

FIRE BEHAVIOUR AND MECHANICAL PROPERTIES OF AN EPOXY HOT-MELT RESIN FOR AIRCRAFT INTERIORS

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Abstract

This study focuses on an epoxy novolac based hot-melt prepreg resin system cured with dicyandiamide for purpose of aircraft interiors. The influence of the phosphorus based reactive flame retardant DOPO in dependence of its concentration on the flammability behaviour of the cured neat resin is investigated by UL 94 testing. In addition the thermal and mechanical properties of the formulations are determined by DMA measurements and fracture toughness testing. Besides this the efficiency of boehmite as synergistic flame retardant to DOPO is evaluated at two levels of phosphorus content as well as its influence on thermal and mechanical properties.

It is shown that the flammability is significantly improved with increasing phosphorus content whereas the glass transition temperature decreases. The fracture toughness is not affected within the considered range of phosphorus content.

The addition of boehmite to the modified resins leads to further improvement in flammability behaviour. Moreover it is presented that the fracture toughness increases with higher content of this mineral microfiller while the glass transition temperature keeps constant.

1 Introduction

Today thermosetting prepreps for aircraft interiors are mainly based on phenolic matrices because of their inherent flame resistance [1]. But indeed there are disadvantages such as shrinking and elusion of volatiles during curing. By contrast epoxy novolac systems show minimal shrinkage during curing and furthermore provide improved adhesive properties beneficial for adhesion to core materials. Nevertheless, the intrinsic burning properties of epoxy resins do not permit them for use in the focused application. Therefore they have to be modified using appropriate flame retardants. Halogen free solutions are needed because of the requirements regarding smoke toxicity.

This study was carried out in the course of the development of a new epoxy novolac based hot-melt prepreg resin system for aircraft interiors. DOPO (9,10- Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) was used as halogen free, phosphorus based flame retardant. Formulations with varying phosphorus content from 0 to 1.9 % by weight were produced to investigate the effect of the flame retardant on the neat resin properties especially the inflammableness. Furthermore the synergistic effect of aluminium monohydrate (boehmite) on the flammability properties was investigated at two levels of phosphorus content. Besides

this the effect of this mineral microfiller on the glass transition temperature and the fracture toughness of the neat resin is discussed in this work.

The flammability behaviour of the resin is a major aspect concerning the focused application. Fire testing for interior parts includes several aspects such as ignitability, heat release properties, smoke density and smoke toxicity. In this comparative study the UL 94 test was used as a first indicator regarding the flammability. It has to be mentioned that related to the application the fire behaviour of the composite part is the crucial criteria. First burning tests on sandwich panels with NOMEX® honeycomb core and two facing plies of carbon fibre prepreg on each side showed that airworthiness requirements for cabin parts can be fulfilled with a resin formulation presented in this work.

2 Materials

In this study a mixture of D.E.N. 438 and D.E.N. 431 epoxy novolac resins provided by DOW Chemical Company was used. The mixing ratio was optimized with regard to the viscosity necessary for a hot-melt prepregging process. Table 1 presents the major characteristics of the resins used.

Resin	EEW [g/eq]	Functionality
D.E.N. 431	172 - 179	2.7
D.E.N. 438	176 - 181	3.6

Table 1. Major characteristics of the epoxy novolac resins used in this work (acc. to datasheets).

A micronized dicyandiamide (DICY) grade provided by Air Products and Chemicals was employed as curing agent and used as received. DICY is a solid latent hardener, which is often used in prepreg formulations [2]. Furthermore an appropriate co-curing agent that enables a 140 °C curing cycle was also used.

9,10- Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was purchased from Krems Chemie Chemical Services AG and used as reactive flame retardant compound for the epoxy resin. The product was provided in the form of white flakes. Thus, in order to improve the mixing and miscibility of the material, the DOPO flakes were crushed in a planetary ball mill. Triethanolamine (98 % purity) supplied by Sigma-Aldrich was used as catalyst for the pre-reaction of the phosphorus based flame retardant with the epoxy resin (see figure 1).

