



Reaction-to-fire parameters of CE/epoxy blend-based CF/FF and BF/FF hybrid composites

C. Dreyer¹ · D. Luca Motoc²

Received: 22 August 2019 / Accepted: 17 January 2020
© Akadémiai Kiadó, Budapest, Hungary 2020

Abstract

The paper investigates and compares the fire reaction of cyanate ester/epoxy polymer blend-based natural/synthetic hybrid composites. Different stacking sequences of carbon or basalt fibres along with flax fabrics were compressed, moulded and subjected to an incident heat flux of 50 kW m^{-2} for reaction-to-fire parameter's identification using cone calorimetry. Considerable reductions in heat release rate, total heat release and CO_2 produced were obtained for cyanate ester/epoxy-based composites compared with an epoxy-based benchmark. On the other hand, the fire growth index improved considerably with the increase in synthetic layers, approx. 70% and 103% for the composite architectures embedding CF reinforcements, 63% and 99% for the BF, respectively. The synthetic fibre content and type did not change significantly time-to-ignition values, but significant differences were recorded at the peak of heat released rate while switching from a resin system to another.

Keywords Cyanate ester · Epoxy resin · Carbon fibre · Basalt fibre · Flax fibre · Reaction-to-fire parameters

Introduction

Significant research has been conducted on natural and synthetic reinforced polymer composites focusing on their reaction-to-fire characteristics, mainly from polymer matrix perspective, proven the alarming increase instances with both domestic and industrial environments [1–4]. Irrespective of the application domain of these composite materials, such as building and construction, transport, aerospace, electric and electronic engineering, etc., numerous standards, regulations or legislations were released on the issue of fire protection and fire resistance in line with the method employed for reaction-to-fire parameters (i.e. ISO 5660:2015) [5–7]. These must be sought not as barriers for novel material development but both necessity and challenge to diminish the incidence of casualties due to fire [8].

In relation with this contribution, the literature reveals relatively numerous contributions on flammability of epoxy

polymer and its composites especially about different fire retardants added to improve or uplift the fire resistivity such as reactive type, additive or some ecological and friendly fire retardants such as natural minerals [9–11].

On the other hand, since its commercialization on mid 70 and systematically approached into a work coordinated by Hamerton [12], cyanate ester resins, apparently, despite their numerous advantages (e.g. high value of glass transition temperature, low moisture absorption, low out gassing, etc.) are ranked as less favourite during material selection in fibre-reinforced composite manufacturing. One major drawback impeding their widespread was represented by their selling price, higher compared with the most common performance thermosetting. To overcome the issue and reconsider as a feasible candidate, by mixing with other polymer resins seem more appropriate and easiest solution to the problem in addition to the co-reaction between di- and multifunctional cyanates with mono-cyanates resulting into new copolymers with adjusted property profiles [13–16].

Thus, extensive research was carried within the group coordinated by Bauer and Dreyer, regarded to the synthesis and characterization of several formulae of difunctional, oligofunctional and/or polyfunctional cyanates and/or their prepolymers with monomeric, oligomeric and/or polymeric silazanes, plain/halogenated epoxy resins, etc., to serve appropriate applications [17–19]. Their studies emphasize

✉ D. Luca Motoc
danaluca@unitbv.ro; danalucamotoc@gmail.com

¹ Fraunhofer Institute for Applied Polymer Research,
14513 Teltow, Germany

² Department of Automotive and Transport Engineering,
Transilvania University of Brasov, Eroilor Av., 50017 Brasov,
Romania

the intrinsic flame resistance of cyanate resin owing to its high nitrogen content and network structure resulted in the low heat release rate and smoke density values as well as low proportion of toxic gases compared with the epoxy resins that exhibit unacceptable smoke emissions or halogenated epoxy resins exhibiting highly toxic and corrosive gases in case of fire.

Closely to the subject approached, studies by Toldy et al. [20, 21], Wang et al. [22], Zhang et al. [23] or Yang [24] concerned with the flame retardant behaviour of various carbon fibres reinforced cyanate ester, cyanate ester/epoxy blends or epoxy resin-based composites. Their conclusions in relation with the reinforcements indicated the significant influence of the carbon fibres lay up on the fire performance and char residue formation without accounting on its structure optimization that can be developed in further studies. Further insights into the carbon fibre orientation and stacking influence on reaction-to-fire properties can be found in the works of Eibl [25], Eibl and Swanson [26] or Grigoriou and Mouritz [27]. Their findings revealed the influence of fibre on the heat released during the fire because of the thermal boundaries created by reinforcements, as well as on the pyrolysis front movement and velocity since the carbon fibres create temperature-resistant boundary layers during combustion.

