and after immersion. The normalised water uptake (W) during immersion was calculated according to

$$W = \left(\frac{m_f - m_o}{m_{\text{epoxy}}}\right) \times 100, \tag{1}$$

where m_0 and m_f are the weight of the sample before and after immersion, respectively, and m_{epoxy} is the weight of the sample without additive.

2.6. Fracture toughness of the cured epoxy

The critical stress intensity factor (K_{Ic}) was 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 × 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.

3. Results and discussion

All cured epoxy sheets were clear, slightly yellow coloured, and were optically homogeneous and transparent.

3.1. Curing behaviour

In order to determine the onset of the curing reaction, non-isothermal DSC measurements of the pure DGEBA-DDS system from −40 to 330°C at a heating rate of 10 K/min were performed. The recorded heat flow as a function of temperature for this system is shown in Fig. 1. The step in the heat flow at around −3°C corresponds to the glass transition of the unreacted mixture. The curing reaction starts at around 130°C and the extrapolated onset of curing is at approx. 180°C. This temperature was chosen as the standard curing temperature for all epoxy formulations.

In order to determine the degree of cure of the various epoxy formulations, isothermal measurements were carried out at 180°C for 240 min. The final steady-state of the heat flow signal was taken as the base line [24]. The time-dependence of the heat of reaction of the epoxy formulations containing the non-reactive DOP-based additives during isothermal curing with increasing additive concentration is shown in Fig. 2a–c. All curves are normalised to 1 mol of epoxy. Two main features can be observed: the maximum of the heat flow shifts to shorter times and decreases in magnitude as the amount of additive in the mixture increases. These effects can be attributed to a dilution of the reactive species in the mixture and/or to an increasing diffusion coefficient of the reactive species in the mixture.

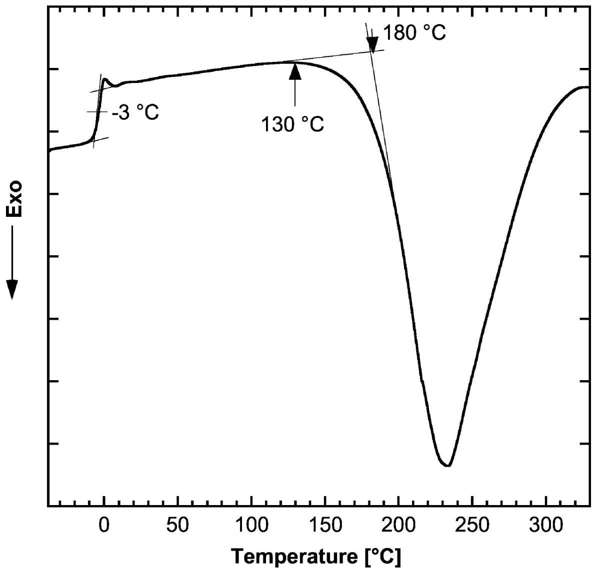


Figure 1 Dynamic DSC thermogram at 10 K/min of the neat DGEBA – DDS mixture.

Assuming that the epoxy curing reaction is a thermal event only and that the heat flow obtained from the DSC (dq/dt) is proportional to the reaction rate (dx/dt) [25], the reaction rate at any given time t is given by the heat flow divided by the overall heat of reaction Q_o

$$\frac{dx}{dt} = \frac{1}{Q_o}\frac{dq}{dt}. \tag{2}$$

The extent of reaction (or the degree of cure) at a time t can be obtained by integration of Equation 2

$$\times = \frac{1}{Q_o}\int_0^t \frac{dq}{dt}dt. \tag{3}$$

The overall heat of reaction, Q_o, was taken as the total heat evolved from the reaction of the neat DGEBA-DDS 1:0.8 system obtained from an isothermal DSC measurement at 180°C. The heat of reaction for the DGEBA-DDS 1:0.8 system was found to be 85 ± 7 kJ/eq, about 21% lower than the reported values for stoichiometric mixtures [25, 26].