Part of the formulations were additionally modified with boehmite (aluminium monohydrate – AlO(OH)) as synergistic flame retardant to DOPO. Boehmite Apyral AOH 30 with a median particle diameter of 1.8 µm was kindly provided by Nabaltec AG and used as received.

3 Experimental

3.1 Preformulation of flame-retardant epoxy resins and preparation of neat resin plates

The chemical incorporation of DOPO into the novolac epoxy resin was made through a pre-formulation process based on the process described by Seibold [3]. The corresponding reaction equation is shown in figure 1. At first D.E.N. 438 and D.E.N. 431 were mixed and degassed under vacuum (10 mbar) in a glass bulb at 100 °C for 1 hour. Afterwards the resin system was heated to 120 °C and the milled DOPO powder was stirred in the resin. 0.1 wt-% of triethanolamine was added as a catalyst to the mixture. Lastly, the temperature was elevated to 140 °C and maintained for 1.5 hours. During the whole preformulation process, the resin system was continuously stirred.

After the preformulation process, the resin was cooled down to 120 °C before adding 3 parts by weight DICY per hundred parts preformulation as well as the boehmite if applicable. The mixture was stirred for 15 to 20 minutes to ensure a homogeneous dispersion of the additives.

Finally, the co-curing agent was added under stirring. The whole formulation was degassed under vacuum (10 mbar) before it was poured in the preheated (120 °C) aluminium moulds. The moulds were pretreated with an external release agent (Loctite Frekote 770-NC, Henkel AG). The neat resin plates were cured for 90 minutes at 140 °C in a convection oven. Demoulding was carried out at room temperature.

With regard to testing methods described below plaques with a thickness of 2, 3 and 4 mm were produced for each formulation, respectively.

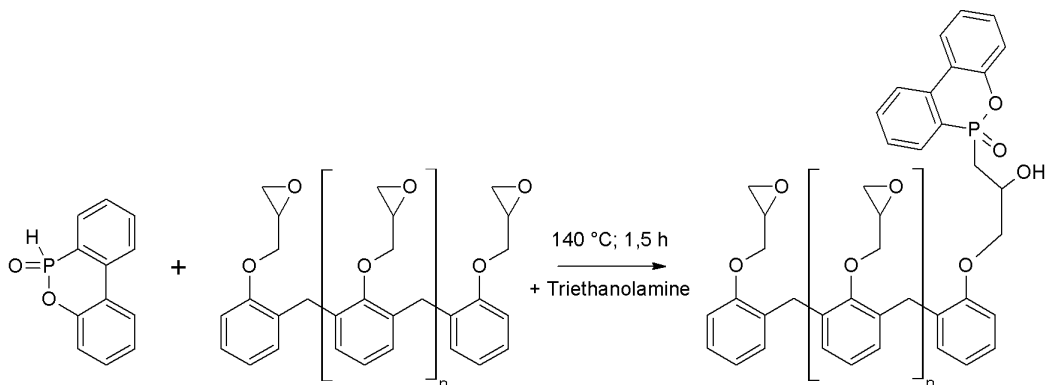


Figure 1. Chemical reaction of DOPO with epoxy novolac resin (acc. to [4]).

3.2 Characterization of cured resins

The flammability behaviour of all cured epoxy resins was characterised by the standardised UL 94 vertical burning test [5]. The sample size for the ignition test was 125 x 12.5 x 3 mm³. Three samples were burned for each formulation. The horizontal burning test (HB) was carried out if classification by vertical burning test (VB) failed.

Dynamic mechanical analysis (DMA) in torsion mode was performed on cured rectangular specimens of 50 x 10 x 2 mm³. Two specimens for each formulation were measured from 25 °C to 250 °C with a heating rate of 3 K/min. The frequency was set to 1 Hz and a deformation of 0.1 % was utilised. The glass transition temperature (T_g) was taken as the temperature at which the loss factor reached its peak.

