COMPARISON OF ADDITIVE AND REACTIVE PHOSPHORUS-BASED FLAME RETARDANTS IN CARBON FIBRE REINFORCED EPOXY RESIN COMPOSITES

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Abstract
The aim of this work was to investigate the effect of phosphorus-based additive and reactive flame retardants (FR) on the flammability and mechanical properties of neat epoxy resins and carbon fibre reinforced composites made thereof. A pentaerythritol-based model epoxy resin system was used as matrix, cured with cycloaliphatic diamine and reinforced with unidirectional woven carbon fibre fabric. Commercially available ammonium polyphosphate (APP) was used as additive and DOPO as reactive flame retardant. The behaviour of these systems was also compared to a recently synthesized phosphorus containing amine (TEDAP), which can be used both as flame retardant and crosslinking agent.

1 Introduction

Epoxy resins are extensively used in various industrial application fields as, for example, adhesives, surface coatings, laminates and matrix materials. Despite their exceptional characteristics like good adhesion to many substrates; moisture, solvent and chemical resistance; low shrinkage on cure; outstanding mechanical and electronic resistant properties, their flammability still represents a limit in structural applications. The use of the parts made of composites of high mechanical loading capability, being suitable for replacing metallic structures, is rapidly increasing in the aircraft industry [1]. In the newest large commercial airliners the fuselage, the wings and the empennage are also made of carbon fibre reinforced composites. In case of fire, the health risk is not the only danger; also the decrease of mechanical properties can be significant [2-4]. Due to environmental reasons, the use of halogen-containing flame retardants needs to be decreased. Their most promising substitutes are the phosphorus-containing flame retardants due to their extremely wide and versatile range, since the P element exists in various oxidation states [5-8]. Epoxy resins that are fire retarded with conventional additives are usually of poorer physical properties than the unmodified ones; therefore the use of reactive comonomers is preferred in many cases. Incorporating them into the polymer structure, they consequently modify the properties of the material, in general decreasing them. The greatest task of actual researches is to create a composite system which has high mechanical performance and shows effective flame retardancy at the same time.

2 Materials and testing methods

2.1 Materials

The epoxy resin matrix consisted of epoxy component type MR 3016 (tetraglycidyl ether of pentaerythritol, properties: non-modified, resin-like reactive dilutant, epoxy equivalent: 156-170; viscosity at 25 ºC: 850-1200 mPa.s; density at 25 ºC: 1.24 g/cm^3) applied with MH 3122 curing agent (3,3'-dimethyl-4,4'-diamino-dicyclohexyl-methane, properties: amine number: 464-490 mg KOH/g; viscosity at 25 ºC: 80-120 mPa.s; density at 20 ºC: 0.944 g/cm^3) supplied by ipox chemicals Ltd., Hungary.

Ammonium polyphosphate produced by Nordmann Rassmann (NORD-MIN JLS APP) was used as additive type flame retardant (properties: phosphorus content: 31-32%, nitrogen content: 14-15%, average particle size: 15 µm).

As reactive flame retardant, Struktol Polydis 3710 (DOPO; 9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide, properties: MM: 216,17 g/mol, mp: 116°C), supplied by Struktol Gmbh was used. In order to form a phosphorus-containing epoxy component, DOPO was reacted with the MR 3016 at 160°C for 6 hours. As two DOPOs were reacted with one molecule of the tetrafunctional epoxy resin, the epoxy equivalent of the product is the double of the original component.

A phosphorus-containing reactive amine, TEDAP (*N,N',N''*-tris(2-aminoethyl)-phosphoric acid triamide, propreties: amine number: 510–530 mg KOH/g; viscosity at 20 °C: 400 mPa) synthesized according to previous publication of the authors [9] was applied as flame retardant curing agent.

For the preparation of fibre-reinforced epoxy resin composites unidirectional woven carbon fibre fabric type PX35FBUD0300 was used (Zoltek, Hungary, fibre surface weight: 300 g/m^2).

2.2 Methods

Preparation of epoxy resin samples: the epoxy and curing agent amine components were mixed at room temperature in a glass beaker in order to obtain a homogenous mixture. In the case of the APP-containing formulations, the flame retardant powder was dispersed homogenously in the epoxy component, and then the amine component was added and mixed as mentioned above. For the mechanical tests composite plates of 3-mm-thick sheets containing 40 mass% of carbon fibres were manufactured using the hand lay-up technique. The fibre-reinforcement consisted of five plies of woven fabric in the case of the mechanical characterization, and of 9 plies for the flammability tests. The specimens were cut to appropriate dimensions with diamond disc.

The fire resistance was characterized by limiting oxygen index measurement (LOI, according to ASTM D-2863), UL-94 test (according to ASTM 1356-90 and ANSI//ASTM D-635/77, respectively), mass loss type cone calorimeter (according to ISO 13927, Fire Testing Technology, heat flux of 50 kW/m^2).

