Polymer Degradation and Stability 128 (2016) 29–38

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

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

A. Toldy [a], [*], Á. Szlancsik [a], B. Szolnoki [b]

[a] *Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, H-1111 Budapest, Műegyetem rkp. 3, Hungary*

[b] *Department of Organic Chemistry and Technology, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, H-1111 Budapest, Budafoki út 8, Hungary*

ARTICLE INFO

Article history:
Received 7 October 2015
Received in revised form
9 February 2016
Accepted 23 February 2016
Available online 27 February 2016

Keywords:
Cyanate ester
Epoxy resin
Reactive flame retardancy
Glass transition temperature
Moisture uptake

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^2.

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

---

* Corresponding author.
E-mail address: atoldy@mail.bme.hu (A. Toldy).

http://dx.doi.org/10.1016/j.polymdegradstab.2016.02.015
0141-3910/

[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_2 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_2-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-phosphaphenantrene-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 form 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^2 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^{-1} 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

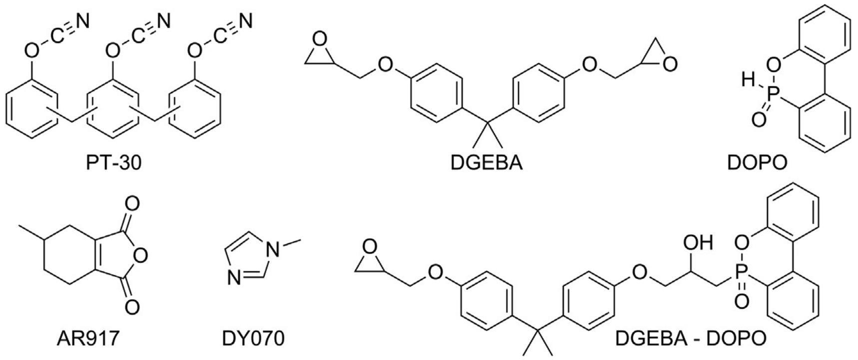

Fig. 1. Chemical structures of the applied polymer components.

Table 1
Compositions of the CE, EP and CE/EP samples.

	Sample composition (mass%)				
	PT-30	DGEBA	DOPO	AR917	DY070
Reference samples					
PT-30	100	–	–	–	–
DGEBA	–	52.3	–	47.1	0.6
20% PT-30 – 80% DGEBA	20	80	–	–	–
40% PT-30 – 60% DGEBA	40	60	–	–	–
Flame retarded samples					
DGEBA – DOPO 2% P	–	56.61	13.94	29.12	0.32
20% PT-30 – DGEBA – DOPO 2% P	20	66.06	13.94	–	–
30% PT-30 – DGEBA – DOPO 2% P	29.8	56.26	13.94	–	–
40% PT-30 – DGEBA – DOPO 2% P	40	46.06	13.94	–	–
20% PT-30 – DGEBA – DOPO 3% P	20	59.1	20.9	–	–
25% PT-30 – DGEBA – DOPO 3% P	24.55	54.56	20.9	–	–
40% PT-30 – DGEBA – DOPO 3% P	40	39.1	20.9	–	–

Samples with stoichiometric ratio of epoxide group and cyanate ester group (1:1) are highlighted in grey

50 ml/min nitrogen flow. Tzero type aluminium pans were used, the sample mass was 5–20 mg. The applied three-step temperature program consisted of heat/cool/heat cycles: after a linear ramp from 25 to 250 °C (in case of pure CE sample up to 400 °C) with 1 °C/min heat rate (first cycle), the sample was cooled down to 0 °C with 50 °C/min cooling rate, followed by a second linear heating ramp from 0 to 250 °C (in case of pure CE sample up to 400 °C) with 1 °C/min heating rate (second cycle) to ensure the proper conversion. The glass transition temperature (T_g) values were determined from the second heating scan and were defined as the inflection point of the transition curve.

2.2.4. Thermogravimetric analysis

TA Q5000 device of TA Instruments (New Castle, DE, USA) was used for thermogravimetric analysis (TGA). TGA measurements were carried out in the temperature range of 25–600 °C at a heating rate of 10 °C/min under nitrogen gas flow rate of 30 ml/min. Platinum-HT sample pan was used, the sample size was about 15 mg.

2.2.5. Characterization of the fire behaviour

The fire behaviour of the reference and flame retarded systems was characterized by limiting oxygen index measurements (LOI, according to ASTM D-2863, specimen size: 150 mm × 10 mm × 4 mm). The LOI value expresses the minimum volume fraction of oxygen in a mixture of oxygen and nitrogen, that supports flaming combustion of a material under specified test conditions.

Standard UL-94 flammability tests (according to ASTM D3081 and ASTM D-635, respectively) were also carried out in order to classify the samples based on their flammability in horizontal and vertical test setups.

Mass loss calorimeter tests were carried out by an instrument made by FTT Inc. using the ISO 13927 standard method. Specimens (100 mm × 100 mm × 4 mm) were exposed to a constant heat flux

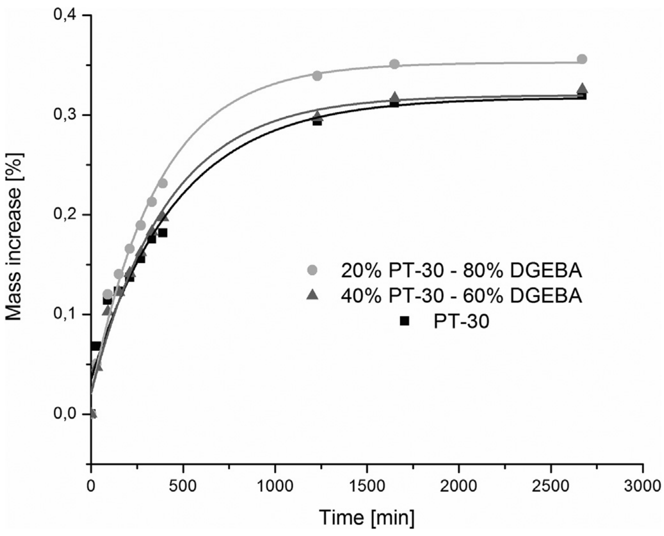

Fig. 2. Moisture uptake of CE and CE/EP blends as a function of time under 30 °C and 80% RH.

of 50 kW/m^2 and ignited. Heat release values and mass reduction were continuously recorded during burning.