Rubber elasticity theory was used to calculate the average molecular weight between crosslinks (M_c) of the formulations by means of the following relationship [6]:

$$M_c = \frac{\phi \rho R T}{G_e} \quad (1)$$

where M_c is the molecular weight between crosslinks, ϕ a front factor, ρ the density at the absolute temperature T , R the gas constant, T the absolute temperature 50 K above T_g and G_e the equilibrium shear modulus. To apply this equation, equilibrium shear modulus G_e is determined from DMA curves at the rubbery state, which is taken at 50 K above T_g . The front factor is the ratio of the mean square end-to-end distance of a network segment to that of a randomly coiled chain, and, following Katz and Tobolsky [7], is taken to be approximately 1.88. The dimension change of the specimens from room temperature to T was also obtained by DMA measurements. Assuming isotropic expansion, the volume of a specimen at T was calculated by adding the appropriate percent volume change to the room temperature volume. The high temperature density was then calculated as the ratio of mass to volume at T .

Based on Linear Elastic Fracture Mechanics (LEFM) the critical stress intensity factor (K_{Ic}) was obtained from the opening mode test according to ISO 13586 [8], performed on compact

tension specimens (CT). A sharp V-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 kN under controlled atmosphere conditions (23 °C and 50 % relative humidity) and a cross-head speed of 10 mm/min. A minimum of four specimens of each formulation was tested.

Moreover, based on the theory of Saxena and Hudak [9] the Young's modulus is also determined from the fracture toughness testing.

A detailed analysis of the fracture surfaces was carried out using a Zeiss 1530 Scanning Electron Microscope equipped with a field emission cathode operating at 5 kV.

4 Results and Discussion

4.1 Formulations with varying phosphorus content – without boehmite

The glass transition temperature in dependence of the phosphorus content is presented in figure 2. As can be clearly observed the glass transition temperature decreases significantly for phosphorus contents above 0.5 wt-%. But it should be mentioned that a phosphorus content of 1.9 wt-% still leads to a glass transition temperature of 156 °C, which is considerably above the needs for interior parts. The drop in T_g can be explained by the decreasing crosslinking density due to the reactive flame retardant. This is confirmed by the increasing average molecular weight between crosslinks with increasing phosphorus content (figure 2). The addition of the reactive flame retardant reduces the number of epoxy reactive sites in the resin (see reaction equation in fig. 1), affecting the network density. This is also reported by Wang et. al. [10] and Hussain et. al. [11].