The mechanical characteristics of the composite specimens were determined with instrumented tensile tester type Zwick Z050 and Z020. Tensile strength measurements were carried out according to ISO 527-4, flexural strength of the composites was determined according to ISO 14125, while the interlaminar shear properties according to ASTM D3846-94.

3 Results and discussion

3.1 Flammability properties

The flame retardant efficacy of an additive and two types of reactive flame retardants was compared. Both matrices and the relevant carbon fibre reinforced composites were tested. In the case of the DOPO-containing resin system, due to the brittleness of the cured matrices, no mechanical evaluation was performed on the samples, and no composites were prepared.

Comparing the results of the matrices containing 3 wt% of phosphorus (**Table 1**), it can be stated that there is practically no difference between the reference resin and the DOPO-containing one, which indicates that the DOPO cannot exercise its beneficial effect in this aliphatic resin system. The samples containing APP and TEDAP reached the same LOI values, but to reach the V-0 rating, the application of the latter one was necessary. Concerning the heat release results, the application of APP resulted in decreased peak of heat release (pHRR) by 40%, while by the incorporation of TEDAP resulted in 85% lower value.

Flame retardant	**LOI (V/V%)**	**UL-94**	**pHRR (kW/m^2)**	**THR (MJ/m^2)**	**residue (%)**
reference	23	HB	706,4	103,5	0
DOPO	23	HB	682,0	106,0	5,6
APP	32	HB	420,8	82,5	13,6
TEDAP	33	V-0	111,4	28,0	40,0

Table 1. Comparison of the flammability properties of different flame retardants at 3 wt% phosphorus content of the matrices

Comparing the values received for the composites (**Table 2**) to those of the matrices, the flame retardant effect of the non-flammable carbon fibres can be observed. By the incorporation of the reinforcement, the LOI value of the reference resin increased from 23 to 31, and the pHRR decreased by 50%. With both flame retardants the V-0 rating could be reached, however, the application of TEDAP resulted in much lower THR (total heat released) value and more residue after the cone calorimetric measurement (60%).

Flame retardant	**LOI (V/V%)**	**UL-94**	**pHRR (kW/m^2)**	**THR (MJ/m^2)**	**residue (%)**
reference	31	HB	341,4	56,9	48
APP	36	V-0	252,8	53,6	51,3
TEDAP	39	V-0	209,1	20,6	59,8

Table 2. Comparison of the flammability properties of the carbon fibre reinforced composites at 3 wt% phosphorus content

3.2 Mechanical characterization

The tensile and the bending properties of the flame retarded matrices were investigated, while for the carbon fibre reinforced composites also the interlaminar shear properties were determined. In the case of the matrices, it can be concluded that the application of APP as flame retardant in different concentrations cause only a slight change in the strength of the samples. This can be explained by the homogenous dispersion of the FR particles, so no aggregates can be found in the matrices. When the flame-retardant crosslinking agent (TEDAP) is used in higher concentrations, the measured strength decreased significantly, due to the lower crosslink-density of this system.

Flame retardant	**Tensile strength (MPa)**	**Bending strength (MPa)**	**Interlaminar shear strength (MPa)**
reference	50,4	82,1	-
APP	42,9	72,7	-
TEDAP	32,0	52,9	-
reference CC	386,9	431,5	17,75
APP CC	383,0	454,7	18,18
TEDAP CC	298,5	228,5	11,54

Table 3. Comparison of the mechanical properties of the matrices and carbon fibre reinforced composites (CC) at 3 wt% phosphorus content

Comparing the results of the matrices and composites containing 3 wt% of phosphorus (**Table 3**), it can be stated that the incorporation of the reinforcing carbon fibres increased the measured strength values, as expected. As the fibres act as load-bearing elements, the role of the matrix is to transmit the load to them, thus the difference between the different compositions is smaller than in the case of the matrices. The interlaminar shear strength of the composites is in good accordance with the other determined mechanical properties. Due to the polar character of TEDAP, the adhesion to the apolar carbon fibres is weaker, so the decreased strength values can be explained by the smaller load transmitter capability of this resin.

Conclusions

In this work, three types of phosphorus-based flame retardants were investigated in a model aliphatic epoxy resin. The application of DOPO in this system did not lead to increased flame retardancy due to the molecular incompatibility of the components. The additive APP and the reactive TEDAP decreased the flammability of the resin. The effectiveness of the TEDAP is proved by the UL-94 V-0 rating even at 3 wt% of P-content, amplified with significantly reduced heat release value and high charred residue. The incorporation of the carbon fibres itself into the resin improved the flame retardant characteristics of the samples to a large extent. Concerning the mechanical properties, it can be concluded that the well-dispersed APP particles did not affect significantly the reached values; however, due to the weak adhesion between the polar TEDAP and the apolar reinforcing fibres, the measured strength did not reached the expected level. As the effective flame retardancy and the appropriate mechanical properties seem to be contradictory requirements, the development of a coated composite, with a slightly flame retarded load bearing core, and a resin coating layer made of the most effective FR system seems to be a good compromise.

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