3. Results and discussion

3.1. Moisture uptake

One major issue in connection with the processing of cyanate esters or their composites is the moisture sensitivity of the cyanate ester curing. The hydrolysis of the cyanate function leads to imidocarbonic acid intermediate, which rearranges to more stable carbamate. Over 190 °C the carbamate structure can decompose to CO_2 and amine [21]. The evolving CO_2 results in voids in the composite structure (especially if the composite is post-cured above the decomposition temperature of the carbamates), while the amine reacts with another cyanate group leading to linear junction instead of cyclotrimerization, leading to lower T_g and decrease in mechanical properties [22,23].

First, the moisture uptake of the uncured reference CE and CE/EP blends was studied at 30 °C and 80% RH (with this climate chamber setting the general storing conditions were intended to be simulated). According to results shown in Fig. 2, the moisture uptake belonging to saturation is approximately the same in case of the reference CE and 40 mass% CE and 60 mass% EP containing stoichiometric CE/EP blend. By increasing the EP content from 60 to 80 mass%, the water uptake increased by approx. 10%. Accordingly, from the point of water uptake lower EP content and stoichiometric ratio is more favourable.

Parallel to the measurement of moisture uptake, FTIR spectra of the samples were taken to detect the possible carbamate formation by the appearance of carbonyl peak at 1745 cm^{-1}. Under these conditions (30 °C and 80% RH) no carbamate formation occurred in any of the samples.

In a next step the moisture uptake was studied under conditions simulating the processing parameters (80 °C to achieve optimal viscosity of the polymer components and as low relative humidity as possible to avoid carbamate formation, in this case 10% RH). In this case not only the reference CE and the favourable stoichiometric 40 mass% CE and 60 mass% EP containing CE/EP blend was examined, but also its versions containing 2 and 3 mass% phosphorus from the reactive flame retardant.

According to results showed in Fig. 3, the moisture uptake of samples increases with increasing phosphorus content. By incorporating phosphorus flame retardants the water uptake of the polymers usually increases due to the polar backbone of the flame retardant, therefore the need for strict moisture control during processing is even more pronounced in case of flame retarded samples. Comparing the moisture uptake at 30 °C and 80% RH and at 80 °C and 10% RH, respectively, it can be concluded that at higher temperature and lower relative humidity the moisture uptake is much smaller (in case of reference CE sample the mass of the sample even decreases, most probably it releases its moisture content gained under storage conditions). Given that the preparation time of samples is not more than 60 min both in case of matrix and composite specimens, based on these results it can be assumed, that the water uptake during processing is less than 0.12%, which is acceptable.

Although the moisture uptake was less pronounced at 80 °C and 10% RH, due to the increased temperature even this low amount of sorbed water can induce carbamate formation in the samples according to the FTIR results. In Table 2 the time of the first appearance of the carbonyl peak at 1745 cm^{-1} related to carbamate formation is listed. According to the results in case of reference and non-flame retarded samples no carbamate formation was detected after 24 h. However, in flame retarded samples, by increasing the amount of CE and phosphorus in the samples, the carbamate formation occurs earlier. Given that the sample preparation takes less than 60 min, it can be assumed that no significant carbamate formation occurs during the processing (after 60 min at 80 °C and 10% RH carbamate formation was detected by FTIR only in 40% PT-30 – DGEBA–DOPO 3%P sample).

As an example the FTIR spectra as a function of time spent in climate chamber under 80 °C and 10% RH in case of the 40% PT-30 – DGEBA–DOPO 2%P sample is showed in Fig. 4. Simultaneously to the increase of carbonyl peak intensity at 1745 cm^{-1}, the intensity of C≡N stretching bands of the cyanate functional group (at 2250–2300 cm^{-1}) is decreasing. Similar tendencies were noticed by Hamerton [21] and Ramirez [24] as well.

Based on the parallel moisture uptake and FTIR studies, it can be concluded that both under stimulated storage and processing conditions no carbamate formation was detected in pure CE. By increasing the EP and phosphorus flame retardant content, the moisture uptake increases, but the carbamate formation at higher temperatures necessary to reach proper polymer viscosities for processing can be greatly reduced or even avoided with strict moisture control and as short processing time as technically possible.

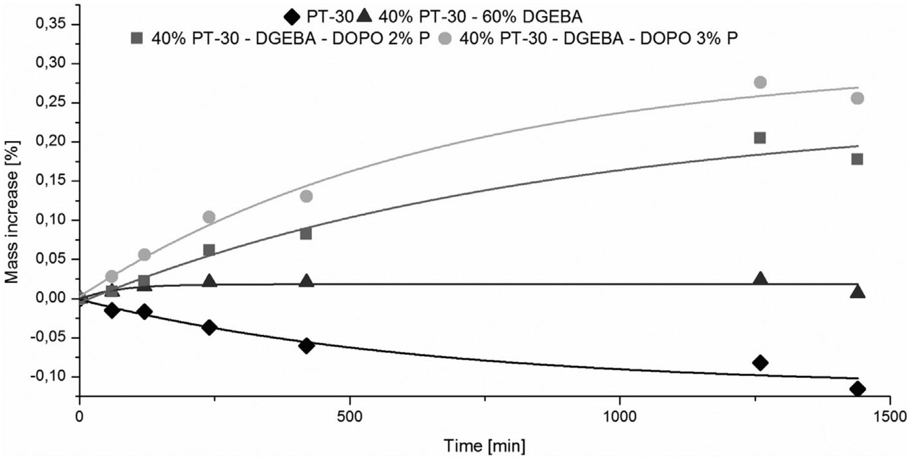

Fig. 3. Moisture uptake of CE and CE/EP blends as a function of time under 80 °C and 10% RH.

Table 2
Time of the first appearance of carbamate FTIR peak in CE and CE/EP blends under 80 °C and 10% RH.