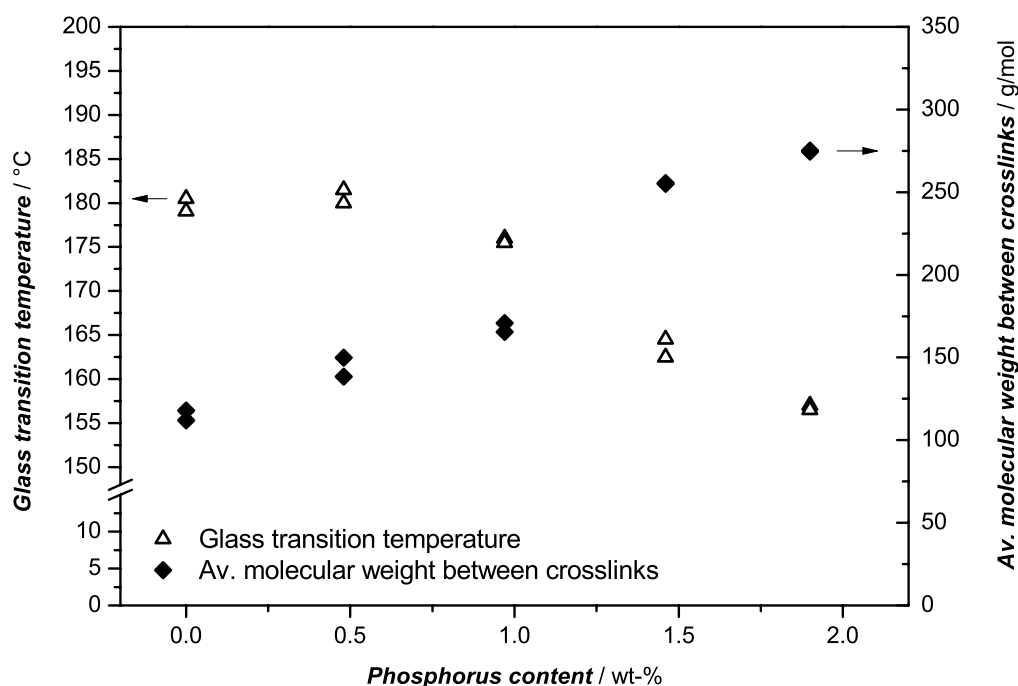


Figure 2. Glass transition temperatures and average molecular weight between crosslinks in dependence of phosphorus content for the formulations without boehmite. Each point represents one DMA measurement.

The mechanical properties of the cured resins are not affected by the decreasing network density as shown in figure 3. All formulations show a very brittle behaviour with K_{Ic} values in the range of 0.4 to 0.5 MPa m^{1/2} and also the modulus keeps constant. The brittleness of this novolac based resin is caused by its high crosslinking density [12]. Even the increase in average molecular weight between crosslinks with increasing amount of DOPO does not improve the fracture toughness.

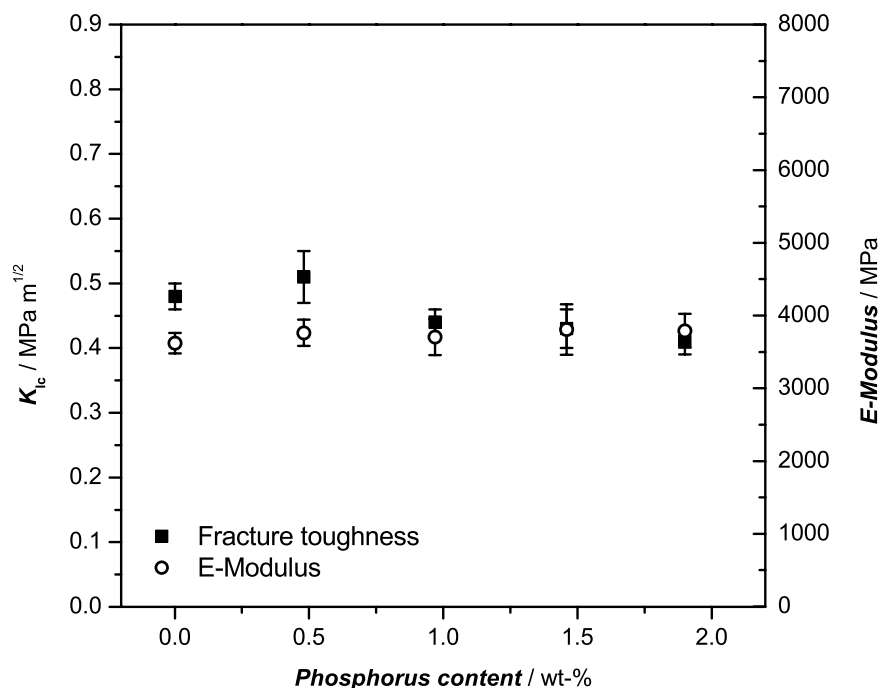


Figure 3. Effect of phosphorus content on mechanical properties.

The flammability behaviour of the cured neat resins is improved with increasing phosphorus content. Table 2 presents the results of the UL 94 testing. For the formulations classified as HB the calculated burning rate is shown, too.

P-content [wt-%]	UL 94 rating	burning rate (HB) [mm/min]
0	HB	20 ± 2
0.5	HB	18 ± 1
1.0	HB	14 ± 1
1.5	HB	self extinguishing
1.9	V-1	-

Table 2. Flammability results from the UL 94 testing for formulations without boehmite.

The burning rate of the HB rated systems decreases significantly with increasing DOPO content. The specimens with a phosphorus content of 1.5 wt-% extinguish before reaching the 25 mm mark. V-1 classification could be obtained for the formulation containing 1.9 wt-% phosphorus.