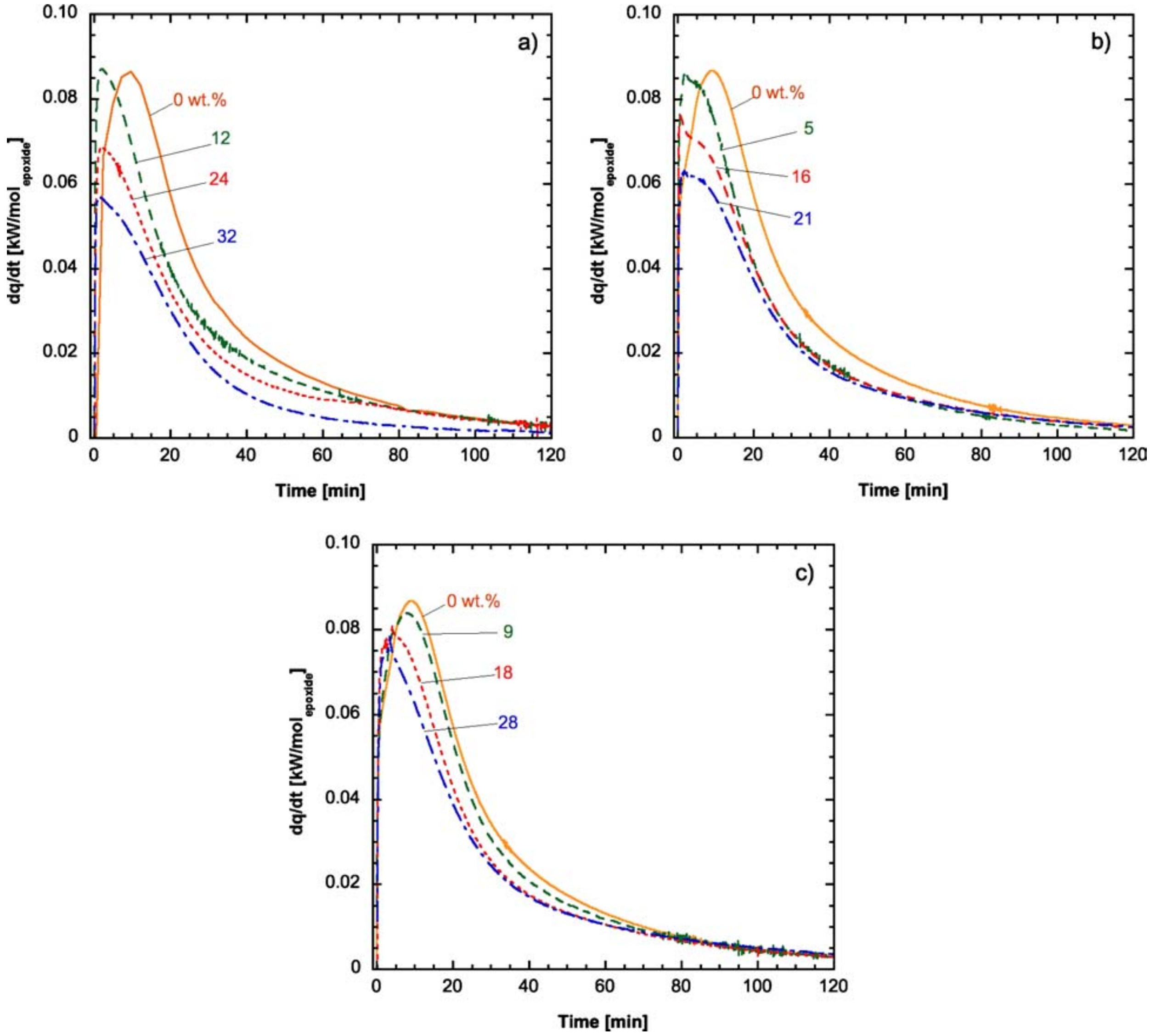


Figure 2 Isothermal DSC scans of epoxy resin formulations containing increasing weight fractions of the non-reactive: (a) DOP-Et, (b) DOP-EtHex, and (c) DOP-Cyan at 180°C.

The degree of cure of the epoxy formulations containing the non-reactive DOP-based additives is shown in Fig. 3a–c as a function of time for the various additive concentrations. For comparison, the time-dependent progress of the curing reaction of the neat epoxy formulation at a lower temperature is included in Fig. 3d. As can be seen, a similar curing profile for all epoxy formulations with increasing amount of the non-reactive DOP-additives is observed. However, as the concentration of the additive in the mixture increases, the degree of cure (at $t = 120$ min) decreased to about 50% and 65% for up to 32 wt.% of the non-reactive DOP-Et or DOP-EtHex additives, respectively, and to about 75% for up to 28 wt.% of the non-reactive DOP-Cyan. As discussed before, this effect is attributed to the dilution of the reactive species in the mixture which leads to a less developed network structure.

In case of the epoxy formulations containing the reactive DOP-based additive, an accelerated curing rate is observed, as shown in Fig. 4a. Contrary to the formulations containing the non-reactive additives, the maximum heat flow during the curing reaction is augmented most likely due to the higher mobility and earlier reaction of the DOP-Gly molecules in the mixture, forming pendant hydroxyl groups which are known to accelerate the subsequent epoxy-amine reaction [10]. The DOP-Gly additive can be considered a reactive diluent which essentially leads to a reduction of the functionality of the curing reaction [10] and to a less cross-linked epoxy network.

From the time-dependent plot of the degree of cure of epoxy formulations containing the reactive DOP-Gly, Fig. 4b, it can be seen that the conversion during the curing reaction also decreases when the amount of additive in the mixture increases. However, in contrast to the epoxy formulations containing the non-reactive DOP-additives, degrees of cure exceeding 80% were achieved at a curing time of 120 min, even at high loadings of the reactive DOP