Sample	Time of the appearance of carbamate FTIR peak (min)
PT-30	–
20% PT-30 – 80% DGEBA	–
40% PT-30 – 60% DGEBA	–
20% PT-30 – DGEBA – DOPO 2%P	1260
30% PT-30 – DGEBA – DOPO 2%P	420
40% PT-30 – DGEBA – DOPO 2%P	420
20% PT-30 – DGEBA – DOPO 3%P	240
25% PT-30 – DGEBA – DOPO 3%P	120
40% PT-30 – DGEBA – DOPO 3%P	60

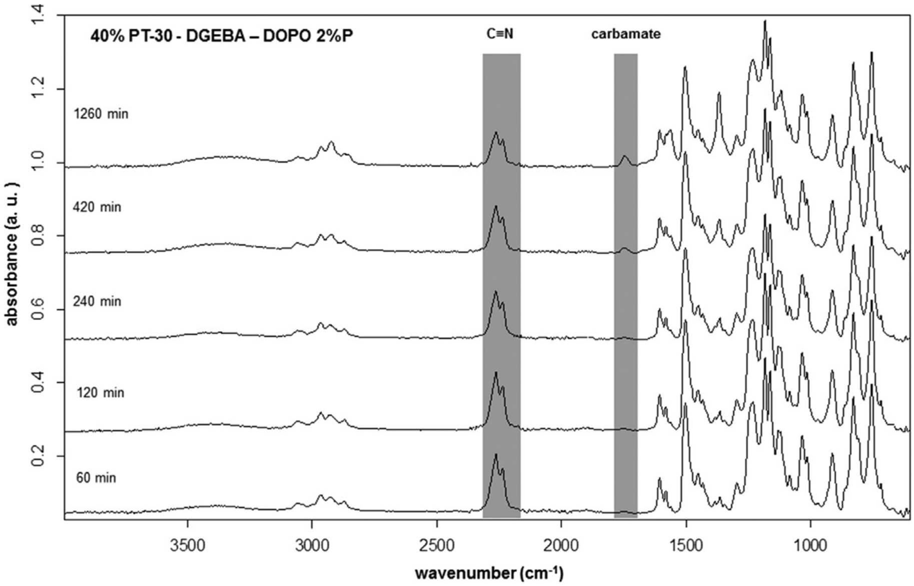

Fig. 4. FTIR spectra of 40% PT-30 – DGEBA–DOPO 2%P sample as a function of time (80 °C and 10% RH).

Table 3
T_g of CE and EP references and their blends determined by DSC method.

Sample	T_g (°C)
PT-30	387
DGEBA	149
20% PT-30 – 80% DGEBA	161
40% PT-30 – 60% DGEBA	214
DGEBA – DOPO 2% P	106
20% PT-30 – DGEBA – DOPO 2% P	129
30% PT-30 – DGEBA – DOPO 2% P	150
40% PT-30 – DGEBA – DOPO 2% P	162
20% PT-30 – DGEBA – DOPO 3% P	108
25% PT-30 – DGEBA – DOPO 3% P	113
40% PT-30 – DGEBA – DOPO 3% P	141

3.2. *Glass transition temperature*

One of the major advantages of CEs is their high T_g, enabling advanced applications as aircraft or electronic industries, therefore it was necessary to determine the effect of EP and flame retardant addition on the T_g. The T_g values of the CE and EP references and their blends determined by DSC are displayed in Table 3.

As expected, DOPO reduced the initial T_g values: the applied DOPO-DGEBA adduct has high EEW and has only one free oxirane ring per molecule, therefore it reduces the crosslinking density of the polymers leading to lower T_g values. On the other hand, by increasing the amount of CE in the blends their T_g increases due to the rigid triazine structure present in CEs. Therefore CEs can be used to increase the T_g of EPs and to compensate the T_g decreasing effect of DOPO. It would be desirable that T_g of the flame retarded systems would approach the T_g of the benchmark systems they would eventually replace, i.e. in this case the T_g of DGEBA (149 °C measured by DSC). To reach this goal in case of 2% P-containing systems at least 30% PT-30 is necessary, while in case of 3% P-containing systems 40% PT-30 is necessary.

As high water uptake can plasticize the resins, lower the T_g value and thus limit their hot/wet service temperature, it was necessary to determine the effect of moisture uptake on the T_g of the polymers. During the moisture uptake measurements samples were taken after 1, 2, 4, 7 and 21 h (reaching moisture saturation under both conditions), After curing these samples (cure schedules were detailed above in Sample preparation section) their T_g was determined by DSC. According to the results no significant differences were measured compared to the T_g values of the dry samples displayed in Table 3, therefore it can be concluded that under the mentioned conditioned the examined CE and CE/EP blends can be stored/processed without detectable decrease in T_g values.

3.3. *Thermogravimetric analysis*

The effect of EP and flame retardants on the thermal stability of CE was determined by thermogravimetric analysis. Table 4 shows the temperature at 5 and 50 mass% loss ($T_{5mass\%}$; $T_{50mass\%}$), the maximum mass loss rate (dTG_{max}), the temperature belonging to

Table 4
$T_{5mass\%}$; $T_{50mass\%}$; dTG_{max}; T_{dTGmax} and char yield values of the CE and EP references and their blends.

Sample	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	dTG_{max} (mass%/°C)	T_{dTGmax} (°C)	Char yield at 600 °C (mass%)
PT-30	415	–	0.64	435	70 (68 at 900 °C)
DGEBA	302	398	1.57	395	10
20% PT-30 – 80% DGEBA	377	426	1.90	422	20
40% PT-30 – 60% DGEBA	373	424	1.24	399	30
DGEBA – DOPO 2% P	311	387	1.43	383	10
20% PT-30 – DGEBA – DOPO 2%P	339	401	1.16	389	25
30% PT-30 – DGEBA – DOPO 2%P	346	411	1.12	398	26
40% PT-30 – DGEBA – DOPO 2%P	351	426	0.94	396	32
20% PT-30 – DGEBA – DOPO 3%P	306	399	0.72	379	26
25% PT-30 – DGEBA – DOPO 3%P	320	408	0.68	376	25
40% PT-30 – DGEBA – DOPO 3%P	347	443	0.68	384	35

$T_{-5\%}$: temperature at 5 mass% loss; $T_{-50\%}$: temperature at 50 mass% loss; dTG_{max}: maximum mass loss rate; T_{dTGmax}: the temperature belonging to maximum mass loss rate.