4.2 Boehmite modified formulations

To investigate the efficiency of boehmite as synergistic flame retardant the formulations containing 0.5 and 1.0 wt-% phosphorus, respectively, were filled with boehmite. Filler levels up to 50 wt-% were investigated. It has to be mentioned that increasing boehmite content leads to decreasing phosphorus content regarding the whole formulation as the phosphorus content keeps constant in the resin excluding the solid fraction.

Figure 4 shows the glass transition temperature in dependence of the boehmite filler content. It can be clearly observed that the additional flame retardant has no significant influence on the glass transition temperature of the formulations.

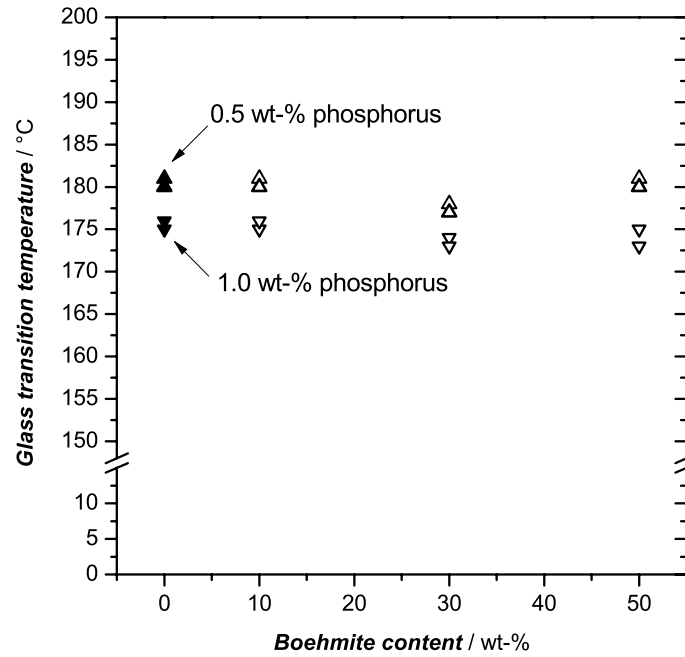


Figure 4. Glass transition temperature of modified formulations in dependence of boehmite content.

The mechanical testing reveals an ascent in fracture toughness with increasing amount of boehmite (see figure 5). The fracture toughness can be raised up to approx. $0.8 \text{ MPa m}^{1/2}$ by adding 50 wt-% boehmite to the formulation including 1.0 wt-% phosphorus. It can further be recognized that the K_{Ic} values of the formulation with 1.0 wt-% phosphorus content exceed those of the system based on the 0.5 % phosphorus containing resin for boehmite contents above 10 wt-%. This might be due to a synergistic effect of boehmite micro particles and network density on toughness, which should be investigated more detailed in further studies. The modulus also grows drastically with increasing boehmite content due to the higher modulus of the rigid filler particles.