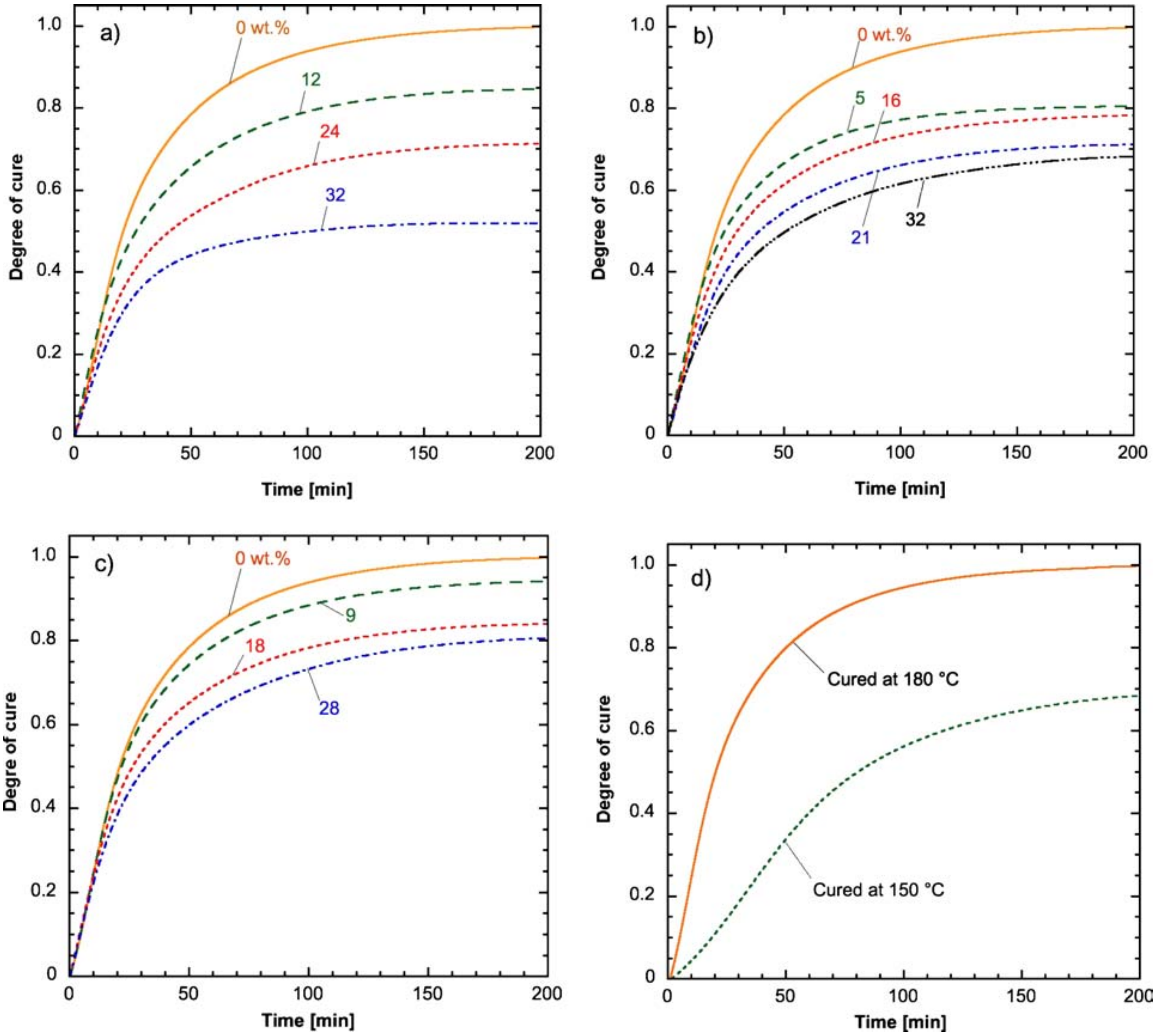


Figure 3 Curing time-dependent conversion of epoxy formulations containing increasing weight fractions of the non-reactive: (a) DOP-Et, (b) DOP-EtHex, and (c) DOP-Cyan at 180°C. For comparison, the time-dependent conversion of the neat epoxy formulation at a lower curing temperature of 150°C is included in (d).

additive. This increased degree of conversion obtained for the epoxy formulations containing the DOP-Gly as compared to the non-reactive additives is related to the higher amount of reacted epoxy-amine groups. Although the additive is acting as a diluent, the epoxy groups in the additive itself will partly react with the amine hardener, reducing the amount of amine groups available to react with the resin. Since the rate of reaction increases with the concentration of the reactive additive, Fig. 4a, it appears reasonable to assume that nearly all molecules of the DOP-Gly reacted with part of the available amine groups. Thus, taking into account the functionality of the DOP-Gly additive (EEW = 272 g/eq), one can find that the epoxy (from DGEBA)-amine ratio reduces from 1:0.8 (without additive) to 1:0.6 (with 26 wt.% of additive). In this case, a rough estimation of the degree of conversion of epoxy groups (from DGEBA) leads to a value of around 60%. As a result, the degree of cross-linking of the fully developed network should also be decreased compared to the pure DGEBA/DDS system.

3.2. DMA analysis of the cured epoxy

Storage modulus and tan δ plots of the cured epoxy resin formulations with varying concentrations of the DOP-based additives are shown in Fig. 5a–d. It can be seen that the storage modulus of this particular epoxy system at 25°C is not significantly affected by the additive content or type, indicating that the rigidity of the cured epoxy below T_g can be maintained although the degree of conversion of all modified systems decreased, as indicated by the DSC results. This effect might be partly attributed to the rigidity of the additive molecules themselves, effectively compensating for the loss in the degree of cross-linking, independent of whether the additive molecules are chemically bound into the network or whether they are located

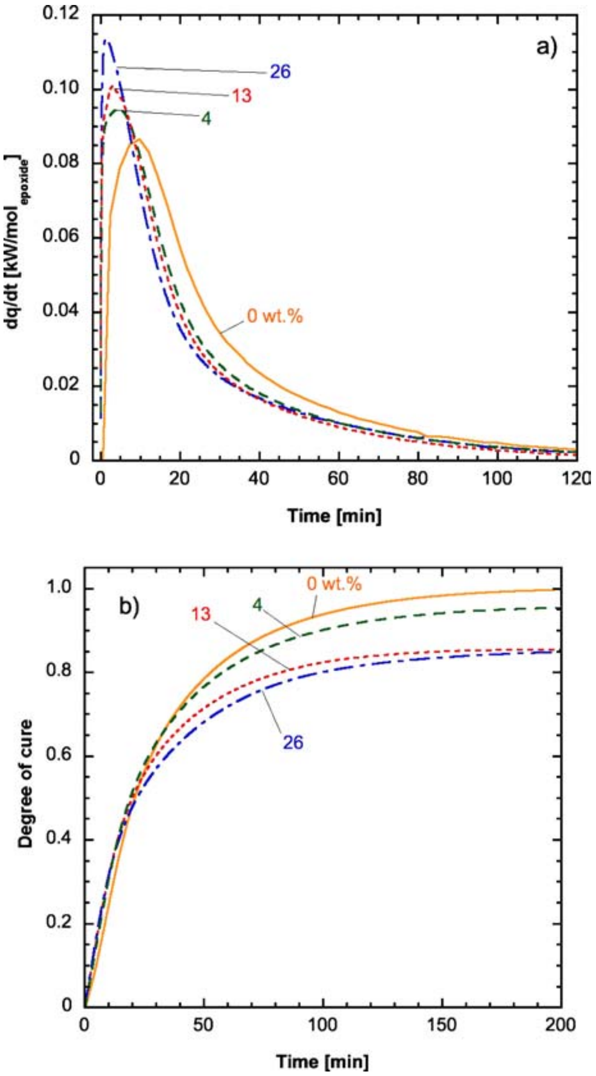


Figure 4 (a) Isothermal DSC scans of epoxy formulations containing increasing weight fractions of the reactive DOP-based additive at 180°C, and (b) corresponding curing time-dependent conversion.

in between cross-linking sites. A similar behaviour is reported in the literature [13, 14], where the DOPO group was chemically incorporated into an epoxy network. From the DMA plots, it can also be observed that the transition from the glassy to the rubbery state of the cured materials shifts to lower temperatures and that the transition occurs over a smaller temperature range for the epoxy formulations containing the non-reactive DOP-Cyan and the reactive DOP-Gly additive. These observations correlate directly with the results obtained from the isothermal DSC measurements.