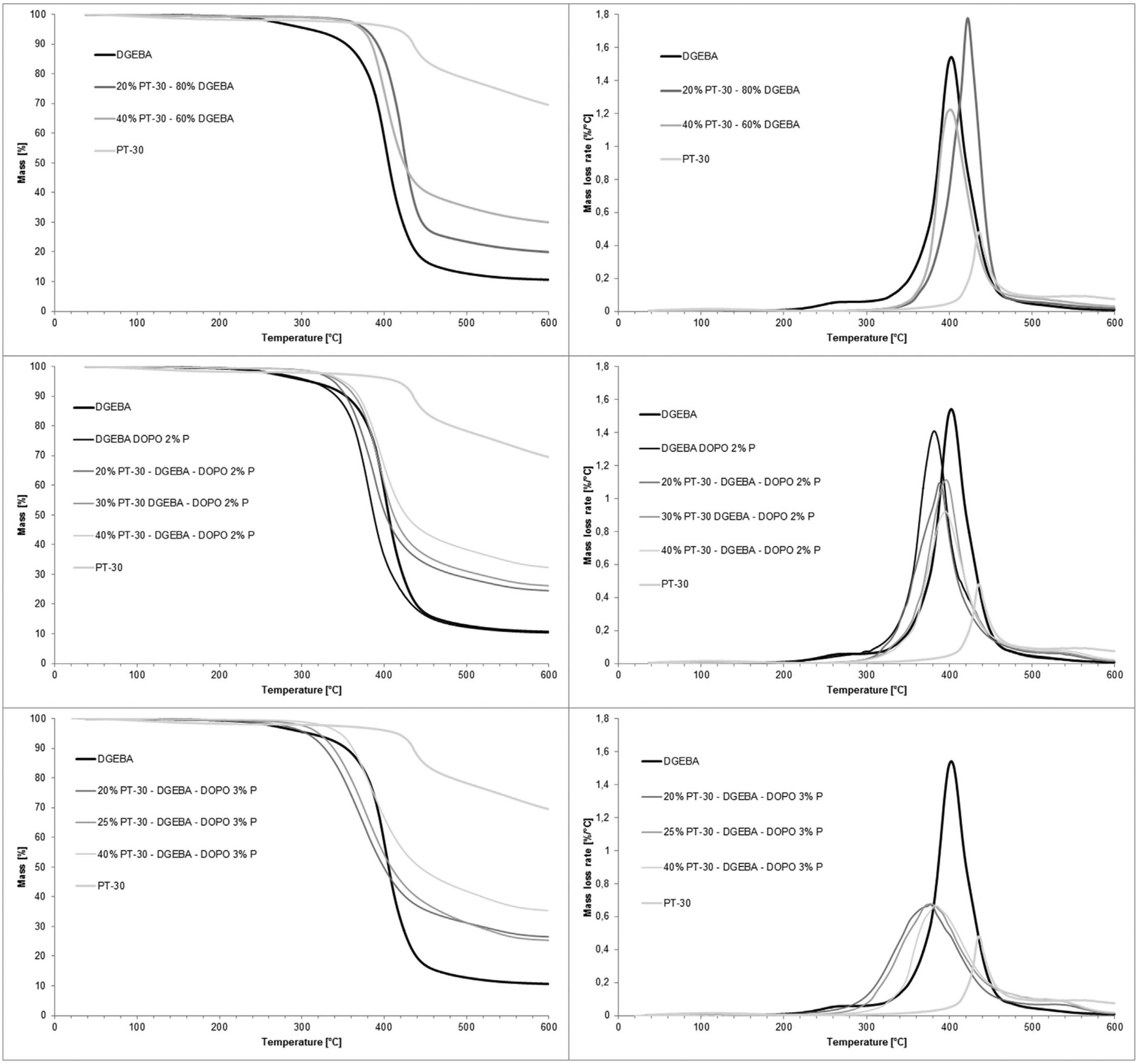

Fig. 5. Mass and mass loss rate curves of the CE and EP references and their blends.

this value (T_{dTGmax}) and the char yield at the end of the TGA test (at 600 °C). Mass and mas loss rate curves are displayed in Fig. 5.

The thermal stability of the CE reference is outstanding: its thermal degradation begins above 400 °C, with a moderate mass loss rate, and it loses only 30% of its mass by reaching 600 °C. By adding PT-30 to DGEBA the temperature belonging to 5% mass loss increases by even 75 °C and the char yield increases from 10 mass% up to 30 mass% due to the rigid triazine structure in CE. On the other hand by increasing the amount of DOPO, the thermal degradation begins earlier and the maximum of mass loss rate was reached at lower temperatures, which can be explained by the gas phase flame retardant mechanism of DOPO [10,25,26]: during the initial phase of degradation phosphorus-containing radicals are formed, which effectively delay the degradation process. DOPO decreases the mass loss rates as well, in 3 mass% P-containing samples the mass loss rate is approximately the same as in case of reference CE.

3.4. Flame retardancy

3.4.1. Flame retardancy of polymer matrices

Limiting oxygen index (LOI), UL-94 and mass loss type cone calorimetry results of the CE and EP references and their blends are summarized in Table 5. By adding PT-30 to DGEBA, its LOI value was increased from 23 up to 33 V/V%, however the UL-94 rate remained HB, as in case of the reference PT-30 and DGEBA. By adding DOPO to DGEBA the UL-94 rate was ameliorated to V-1, however the LOI value was lower than in case of PT-30 (28 vs. 30 V/V%). All blends consisting of EP, CE and phosphorus-containing flame retardant reached the V-0 UL-94 classification, and their LOI values usually improved with increasing CE and FR content, reaching even LOI of 45 V/V% with 40 mass% CE and 2 mass% phosphorus. Phosphorus-containing samples exhibited intensive intumescent charring.

As for the heat release rates (HRRs) (Fig. 6), by adding PT-30 to DGEBA the HRR curves were shifted in time by 10 s and the peak of heat release rate (pHRR) values was lowered from 743 up to 238 kw/m^2 with 40 mass% PT-30.