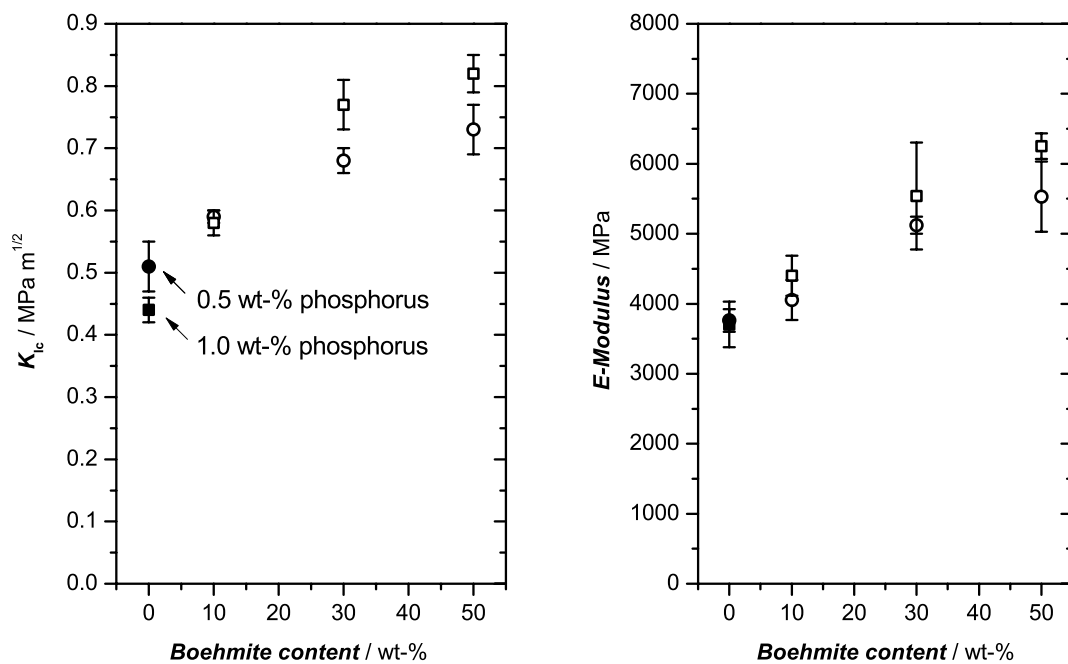


Figure 5. Mechanical properties of modified formulations based on K_{Ic} fracture toughness testing in dependence of boehmite content.