In the rubbery region, the storage modulus decreases with increasing content of DOP-additive due to the reduced degree of cross-linking for all epoxy formulations (as confirmed by the increasing height of the tan δ peak with additive content and also by the degree of cure obtained from the isothermal DSC measurements). According to the theory of rubber elasticity [27, 28], the cross-linking density is proportional to the storage modulus at $T_g + 45$ K; thus, Fig. 6 shows a semi-log plot of the storage modulus at $T_g + 45$ K as a function of additive concentration. The linear and similar decrease of the rubbery modulus of all cured materials indicates a comparable decrease of the number of effective cross-link points, independent of the type of organo-phosphorus compound under investigation here. More specifically, from the rubbery modulus measurements, there appears to be no significant difference between the number of effective cross-link points of epoxy formulations with either the reactive DOP-Gly or non-reactive DOP-Et and DOP-EtHex above 10 wt.% of additive. This result confirms that the higher degree of conversion observed for the epoxy mixtures containing the DOP-Gly in the isothermal DSC measurements is partly due to a conversion of epoxy groups located in the additive itself. In contrast, the higher rubbery modulus obtained for the epoxy containing the DOP-Cyan can be attributed to a higher number of cross-link sites in the developed network.

Plots of the glass transition temperature, defined as the temperature of the maximum of tan δ, as a function of DOP-additive concentration for dry and conditioned epoxy samples are shown in Fig. 7a and b, respectively. The T_g was found to decrease continuously with additive concentration for both the dry and the conditioned samples. For the conditioned samples, two major transitions in the tan δ curves are observed: a transition at low temperatures attributed to the plasticizing effect of the absorbed water [10], shown in Fig. 7b, and a transition which occurs after the water is removed from the epoxy at high temperatures during the experiment. This second transition temperature agrees well with the T_g of the dry samples, indicating that the absorbed water has been completely removed. It should be noted that the lowest rate of decrease in T_g occurred for the epoxy formulations containing the non-reactive DOP-Cyan additive.

The decrease of T_g with increasing DOP-additive content highlighted in Fig. 7 is attributed to the decreasing effective number of cross-link points in the epoxy network estimated from the rubbery modulus, Fig. 6. A further confirmation of this explanation is provided by the decreasing degree of cure observed by the isothermal DSC experiments, Figs 3 and 4. Decreasing glass transition temperatures of epoxy systems with increasing concentration of organo-phosphorus compounds are well-known, independent of whether the flame retardants are chemically incorporated into the network or are a plain additive [13–17]. However, significantly less pronounced decreases in T_g were observed for the epoxy formulations containing the DOP-Gly and DOP-Cyan. This effect can be related to: (1) the chemical bonding of the reactive additive to the epoxy network which decreases the amount of pendant chains, (2) restrictions to molecular motion imposed by the bulky structure of the DOP-Cyan molecule and (3) the higher extent of the cross-linking reaction.

An even higher T_g can be obtained for the epoxy formulation containing the reactive DOP-Gly by adjusting the amount of hardener in the reacting mixture to take into account the functionality of the additive. Following

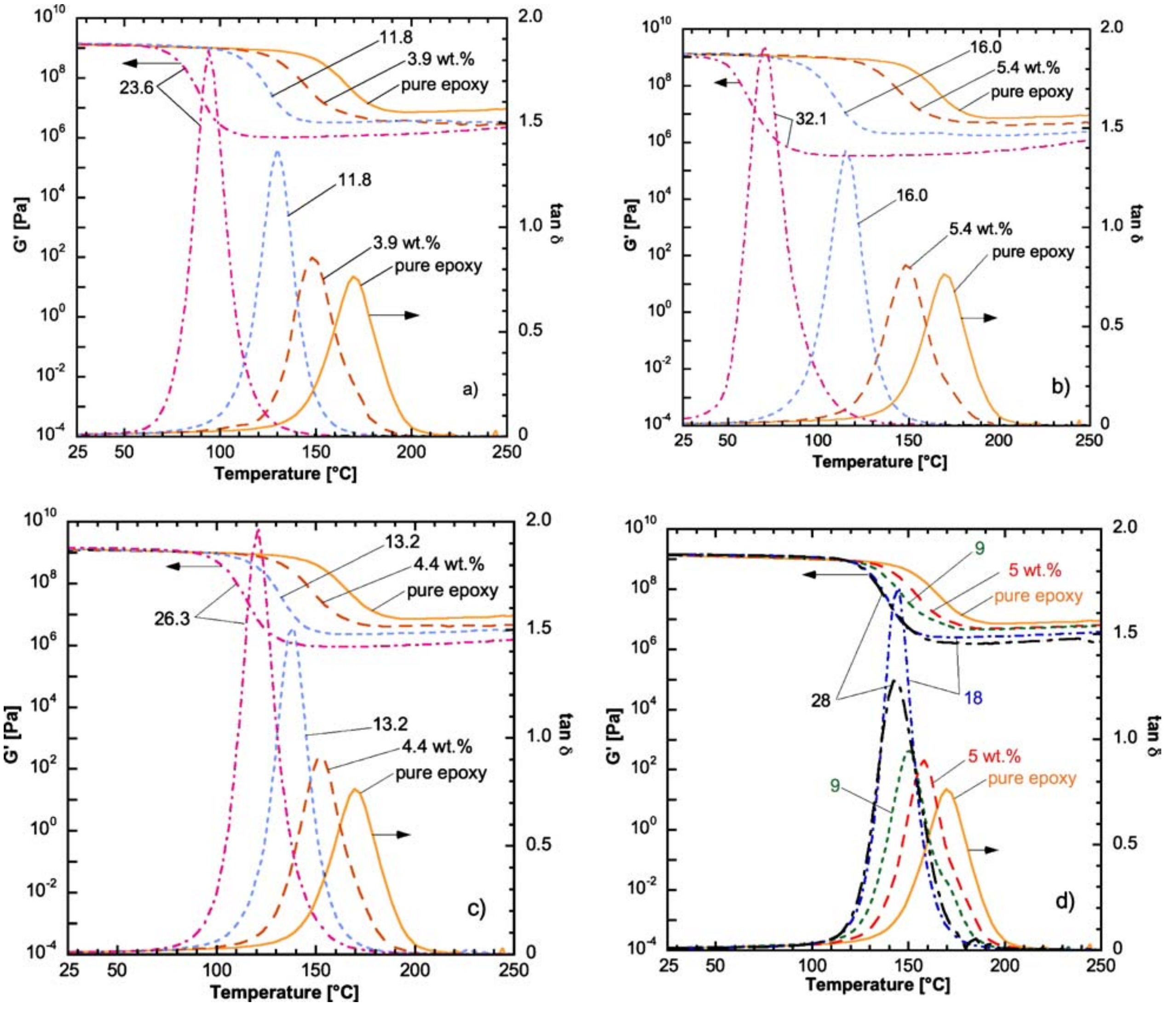


Figure 5 Results of the dynamical mechanical analysis of the cured epoxy formulations containing increasing weight fractions of: (a) DOP-Et, (b) DOP-EtHex, (c) DOP-Gly, and (d) DOP-Cyan.