By adding DOPO to CE/EP blends, the pHRR and total heat release (THR) values decreased further. By comparing the heat release of the DGEBA reference and 2 mass% P-containing samples (Fig. 7), it can be concluded that by increasing the amount of PT-30, the pHRR and THRR values decreased significantly. By increasing the phosphorus-content to 3 mass% no further decrease in flammability was experienced, which can be explained by the lower crosslinking density (in order to reach 3 mass% phosphorus-content, 1.5 times higher amount of pre-reacted DOPO-DGEBA adduct is necessary, which contains only one oxirane ring and one less reactive OH-group from the ring opening of the oxirane ring, in contrast to the two oxirane functionalities per molecule of DGEBA).

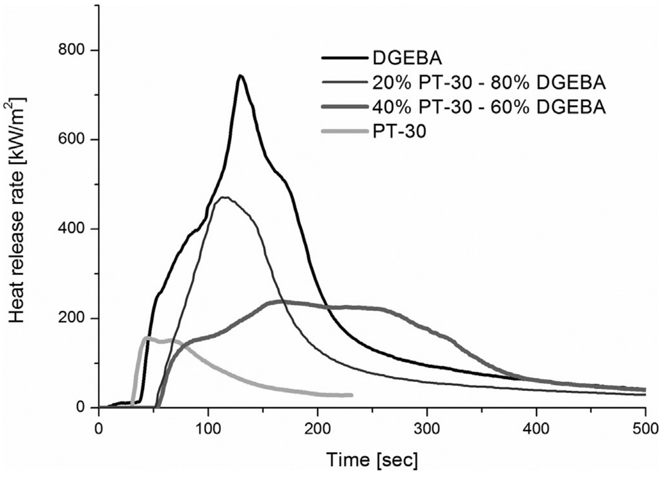

Fig. 6. HRR curves of CE and EP references and their blends.

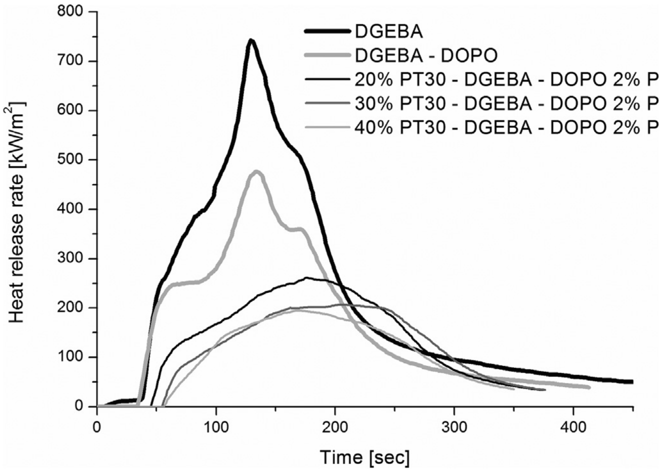

Fig. 7. HRR curves of EP reference, flame retarded EP and CE/EP blends with 2 mass% phosphorus-content.

Table 5
LOI, UL-94 and mass loss type cone calorimetry results of the CE and EP references and their blends.

Sample	LOI (V/V%)	UL-94[a]	TTI (s)	pHRR (kW/m^2)	Time of pHRR (s)	FIGRA (kW/m^{2}s)	Burning time (s)	THR (MJ/m^2)	EHC (MJ/kg)	MARHE (kW/m^2)	Residue (mass%)
PT-30	30	HB	26	156	44	3.5	180	15.5	11.9	91.7	48
DGEBA	23	HB (17.1 ± 2)	40	743	129	6.6	217	91.0	19.4	364.3	0
20% PT-30 – 80% DGEBA	33	HB	50	471	113	4.2	176	59.5	18.5	223.9	0
40% PT-30 – 60% DGEBA	28	HB	50	238	167	1.4	345	55.1	13.2	160.5	14
DGEBA – DOPO 2%P	29	V-1	32	477	134	3.6	226	65.1	13.5	252.6	0
20% PT-30 – DGEBA – DOPO 2% P	42	V-0	42	261	177	1.5	279	49.0	12.3	161.8	15
30% PT-30 – DGEBA – DOPO 2% P	40	V-0	50	207	207	1.0	309	42.0	11.4	130.8	18
40% PT-30 – DGEBA – DOPO 2% P	43	V-0	53	195	168	1.2	301	36.3	11.6	116.2	23
20% PT-30 – DGEBA – DOPO 3% P	40	V-0	27	218	156	1.4	380	50.3	11.8	150.5	14
25% PT-30 – DGEBA – DOPO 3% P	42	V-0	45	218	155	1.4	375	46.0	12.1	134.6	17
40% PT-30 – DGEBA – DOPO 3% P	45	V-0	44	234	179	1.3	315	47.5	13.3	142.9	22

LOI: limiting oxygen index, TTI: time to ignition, pHRR: peak of heat release rate, FIGRA: fire growth rate, THR: total heat release, EHC: average effective heat of combustion, MARHE: maximum of average rate of heat emission.
Average standard deviation of the measured mass loss calorimeter values: TTI: ±2, pHRR: ±15, time of pHRR: ±5, residue: ±2.
[a] In parenthesis the horizontal burning rate is showed, where measurable.

The pHRR of the DOPO-containing CE/EP blends was in the range of 195–261 kW/m^2, not much higher than pHRR value of 156 kW/m^2 of CE reference. Furthermore the time to ignition (TTI) and time of pHRR values significantly increased in DOPO-containing CE/EP blends (up to TTI of 53 s and time of pHRR of 207 in comparison to 26 s and 44 s, respectively, in case of CE reference).

As for the fire growth rate (FIGRA) values, by blending 40% PT-30 to DGEBA FIGRA decreased to 1.4 kW/m^{2}s compared to 3.5 kW/m^{2}s in case of PT-30 and 6.6 kW/m^{2}s in DGEBA. By adding DOPO adduct to this composition, FIGRA decreased further slightly (1.2 in case of 2% P containing sample and 1.3 in case of 3% P containing sample). Effective heat of combustion (EHC) and maximum of average rate of heat emission (MARHE) values were the closest to the values of PT-30 in case of 40% PT-30 – DGEBA–DOPO 2% P sample. Compared to the DGEBA DOPO 2%P sample the inclusion of 40% PT-30 significantly reduced the EHC (from 13.5 to 11.6 MJ/kg) and MARHE values (from 252.6 to 116.2 kW/m^2).

