



# Reactive flame retardancy of cyanate ester/epoxy resin blends and their carbon fibre reinforced composites



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## ABSTRACT

Cyanate ester/epoxy resin (CE/EP) blends consisting of diglycidyl ether of bisphenol A (DGEBA) and novolac type cyanate ester (CE) were prepared and reactively flame retarded using an epoxy functional adduct of DGEBA and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). Moisture uptake was measured by the gravimetric method; consequent carbamate formation was detected by infrared spectrometry. Effects of cyanate ester : flame retardant ratio were determined on glass transition temperature ( $T_g$ ), thermal stability and flammability. The addition of CE compensated the  $T_g$  decreasing effect of DOPO. Reactively flame retarded CE/EP carbon fibre reinforced composites had LOI of 48 V/V%, V-0 UL-94 rate and peak of heat release rate of 84 kW/m<sup>2</sup>.

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## 1. Introduction

Cyanate esters (CEs) offer several advantages over the commonly used high performance and high heat resistant epoxy resins (EPs). They have high glass transition temperature ( $T_g$ ) (up to 400 °C), low moisture absorption and low outgassing providing great dimensional stability. These properties make CEs good candidates for applications such as printed circuit boards, capacitors and structural aircraft components. Despite the numerous advantages and the four decades past since their commercialization in 1976, they are not yet abundantly used in the composite industry [1,2]. Compared to high performance EPs their price is still more than twice as high, and the lack of formulation knowledge, especially issues connected with their moisture sensitivity during curing [3] and toughness [4], also hinders their wide-spread application as polymer matrix material.

One feasible way to reduce the associated material costs and facilitate the headway of CEs in the composite industries is to blend them with other thermosetting matrices. For this purpose EPs are an optimal candidate, not only because of their moderate price

level, but also because they can be crosslinked with CEs instead of the commonly applied amine or anhydride type hardeners, and this results in primary chemical bonds instead of simple blend formation. Consequently, from point of view of EPs, CEs can be considered as multifunctional reactive modifiers: Besides replacing the hardeners, representing practically the same price level as CEs, they also enhance numerous properties of EPs as thermal stability, glass transition temperature, moisture absorption, etc. Although CEs possess a thermally stable backbone, their flame retardancy is still an issue to be solved, especially in advanced sectors with strict fire safety standards as electrical and aircraft industry. By combining them with EPs having even lower thermal stability [5], this problem is even more emerging. There exist two main approaches to achieve flame retardancy: the additive and the reactive one. Lately the reactive approach was given much attendance because of its numerous advantages: it provides a more stable effect compared to the additive method, because the flame retardant is chemically incorporated into the polymer structure, so it does not migrate to the surface of the polymer either during high temperature processing or application. The increasing emphasis on the health and environmental compatibility of flame retardants has drawn the attention to organophosphorus reactive flame retardants [6–10], providing in most cases a combined gas and solid phase effect

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[11,12].

In the case of CE/EP blends the phosphorus (P) -containing chemical unit, providing the flame retardant effect, can be incorporated into the EP, CE component or separate reactive modifiers (in most cases with –OH and –NH<sub>2</sub> functions) can be applied as well. Chang et al. [13] reacted 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) with benzoxazines to form **P-containing reactive flame retardant with –OH functions**. V-0 UL-94 rate was reached with 1.5 or 2.0 mass% P-content, respectively, depending from the benzoxazines backbone. Ho et al. reacted DOPO with naphthoquinone [14] and benzoquinone [15], respectively, and the gained–OH functional adducts were reacted with diglycidyl ether of bisphenol A (DGEBA) to form **P-containing EP components**. The CE/EP blends made thereof reached V-0 UL-94 rate with 2 mass% P. Lin et al. [16] reacted DOPO with bisphenol-A, to form a P-containing adduct with OH-functions, which were reacted with cyanogen bromide to result in **P-containing CE**. In this case V-0 UL-94 rate was reached with 1.5 mass% P. Lin [17] reacted DOPO with bisphenol A dicyanate (BADCY) to form **P-containing CE**. When self-cured 1.5 mass% P-content was enough to reach V-0 rate, while if blended with DGEBA, 1.6 mass% P was necessary to reach V-0 rate. Chen et al. [18] reacted commercially available dihydroxyphenyl-DOPO with CE to form **P-containing CE** and reached V-0 rate with 1.4 mass% P. Krishnadevi et al. [19] synthesized hexa(aminophenyl)cyclotriphosphazene, a **P-containing reactive flame retardant with NH<sub>2</sub>-functions**. By adding 15 mass% of it (equivalent to 1.9 mass% P) to BADCY, LOI of 44 V/V% was reached. The above mentioned literature examined the flame retardant effect only in polymer matrices, no results related to applications in fibre reinforced composites were disclosed yet.