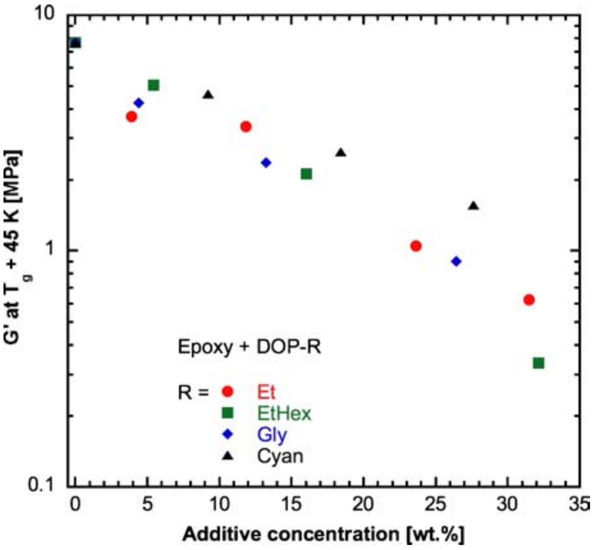


Figure 6 Storage modulus at $T_g + 45$ K of cured epoxy formulations containing increasing weight fractions of the DOP-based additives.

this approach for an epoxy containing 13 wt.% of DOP-Gly, the glass transition temperature of the cured material increased from 140°C to 160°C, indicating a further improved cross-linking reaction.

3.3. Thermal stability and flammability of the cured epoxy

The results of the thermal analysis of the cured epoxy formulations containing the DOP-based additives are shown in Fig. 8. All cured epoxy samples decomposed in a single step. Tables II and III summarise the characteristics of the decomposition step for epoxies containing the non-reactive and reactive additives, respectively. In all cases, approx. 80 wt.% of the epoxy matrix is decomposed and the remainder is residue. A maximum increase of the char yield at 700°C from 2 to 3 wt.% was observed when the DOP-Et and DOP-EtHex additives were used. In contrast, a 7 wt.% increase for the DOP-Gly and DOP-Cyan was

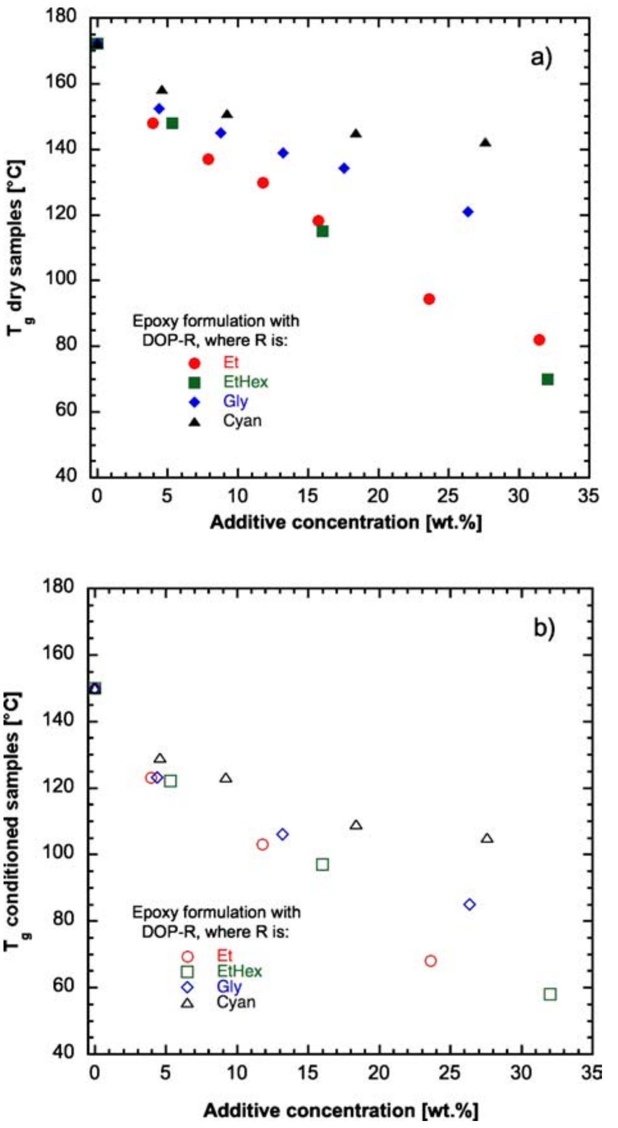


Figure 7 Glass transition temperature of the epoxy formulations as a function of weight content of the DOP-based additives for: (a) dry samples, and (b) conditioned samples.

found. It has been reported that organo-phosphorus compounds increase the char yield of cured epoxy systems during thermal decomposition [11, 13, 14].

According to the results summarised in Tables II and III, the epoxy containing the non-reactive DOP-additives appears to have a higher resistance to thermal decomposition (higher maximum temperature of dTG) than the epoxy containing the reactive DOP-additive. However, it should also be noted that the maximum weight loss rate decreased faster with increasing DOP-Gly content. This observation explains the slightly higher char yields obtained for the epoxy formulations containing the DOP-Gly additive. Char formation during combustion limits the production of combustible gases, decreases the exothermicity of the combustion reactions, and consequently limits the flammability of the material [16, 18, 22]. Taking into account the small overall improvements in char formation, no convincing increase in flame retardancy due to charring can be determined from the thermogravimetric analysis.

However, a significant increase of the LOI value (from 26 up to 35) was obtained for increasing additive contents from 10 to 15 wt.% (about 1.5 wt.% of phosphorus) using the non-reactive additives. In comparison, using the reactive DOP additive, similar improvements in the flammability can only be achieved at higher phosphorus concentrations. This discrepancy might be related to the different chemical environment of the additives which affects their ability to act as a flame retardant. In principal, two mechanisms are possible: in the gas-phase, PO radicals can quench flammable particles such as H and OH radicals [11]; and in the condensed phase, the condensation of non-volatile products can promote char formation. Without a more detailed analysis of the decomposition products during thermal decomposition no fundamental evaluation of the flame retardancy mechanism of the different organo-phosphorus additives in the epoxy samples is possible. However, it is noteworthy that only 10 wt.% of DOP-Et or DOP-EtHex (about 1 wt.% of phosphorus) in the mixture are needed in order to achieve the UL94-V0 classification, while 20 wt.% (about 2 wt.% of phosphorus) of the DOP-Gly or DOP-Cyan are needed to reach the same classification, as shown in Table IV.