The inclusion of PT-30 and DOPO also increased the residual mass after mass loss calorimetry. The CE/EP blends exhibited slight charring, while the thickness of the flame retarded CE/EP samples manifested a 10-fold increase due to the intumescent charring phenomena (Fig. 8).

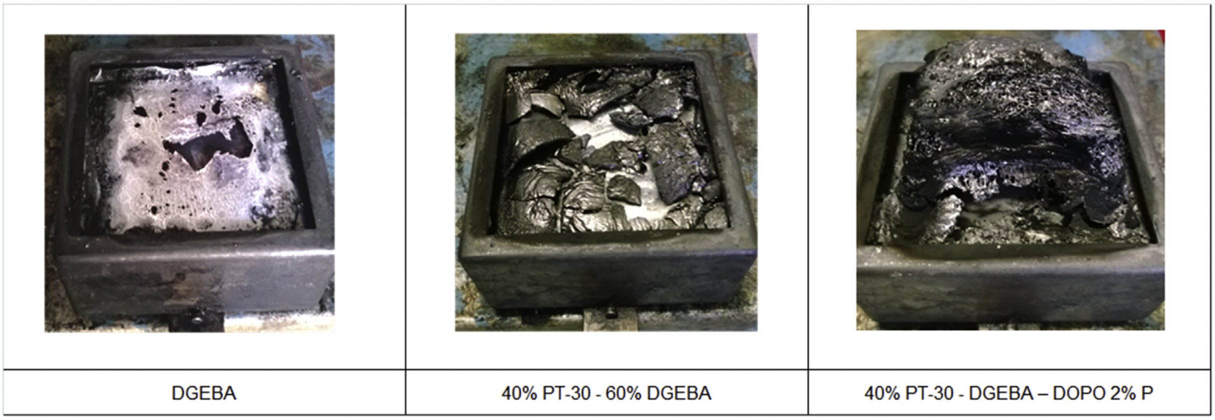
DGEBA | 40% PT-30 - 60% DGEBA | 40% PT-30 - DGEBA – DOPO 2% P

Fig. 8. Cone calorimetry residue of DGEBA, 40% PT-30 – 60% DGEBA and 40% PT-30 – DGEBA–DOPO 2% P samples.

3.4.2. Flame retardancy of polymer composites

According to the flame retardancy results of the matrices, the best performing CE/EP blends were chosen for composite preparation along with the CE and EP reference. LOI, UL-94 and mass loss calorimetry results of the composites made of CE and EP references and their blends are summarized in Table 6. The higher LOI values in comparison to the neat matrices are the result of the decrease of flammable matrix material due to the inclusion of 50–55 mass% of carbon fibre reinforcement (considered as inert material under the conditions of the LOI, UL-94 and mass loss calorimetry tests). By increasing the amount of PT-30 and DOPO, the LOI increases in the case of composites as well. As for the UL-94 results, in case of composites 40 mass% of PT-30 is already sufficient to reach the V-0 rate. As expected, the inclusion of carbon fibres drastically decreased the pHRR and THR values (Fig. 9), and increased the residual mass. By increasing the amount of CE and phosphorus, the pHRR values showed further decrease. In contrast to matrix samples, where no further decrease in flammability was experienced when the phosphorus-content was increased to 3 mass%, in case of the composite samples the 40% PT-30 – DGEBA–DOPO 3%P composite sample showed the best performance: it had the same pHRR value, 84 kW/m^2 as the PT-30 reference composite. Its THR and MARHE values were still higher than that of the PT-30, however it had lower FIGRA and EHC values than PT-30. The increasing P-content slightly decreased the TTI values, which can be explained by the gas phase mechanism of DOPO [11,25,26]: due to inclusion of DOPO the thermal stability of the system decreases, so it ignites earlier, on the other hand the formed P-containing radicals effectively postpone the time of pHRR and reduce the pHRR values. These latter effects led to significant decrease in FIGRA values, as observed in case of the matrices as well. The charring experienced at matrix samples was hindered by the included carbon fibre plies [27], no charring at all was detected on the surface of the mass loss calorimetry residual composite samples.

4. Conclusions

Reactively flame retarded CE/EP blends and their composites were prepared and their moisture uptake, glass transition temperature, thermal degradation and fire behaviour were tested.

Moisture uptake of neat polymer matrices was measured under stimulated storage (30 °C and 80% RH) and processing (80 °C and 10% RH) conditions. At the latter the moisture uptake was much smaller due to the lower relative humidity. By increasing EP and flame retardant content, the moisture uptake increases, and this

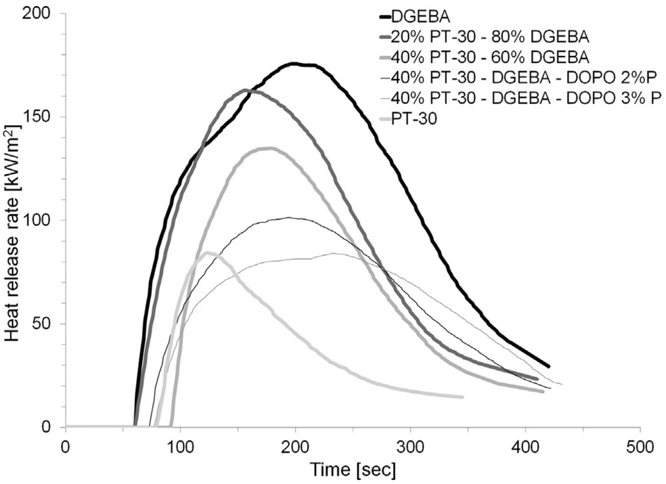

Fig. 9. HRR curves of the composites made of CE and EP references and their blends.