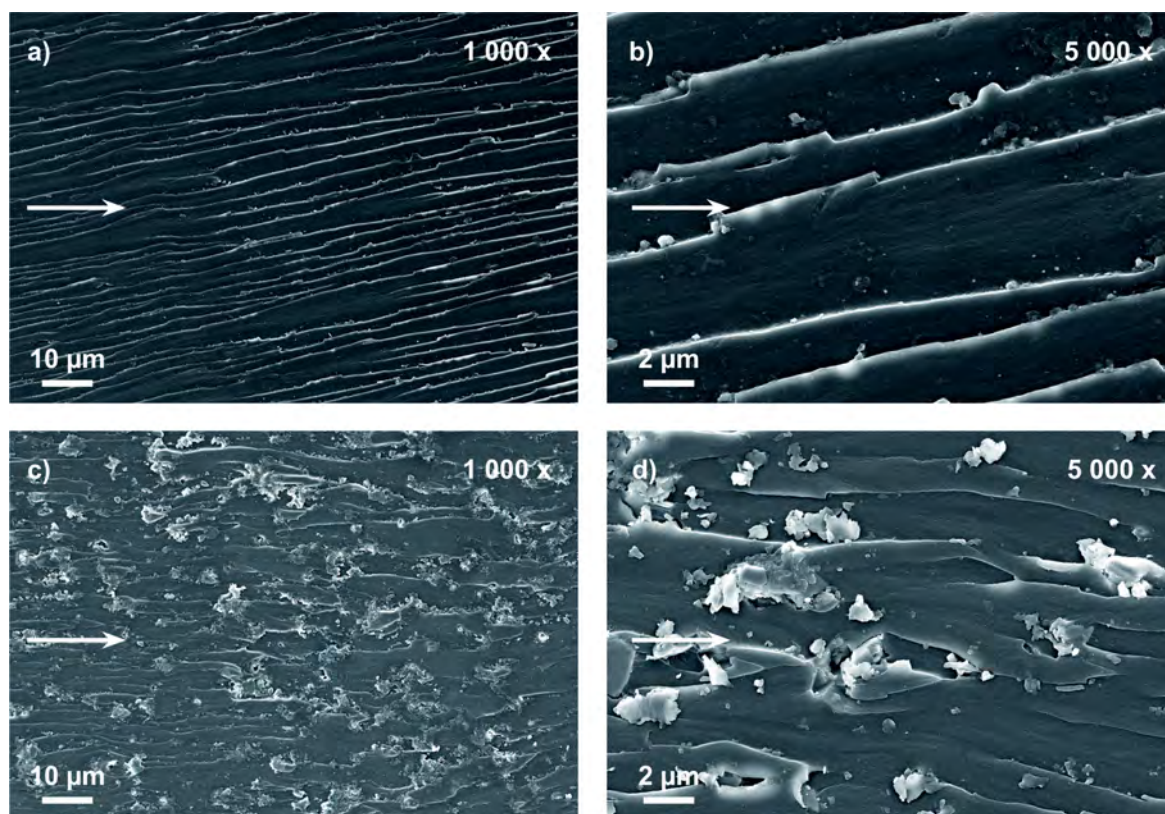


Figure 6. SEM micrographs of fracture surfaces. The arrows indicate the direction of crack propagation. Pictures a) and b) show the system with 0.5 wt-% phosphorus content without boehmite. Pictures c) and d) present fracture surfaces of the same system filled with 10 wt-% boehmite.

Observing the SEM pictures (figure 6) at an amplification of 1 000 x and 5 000 x it can be seen that the fracture surface changes from the brittle failure bands in the modification without boehmite (fig. 6.a) and 6.b)), to a tortuous surface for the system containing 10 wt-% boehmite (fig. 6.c)). The micrograph of the boehmite modified resin at an amplification of 5 000 x (fig. 6.d)) depicts the occurrence of crack deviation and crack pinning by the presence of particles. These observed mechanisms improve the fracture toughness, as they impose higher energy expenditure for the crack transmission.

P-content of unfilled resin	0 wt-% boehmite	10 wt-% boehmite	30 wt-% boehmite	50 wt-% boehmite
0.5 wt-%	HB 18 ± 1 mm/min	HB 12 ± 2 mm/min*	HB self extinguishing	HB self extinguishing
1.0 wt-%	HB 14 ± 1 mm/min	HB self extinguishing	HB self extinguishing	HB self extinguishing

Table 3. Flammability results from the UL 94 testing for formulations filled with boehmite.

* Average of 2 samples. 3rd sample was self extinguishing.

In the UL 94 flammability testing all regarded boehmite modified systems were classified to HB. With a closer look on the results (see table 3) an improvement of burning behaviour due to the mineral filler can be clearly observed. All tested specimen of the resin system containing 1.0 wt-% phosphorus filled with 10 wt-% boehmite extinguished before reaching the 25 mm mark (phosphorus content of the whole formulation: 0.9 wt-%). For the resin system containing 0.5 wt-% phosphorus the same was the fact at a boehmite filler level of 30 % (phosphorus content of the whole formulation: 0.4 wt-%). Within the formulations without boehmite the identical result was observed for 1.5 wt-% phosphorus content (see

table 2). Therefore it can be concluded that the boehmite acts as a synergistic flame retardant to DOPO and furthermore reduces the phosphorus content needed in the whole formulation.

5 Conclusions and Outlook

This work investigates the influence of DOPO, a reactive phosphorus flame retardant, on the neat resin properties of an epoxy novolac based hot-melt prepreg resin cured with DICY. It is shown that the glass transition temperature decreases for phosphorus contents higher than 0.5 wt-% with increasing amount of DOPO. This is caused by lowering the network density due to the reaction of DOPO with the epoxy groups. The fracture toughness and the modulus of the neat resin are not affected by the incorporation of DOPO in the focused range. The flammability characterized by UL 94 is ameliorated with increasing phosphorus content.

Besides this, formulations with 0.5 and 1.0 wt-% phosphorus content, respectively, were filled with boehmite to evaluate its influence on burning behaviour as well as on thermal and mechanical properties. The results present that the glass transition temperature is not affected by the boehmite. The mineral filler acts as a synergistic flame retardant to DOPO and furthermore increases the fracture toughness considerably.

In further studies the tensile properties of the boehmite modified resins will be investigated to see the effect of the filler on the elongation at break. Afterwards the processability and resins mechanical performance in the fibre reinforced composites should be evaluated. The burning behaviour should be characterized using sandwich specimens and the appropriate fire testing methods for aircraft interior parts.

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