3.4. Water uptake of the cured epoxy

The water uptake of epoxies containing the different DOP-additives measured after 14 days of immersion as a function of additive content is summarised in Fig. 9. An increased water absorption with DOP-additive content for all epoxy formulations can be seen. Owing to the complete recovery of the T_g of the conditioned samples, single hydrogen bonds with the epoxy network are expected to be the dominant form of absorbed water [30] for the epoxy formulations under investigation here.

The difference in the moisture absorption between the epoxy containing the DOP-Et and epoxies based on DOP-EtHex or DOP-Cyan is attributed to the higher hydrophobicity and a hindering effect of the DOP-EtHex and DOP-Cyan which prevents the water molecules from being absorbed (as hydrogen bonds) at the hydrophilic sites of the epoxy network.

A higher concentration of hydrophilic sites is expected in the epoxy network containing the DOP-Gly additive due to the higher extent of reacted epoxy groups. Indeed, an increased moisture absorption is observed for the epoxy formulations containing the DOP-Gly.

3.5. Fracture toughness of the cured epoxy

The fracture toughness of the cured epoxy systems at room temperature as a function of DOP-additive content is summarised in Table V. The resulting fracture toughness of the epoxy system containing DOP-Et or DOP-EtHex does not seem particularly affected by additive contents up to 24 and 21 wt.%, respectively, although the

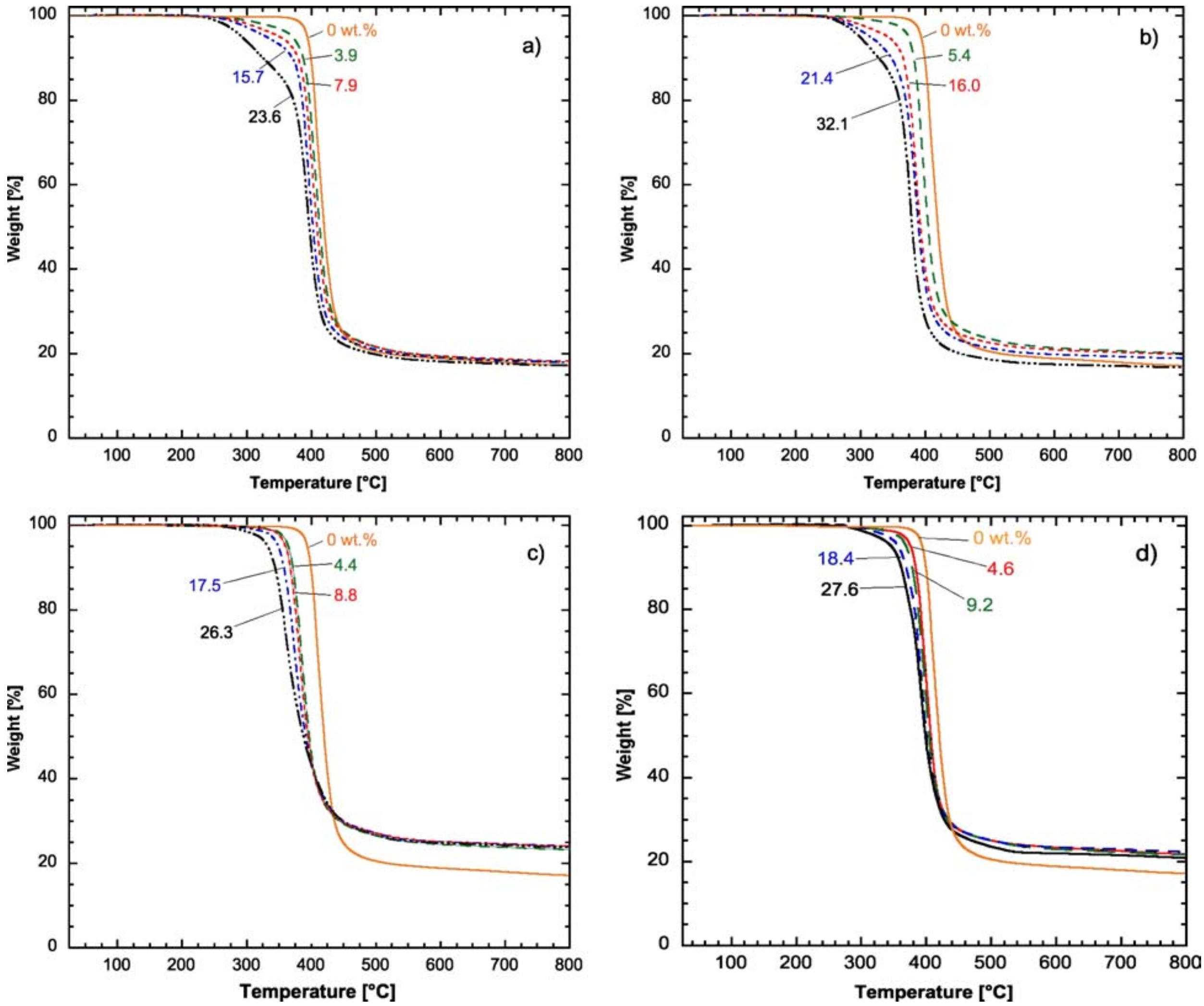


Figure 8 Decomposition profile of epoxy formulations containing increasing weight fractions of: (a) DOP-Et, (b) DOP-EtHex, (c) DOP-Gly, and (d) DOP-Cyan.

T_g decreased significantly. Above these additive concentrations, the degree of conversion of the epoxy falls below 65%, as shown in Fig. 3a and b, and the brittleness of the specimens is observed to increase significantly. The increasing concentration of unreacted epoxy groups introduces a critical number of defects into the network which, in turn, induce a non-uniform stress distribution. At some point, the fracture toughness of the material decreases as a consequence of the high degree of imperfection of the network structure. The higher scatter of the data observed for some of the fracture toughness values at the highest additive contents is attributed to the experimental difficulties faced when preparing such brittle specimens (inducing a straight pre-crack).