Table 6
LOI, UL-94 and mass loss type cone calorimetry results of the composites made of CE and EP references and their blends.

sample	LOI (V/V%)	UL-94	TTI (s)	pHRR (kW/m^2)	Time of pHRR (s)	FIGRA (kW/m^2s)	Burning time (s)	THR (MJ/m^2)	EHC (MJ/kg)	MARHE (kW/m^2)	Residue (mass%)
PT-30	58	V-0	80	84	124	0.7	257	9,8	10.4	38.0	81
DGEBA	33	HB	55	176	197	0.9	355	37,9	13.8	112.2	50
20% PT-30 – 80% DGEBA	41	HB	51	162	156	1.0	301	29,9	14.7	95.8	61
40% PT-30 – 60% DGEBA	42	V-0	87	134	178	0.8	308	21,8	13.2	69.1	70
40% PT-30 – DGEBA – DOPO 2%P	46	V-0	72	101	195	0.5	401	20,1	11.2	61.1	67
40% PT-30 – DGEBA – DOPO 3%P	48	V-0	70	84	233	0.4	372	18,7	10.1	53.6	67

LOI: limiting oxygen index, TTI: time to ignition, pHRR: peak of heat release rate, FIGRA: fire growth rate, THR: total heat release, EHC: average effective heat of combustion, MARHE: maximum of average rate of heat emission).
Average standard deviation of the measured mass loss calorimeter values: TTI: ±2, pHRR: ±15, time of pHRR: ±5, residue: ±2.

can lead to carbamate formation at higher temperatures necessary to reach proper processing viscosities. This effect can be greatly reduced or even avoided with strict moisture control and as short processing time as technically possible.

According to the glass transitions temperatures CEs can be used to increase the T_g of EPs and to compensate the T_g decreasing effect of DOPO. The moisture uptake did not affect the T_g of CE and CE/EP blends under the stimulated storage (30 °C and 80% RH) and processing (80 °C and 10% RH) conditions, therefore they could be stored/processed without detectable decrease in T_g values.

TGA measurements showed that the rigid structure of the CE increased the thermal stability of the CE/EP blends. By increasing the amount of DOPO, the thermal degradation begins earlier, due to the gas phase flame retardant mechanism during the initial phase of degradation, but it effectively delays the degradation process, leading to lower mass loss rates as well.

Addition of PT-30 to DGEBA increased the LOI value from 23 up to 33 V/V%, however it was not sufficient to improve the UL-94 rate, which remained HB, as in case of PT-30 and DGEBA reference samples. All blends consisting of EP, CE and phosphorus-containing flame retardant reached the V-0 UL-94 classification, and their LOI values usually improved with increasing CE and FR content, reaching even LOI of 45 V/V%. Phosphorus-containing samples exhibited intensive intumescent charring and increased residual mass. By adding PT-30 to DGEBA the pHRR values were lowered from 743 up to 238 kw/m^2 with 40 mass% PT-30, which was further decreased to 195 kW/m^2 with 2 mass% phosphorus from DOPO.

Although the solid phase intumescent mechanism is hindered by the carbon fibre reinforcement plies, the composite specimens showed even better flame retardant properties owing to their inflammable reinforcement. 40 mass% of PT-30 alone is sufficient to reach the V-0 UL-94 rate. By increasing the amount of PT-30 and DOPO, the LOI increased and the pHRR values showed further decrease. The 40% PT-30 – DGEBA–DOPO 3%P composite had the same pHRR value – 84 kW/m^2 - as the PT-30 reference composite.

Acknowledgements

This work is connected to the scientific program of the “Development of quality-oriented and harmonized R + D + I strategy and functional model at BME” project. This project is supported by the New Széchenyi Plan (Project ID: TÁMOP-4.2.1/B-09/1/KMR-2010-0002). The work reported in this paper has been developed in the framework of the project “Talent care and cultivation in the scientific workshops of BME” project. This project is supported by the grant TÁMOP–4.2.2.B-10/1–2010-0009. Andrea Toldy acknowledges the financial support received through János Bolyai Scholarship of the Hungarian Academy of Sciences.

References

[1] I. Hamerton, J.N. Hay, Recent developments in the chemistry of cyanate esters, Polym. Int. 47 (4) (1998) 465–473. http://dx.doi.org/10.1088/0954-0083/10/2/001.

[2] A. Toldy, Cyanate ester resins – ‘old newcomers’ among high performance composite materials, Express Polym. Lett. 7 (9) (2013), 722–722, http://dx.doi.org/10.3144/expresspolymlett.2013.69.

[3] L.J. Kasehagen, C.W. Macosko, Structure development in cyanate ester polymerization, Polym. Int. 44 (3) (1997) 237–247 http://dx.doi.org/10.1002/(SICI)1097-0126(199711)44:3<237::AID-PI868>3.0.CO;2-L.

[4] M. Thunga, M. Akinc, M.R. Kessler, Tailoring the toughness and CTE of high temperature bisphenol E cyanate ester (BECy) resin, Express Polym. Lett. 8 (5) (2014) 336–344. http://dx.doi.org/10.3144/expresspolymlett.2014.37.

[5] B. Perret, B. Schartel, K. Stöß, M. Ciesielski, J. Diederichs, M. Döring, J. Krämer, V. Altstädt, Novel DOPO-based flame retardants in high-performance carbon fibre epoxy composites for aviation, Eur. Polym. J. 47 (5) (2011) 1081–1089. http://dx.doi.org/10.1016/j.eurpolymj.2011.02.008.

[6] S.V. Levchik, G. Camino, M.P. Luda, L. Costa, G. Muller, B. Costes, Y. Henry, Epoxy resins cured with aminophenylmethylphosphine oxide 1: combustion performance, Polym. Adv. Technol. 7 (1996) 823–830 http://dx.doi.org/10.1002/(SICI)1099-1581(199611)7:11<823::AID-PAT498>3.0.CO;2-X.

[7] J. Artner, M. Ciesielski, O. Walter, M. Döring, R.M. Perez, J.K.W. Sandler, V. Altstädt, B. Schartel, A Novel DOPO-based diamine as hardener and flame retardant for epoxy resin systems, Macromol. Mater. Eng. 293 (2008) 503–514. http://dx.doi.org/10.1002/mame.200700287.