In this particular case, the EP component, DGEBA was pre-reacted with DOPO to form an epoxy functional adduct, and a novolac type CE having high glass transition temperature was reactively blended with it. As the inclusion of flame retardants usually decreases the glass transition temperature of EP systems, the hybrid system consisting of CE, EP and reactive flame retardant would potentially provide higher glass transition temperature than in case of flame retarded EP itself and besides it offers a balance between properties and price level. Effect of CE and flame retardant ratio was determined on moisture uptake, and consequent carbamate formation during curing, glass transition temperature ( $T_g$ ), thermal stability and flammability. From the best performing blends reactively flame retarded CE/EP carbon fibre reinforced composites were made and their flame retardancy was tested and compared to CE and EP benchmarks.

## 2. Materials and methods

### 2.1. Materials

Novolac type cyanate ester (Primaset PT-30) was obtained from Lonza Ltd. (Basel, Switzerland).

Diglycidyl ether of bisphenol A (DGEBA, IpoX ER 1010) with 188 g/eq epoxy equivalent weight was obtained from IPOX Chemicals Ltd. (Budapest, Hungary).

The used reactive flame retardant, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO, Struktol Polydis 3710, properties: molecular mass: 216.17 g/mol, melting point: 116 °C) was supplied by Struktol GmbH.

In order to form a phosphorus-containing epoxy component, DOPO was reacted with DGEBA in 1:1 M ratio. Prior to the reaction DOPO was kept at 85 °C for 12 h, in order to remove the traces of moisture. DGEBA was kept under vacuum at 110 °C to remove air and traces of moisture, and after adding DOPO, the mixture was

stirred at 160 °C for 5 h. After cooling to room temperature a solid adduct was obtained. This synthesis was based on the method previously published by Wang and Lin [20].

In case of DGEBA-based systems methyl-tetrahydrophthalic-anhydride with minimal tetrahydrophthalic anhydride content (Aradur 917 – AR917) was used as hardener with 1-methylimidazole (DY070) accelerator by Huntsman Advanced Materials (Basel, Switzerland). The equivalent mass of the anhydride type curing agent, calculated from its molecular mass, was 160 g/eq. The accelerator was applied in 2 mass% related to the mass of the epoxy resin component.

The chemical structures of the applied polymer components are shown in Fig. 1.

As fibre reinforcement Zoltek Panex 35 type unidirectional carbon weave with 300 g/m<sup>2</sup> aerial weight provided by Zoltek Ltd. (Nyergesújfalu, Hungary) was used.

### 2.2. Methods

#### 2.2.1. Sample preparation

Besides the reference CE, EP and CE/EP blend samples, flame retarded EP and CE/EP blend samples were prepared using the synthesized DGEBA–DOPO adduct. CE/EP blends with 2 and 3 mass % phosphorus were made. The compositions of samples are summarized in Table 1. Samples with stoichiometric ratio of epoxide group and cyanate ester group (1:1) are highlighted in grey.

For the preparation of cured specimens appropriately sized heat resistant silicone moulds were used. Samples containing PT-30 were cured 1 h at 150 °C, 3 h at 200 °C and 1 h 260 °C according to the suggestion of CE supplier. In case of DGEBA and DGEBA–DOPO the heat treatment consisted of a 1 h 80 °C and a 3 h 140 °C isothermal step.

The composite laminates were made by hand lamination in a press mould. Each carbon weave layer was separately impregnated, in case of high viscosity matrices the polymer and the mould were heated to 80 °C. The prepared laminates were put under compression with 180 bar hydraulic pressure in T30 type platen press (Metal Fluid Engineering s. r. l., Verdello Zingonia, Italy) to achieve high and uniform fibre content in the composites. 4 mm thick specimens were made using 10 layers of carbon weave in [0/0] layer order. The heat treatment of the laminates (same as curing cycles in polymer matrix samples) was carried out during the pressing. The measured fibre content was in the range of 50–55 mass%.

#### 2.2.2. Moisture uptake during curing

For the measurement of moisture uptake 10 g of uncured sample was poured into 50 mm × 50 mm × 3 mm aluminium sample holders. The specimens were conditioned in Memmert HCP153 type climate chamber under the following conditions: 30 °C and 80% relative humidity (RH), 80 °C and 10% RH. The moisture uptake of the uncured specimens was measured by Ohaus Explorer type scale (Nänikon, Switzerland). Parallel to moisture uptake measurements ATR-FTIR spectra were recorded using a Bruker Tensor 37 type Fourier transform infrared (FTIR) spectrometer (Bruker Corporation, Billerica, MA, USA) in the spectral range of 600–4000 cm<sup>-1</sup> in order to detect the carbamate formation.

In order to detect the effect of moisture uptake on other properties these samples were subjected to curing cycles detailed above in Sample preparation section and the relevant measurements were carried out on them afterwards.

#### 2.2.3. Differential scanning calorimetry

The Differential scanning calorimetry (DSC) tests were carried out with Q2000 device of TA Instruments (New Castle, DE, USA) in

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