TABLE II Results of the thermogravimetric analysis of the cured epoxy formulations containing increasing amounts of the non-reactive organophosphorus compounds

EP + DOP-Et				EP + DOP-EtHex				EP + DOP-Cyan			
wt.% Add	Residue at 700°C (wt.%)	T_{max}dTG (°C)	dmass/dT at T_{max}dTG (wt.%/°C)	wt.% add	Residue at 700°C (wt.%)	T_{max}dTG (°C)	dmass/dT at T_{max}dTG (wt.%/°C)	wt.% add	Residue at 700°C (wt.%)	T_{max}dTG (°C)	dmass/dT at T_{max}dTG (wt.%/°C)
0	16.9±1.2	409 ± 1	2.16 ± 0.05	0	16.9 ± 1.2	409 ± 1	2.16 ± 0.05	0	16.9 ± 1.2	409 ± 1	2.16 ± 0.05
4	18.4 ± 0.7	407 ± 2	2.02 ± 0.12	5	20.2 ± 0.9	396 ± 1	2.12 ± 0.10	5	22.5 ± 0.4	403 ± 1	1.95 ± 0.06
8	18.2 ± 1.0	400 ± 2	1.98 ± 0.07	–	–	–	–	9	22.2 ± 0.7	400 ± 1	1.93 ± 0.04
16	18.7 ± 0.4	397 ± 2	1.94 ± 0.07	16	20.1 ± 0.7	385 ± 1	2.02 ± 0.10	18	22.9 ± 0.4	395 ± 1	1.78 ± 0.05
24	17.2 ± 0.4	393 ± 1	1.80 ± 0.06	21	19.3 ± 0.6	385 ± 1	1.98 ± 0.08	–	–	–	–
32	16.3 ± 0.1	387 ± 1	1.83 ± 0.10	32	17.4 ± 0.2	378 ± 2	2.05 ± 0.09	28	21.5 ± 0.2	394 ± 1	1.60 ± 0.01

TABLE III Results of the thermogravimetric analysis of the cured epoxy formulations containing increasing amounts of the reactive organo-phosphorus compound

EP + DOP-Gly			
wt.% Add	Residue at 700°C (wt.%)	T_{max}dTG (°C)	dmass/dT at T_{max}dTG (wt.%/°C)
0	16.9 ± 1.2	409 ± 1	2.16 ± 0.05
4	23.6 ± 0.7	387 ± 2	1.79 ± 0.05
9	23.7 ± 0.9	381 ± 1	1.79 ± 0.02
18	23.7 ± 0.8	374 ± 3	1.52 ± 0.04
26	24.3 ± 1.0	360 ± 1	1.18 ± 0.02

TABLE IV Limiting oxygen index and UL94-V classification of the epoxy formulations containing the different organo-phosphorus compounds as a function of phosphorus content in the cured specimens

	EP+DOP-Et		EP+DOP-EtHex		EP+DOP-Cyan		EP+DOP-Gly	
wt.% P	UL94	LOI	UL94	LOI	UL94	LOI	UL94	LOI
0	V2	26	V2	26	V2	26	V2	26
0.5	V1	30	V1	30	–	28	V1	30
1	V0	–	V0	–	V1	–	V1	–
1.5	V0	35	V0	33	–	33	V1	29
2	V0	–	V0	–	V0	–	V0	–
3	V0	31	V0	29	V0	32	V0	27

The cured epoxy formulations containing the non-reactive DOP-Cyan were found to show a less pronounced decrease of fracture toughness at a high additive concentration. Using up to 28 wt.% of DOP-Cyan, a less than 30% decrease of the fracture toughness was observed, while similar concentrations of the other additives led to a decrease of at least 60% in comparison to the neat epoxy. A comparison of different epoxies containing the highest additive concentration reveals that the formulation containing the DOP-Cyan has a definitely higher K_{Ic} value. It is important to remember that, at $t = 120$ min, a higher degree of conversion of epoxy groups (approx. 75%) was observed for this material, Fig. 3c; therefore, a more developed and defect-free network capable of undergoing a greater amount of localised plastic deformation [10] was formed.

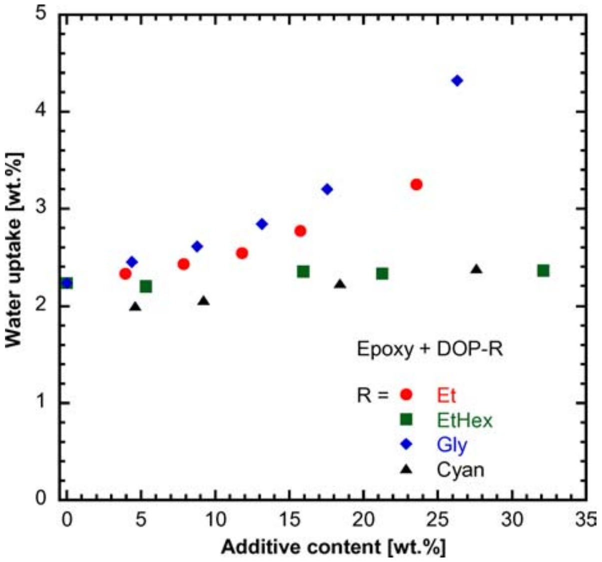


Figure 9 Water uptake of epoxy formulations containing increasing weight fractions of the different DOP-additives.

Similar to the epoxy systems containing the non-reactive additives, the formulation containing the reactive DOP-Gly showed a decreasing fracture toughness at additive concentrations above 18 wt.%, regardless of the higher degree of conversion (>80%) obtained for this system. It should be noted that part of the amine groups were consumed by the reaction with the additive, as discussed in Section 3.1. Thus, the available molar amount of amine for the network development is less than 0.7 when the additive content is above 18 wt.%. Given that the degree of conversion of the epoxy groups should be less than 70%, the poorly developed epoxy network leads to an extremely brittle material.