[8] P.M. Hergenrother, C.M. Thompson, J.G. Smith Jr., J.W. Connell, J.A. Hinkley, R.E. Lyon, Richard Moulton, Flame retardant aircraft epoxy resins containing phosphorus, Polymer 46 (14) (2005) 5012–5024. http://dx.doi.org/10.1016/j.polymer.2005.04.025.

[9] C. Gérard, G. Fontaine, S. Bourbigot, New trends in reaction and resistance to fire of fire-retardant epoxies, Materials 3 (2010) 4476–4499. http://dx.doi.org/10.3390/ma3084476.

[10] S.Y. Lu, I. Hamerton, Recent developments in the chemistry of halogen-free flame retardant polymers, Prog. Polym. Sci. 27 (8) (2002 10.1) 1661–1712. http://dx.doi.org/016/S0079-6700(02)00018-7.

[11] B. Schartel, Phosphorus-based flame retardancy mechanisms—old hat or a starting point for future development? Materials 3 (2010) 4710–4745. http://dx.doi.org/10.3390/ma3104710.

[12] P. Joseph, S. Tretsiakova-Mcnally, Reactive modifications of some chain- and step-growth polymers with phosphorus-containing compounds: effects on flame retardance—a review, Polym. Adv. Technol. 22 (2011) 395–406. http://dx.doi.org/10.1002/pat.1900.

[13] Hou Chien Chang, Hung Tse Lina, Ching Hsuan Lin, Benzoxazine-based phosphinated bisphenols and their application in preparing flame-retardant, low dielectric cyanate ester thermosets, Polym. Chem. 3 (2012) 970–978. http://dx.doi.org/10.1039/c2py00528j.

[14] Tsung-Han Ho, Hann-Jang Hwang, Jeng-Yueh Shieh, Ming-Chin Chung, Thermal and physical properties of flame-retardant epoxy resins containing 2-(6-oxido-6H-dibenz⟨c,e⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-naphthalenediol and cured with dicyanate ester, Polym. Degrad. Stab. 93 (12) (2008) 2077–2083. http://dx.doi.org/10.1016/j.polymdegradstab.2008.09.002.

[15] Tsung-Han Ho, Hann-Jang Hwang, Jeng-Yueh Shieh, Ming-Chin Chung, Thermal, physical and flame-retardant properties of phosphorus-containing epoxy cured with cyanate ester, React. Funct. Polym. 69 (3) (2009) 176–182. http://dx.doi.org/10.1016/j.reactfunctpolym.2008.12.019.

[16] C.H. Lin, H.T. Lin, Y.W. Tian, S.A. Dai, W.C. Su, Preparation of phosphinated bisphenol from acid-fragmentation of 1,1,1-tris(4-hydroxyphenyl)ethane and its application in high-performance cyanate esters, J. Polym. Sci. A Polym. Chem. 49 (2011) 4851–4860. http://dx.doi.org/10.1002/pola.24936.

[17] Ching Hsuan Lin, Synthesis of novel phosphorus-containing cyanate esters and their curing reaction with epoxy resin, Polymer 45 (23) (2004) 7911–7926. http://dx.doi.org/10.1016/j.polymer.2004.09.023.

[18] Xiangxiu Chen, Guozheng Liang, Aijuan Gu, Li Yuan, Flame retarding cyanate ester resin with low curing temperature, high thermal resistance, outstanding

dielectric property, and low water absorption for high frequency and high speed printed circuit broads, Ind. Eng. Chem. Res. 54 (6) (2015) 1806–1815. http://dx.doi.org/10.1021/ie504333f.

[19] K. Krishnadevi, A. Nirmala Grace, M. Alagar, V. Selvaraj, Development of hexa (aminophenyl)cyclotriphosphazene-modified cyanate ester composites for high-temperature applications, High. Perform. Polym. 26 (2014) 89–96. http://dx.doi.org/10.1177/0954008313500058.

[20] C.S. Wang, C.H. Lin, Synthesis and properties of phosphorus-containing epoxy resins by novel method, J. Polym. Sci. Part A Polym. Chem. 37 (1999) 3903–3909. http://dx.doi.org/10.1002/(SICI)1099-0518(19991101)37:21<3903::AID-POLA4>3.0.CO;2-X.

[21] I. Hamerton, Chemistry and Technology of Cyanate Ester Resins, Blackie Academic & Professional (Chapman & Hall), London, 1994.

[22] A. Chaplin, I. Hamerton, H. Herman, A.K. Mudhar, S.J. Shaw, Studying water uptake effects in resins based on cyanate ester/bismaleimide blends, Polymer 41 (11) (2000) 3945–3956. http://dx.doi.org/10.1016/S0032-3861(99)00603-5.

[23] I. Hamerton, H. Herman, K.T. Rees, A. Chaplin, S.J. Shaw, Water uptake effects in resins based on alkenyl-modified cyanate ester–bismaleimide blends, Polym. Int. 50 (4) (2001) 475–483. http://dx.doi.org/10.1002/pi.664.

[24] Michael L. Ramirez, Richard Walters, Edward P. Savitski, Richard E. Lyon, Thermal Decomposition of Cyanate Ester Resins, U.S. Department of Transportation Federal Aviation Administration Office of Aviation Research Washington, DC 20591, Final Report, 2001.

[25] A. Schäfer, S. Seibold, W. Lohstroh, O. Walter, M. Döring, Synthesis and properties of flame-retardant epoxy resins based on DOPO and one of its analog DPPO, J. Appl. Polym. Sci. 105 (2007) 685–696. http://dx.doi.org/10.1002/app.26073.

[26] Wenchao Zhang, Xiangdong He, Tinglu Song, Qingjie Jiao, Rongjie Yang, The influence of the phosphorus-based flame retardant on the flame retardancy of the epoxy resins, Polym. Degrad. Stab. 109 (2014) 209–217. http://dx.doi.org/10.1016/j.polymdegradstab.2014.07.023.

[27] A. Toldy, B. Szolnoki, Gy Marosi, Flame retardancy of fibre-reinforced epoxy resin composites for aerospace applications, Polym. Degrad. Stab. 96 (3) (2011) 371–376. http://dx.doi.org/10.1016/j.polymdegradstab.2010.03.021.