The degree of conversion of the epoxy without additive cured for 2 h at 150°C was found to be approximately 60%, Fig. 3d. The fracture toughness of this material was 0.22 ± 0.02 MPa m$^{0.5}$, in very good agreement with those values obtained for the epoxy containing the DOP-Et, DOP-EtHex or DOP-Gly with a similar degree of conversion. Although the influence of the type of additive on the fracture toughness cannot be established, it can be observed that the fracture toughness of modified epoxies

TABLE V Fracture toughness and modulus values of the epoxy formulations containing increasing weight fractions of the different organo-phosphorus compounds at room temperature

EP+DOP-Et			EP+DOP-EtHex			EP+DOP-Cyan			EP+DOP-Gly		
wt.% Add	K_{Ic} (MPa m$^{0.5}$)	E_{KIc} (GPa)	wt.% Add	K_{Ic} (MPa m$^{0.5}$)	E_{KIc}(GPa)	wt.% Add	K_{Ic} (MPa m$^{0.5}$)	E_{KIc} (GPa)	wt.% Add	K_{Ic} (MPa m$^{0.5}$)	E_{KIc} (GPa)
0	0.56 ± 0.04	3.8 ± 0.3	0	0.56 ± 0.04	3.8 ± 0.3	0	0.56 ± 0.04	3.8 ± 0.3	0	0.56 ± 0.04	3.8 ± 0.3
4	0.53 ± 0.07	4.2 ± 0.4	5	0.52 ± 0.05	4.1 ± 0.3	5	0.52 ± 0.03	3.8 ± 0.1	4	0.50 ± 0.05	4.5 ± 0.5
8	0.52 ± 0.07	4.2 ± 0.2	–	–	–	9	0.51 ± 0.01	3.9 ± 0.3	9	0.54 ± 0.04	4.4 ± 0.4
12	0.55 ± 0.06	4.8 ± 0.4	–	–	–	–	–		13	0.51 ± 0.01	4.9 ± 0.5
16	0.55 ± 0.04	4.5 ± 0.2	16	0.55 ± 0.04	4.5 ± 0.4	18	0.47 ± 0.02	3.9 ± 0.1	18	0.50 ± 0.03	4.5 ± 0.4
24	0.51 ± 0.03	4.3 ± 0.1	21	0.53 ± 0.04	4.1 ± 0.2	–	–	–	26	0.23 ± 0.06	–
32	0.16 ± 0.02	–	32	0.18 ± 0.04	–	28	0.41 ± 0.03	4.3 ± 0.2	–	–	–

is significantly affected by the network development (extent of curing reaction), which, in turn, is influenced by the amount of additive. A degree of conversion of around 70% appears to be a critical number of reacted epoxy groups. Therefore, the amount of additive that can be used without affecting the fracture toughness of the cured material at room temperature is limited.

The modulus values reported in Table V were estimated from the slope of the load-displacement curve obtained when measuring the fracture toughness of the specimens. The slope of the curve was calculated for displacements between 0.02 to 0.05 mm; for the very brittle samples, the maximum displacement was less than 0.03 mm and the modulus value was not derived in this case. The observed trends can again be correlated with the decreasing degree of cross-linking of the epoxy network. Note, that the increasing trend of the modulus value is less pronounced for the epoxy containing the DOP-Cyan additive which was found to have the highest degree of cross-linking. An increase of the room temperature modulus with a decreasing degree of conversion of a stoichiometric DGEBA-DDS system has been reported in the literature [32]. Here, this change in the modulus was correlated with the β-transition in the temperature range between –100 and –40°C which is related to the incorporation of the diphenyl sulphone moiety in the epoxy network. Although the storage modulus below room temperature has not been measured, the reason for the observed increase in the modulus from the K_{Ic} measurements might also be related to this β-transition.

4. Conclusions

The present study was focused on a systematic investigation of the structure-property relationships of a substoichiometrically cured DGEBA/DDS epoxy system containing various organo-phosphorus compounds as flame retardants. Three non-reactive (DOP-Et, DOP-EtHex and DOP-Cyan) and one reactive (DOP-Gly) organo-phosphorus compounds were evaluated. The total phosphorus content in the resin system was up to 3 wt.%. The processing behaviour as well as the optical appearance of the cured product were not significantly affected.

Coupled thermal stability analysis, LOI, and UL94-V tests showed that the flame retardancy of such epoxy systems increases with both the non-reactive and the reactive DOP-based additives. More specifically, a low additive content of 10 wt.% of DOP-Et or DOP-EtHex (1 wt.% of phosphorus) is sufficient to reach the UL94-V0 rating, while at least 20 wt.% of DOP-Gly or DOP-Cyan (2 wt.% of phosphorus) are required to obtain the same classification. These results imply that the flame retardancy of such organo-phosphorus containing epoxies is related to the chemical structure of the additive; however, further detailed investigations of the flame retardancy mechanism are required to elucidate these differences.

The addition of such compounds leads to a decrease of the effective cross-link sites in the epoxy network, an effect that can be correlated with the resulting mechanical and physical properties of the material. This decreasing degree of cross-linking, as verified by isothermal DSC measurements, depends on the molecular structure of the additive as well as on the additive concentration (a dilution effect of the reactive species). The reactive DOP-Gly and the non-reactive DOP-Cyan additives lead to the lowest decrease of the glass transition temperature due to a higher extent of the cross-linking reaction and to restrictions in molecular motions induced by the molecular structure of the additive.

A flame retardant epoxy resin can be obtained by incorporating additive concentrations below 20 wt.% of either the non-reactive DOP-Cyan or the reactive DOP-Gly without significantly affecting its mechanical and thermomechanical properties. Furthermore, the T_g of the system containing the reactive DOP-Gly can be fine-tuned by adjusting the amount of hardener in the mixture.

The addition of DOP-EtHex or DOP-Cyan to the epoxy did not significantly affect the water uptake of the cured material, most likely due to the hydrophobicity of these additives. However, an increasing water absorption was observed for the epoxies containing the DOP-Et or DOP-Gly additives due to a less pronounced hydrophobicity and a higher degree of conversion of the epoxy groups, respectively.

In summary, the study has shown that the resulting mechanical properties, the fracture toughness especially, and the flame retardancy of modified epoxies can be optimised by adjusting the chemical structure of the organo-phosphorus additive. This approach should allow the development of enhanced epoxy systems for liquid composite moulding applications which will fulfil the stringent requirements for aircraft applications.

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