Supplementary, with the increase in environmental consciousness, the use of natural reinforcements (e.g. flax, hemp, bamboo, coir, jute, sisal, etc.) in bio-composites received attention to various aspects concerning their mechanical and thermal performances, but a limited number of references can be tracked in the literature on their fire behaviour [28–30]. Several reasons are related to the toxic fume and smoke large emissions with direct consequences on environments and humans, technological challenges and increased costs due to fibres' surface conditioning by flame retardant materials. Recent contributions of Fan et al. [31], Kim et al. [30] or Das et al. [32] suggest disparities on the fire performance particularly about natural reinforced polymer under scrutiny owing to reinforcement and matrix type as well as to the interaction between them. In addition, the incorporation of reinforcement results on the increase in the mass residue corresponding to the formation of a char barrier with less effects on time-to-ignition values (TTI) but significant consequences on the peak of heat release rates (pHRR).

The overall goal of this work is to understand the reaction-to-fire properties of flax/carbon and flax/basalt reinforced cyanate ester/epoxy polymer composites and selected benchmark and to estimate the specific influences of both matrix and reinforcements (e.g. type and vol% content) during assessment of fire performances. This systematic approach aims to bring insights into the behaviour of generic, natural and natural/synthetic reinforced composites, particularly

differently stacked flax, carbon and basalt layers embedded into a sophisticated, tailored polymer blend out of cyanate ester and epoxy resins. No additional flame retardants were considered to apply to these hybrid composite architectures, either with matrix or reinforcements as their intrinsic natural retardancy is exploited and further considered as reference samples for supplementary investigations.

Experimental research

Materials selection and resin blend formulation

A plain weave 1/1 flax fibre (n. FF) with a $175 \pm 10 \text{ g} \cdot \text{m}^{-2}$ fabric areal mass and $0.400 \pm 0.05 \text{ mm}$ fabric thickness, supplied by Leinenweberei Hoffmann GmbH (Germany), was chosen as natural reinforcement. The synthetic fibres used were: carbon fibre (n. CF, KDK 8003) with a fabric areal mass of $200 \pm 10 \text{ g} \cdot \text{m}^{-2}$ and fabric thickness of $0.30 \pm 0.05 \text{ mm}$, commercially available as SIGRATEx[®], supplied by SGL Technologies GmbH (Germany) and basalt fibre (n. BF) from DBF Deutsche Basalt Faser GmbH (Germany) with the following specifications—fabric areal mass of $475 \pm 10 \text{ g} \cdot \text{m}^{-2}$ and fabric thickness of $0.35 \pm 0.05 \text{ mm}$.

The matrix's polymer blends were formulated by intimately mixing a dicyanate ester pre-polymer (n. CE, Primaset[™] BA 230 S) from Lonza Ltd. (Basel, Switzerland) with methyl ethyl ketone (MEK) solution and further stirring with diglycidyl ether of bisphenol F (n. DGEBF, Epikote[™] 862) epoxy resin, from Momentive (Geesthacht, Germany), under a 70:30 (vol%) ratio in the presence of a bisphenol A hardener. No supplementary flame retardants were added either to the natural/synthetic reinforcements or polymer blends.

Additionally, an epoxy resin (n. DGEBF, Epikote[™] 04434) is employed with FF reinforcements and benchmarked for further comparisons related to the polymer matrix's reaction to fire. The resin was selected due to its high thermoforming stability during laminate manufacturing.

Reference and hybrid composites preparation

Both reference (solely FF reinforced CE/DGEBF epoxy polymer) and hybrid composites were produced in situ by stacking individually nine prepreg sheets. Each prepreg sheet was obtained by exposing singly the resin impregnated fabrics to $80 \text{ }^{\circ}\text{C}$ for about 5 min within a temperature-controlled oven. A 5% mean value of resin flow was measured in all specimens in accordance with ISO 15034:1999 procedures. Gel time was estimated in accordance with ISO 15040:1999.

A temperature-controlled press was used to compress (50 kN) and fully cure the composite plates at constant temperature of $180 \text{ }^{\circ}\text{C}$, for 1 h. High-quality surfaces, high

and uniform reinforcement contents were obtained in all composite panels (310 mm × 310 mm). Sample's thickness fluctuated roughly around 3 ± 0.25 mm. Visual inspection of the final laminates indicated the absence of any apparent shrinkage from the processing stage.

The hybrid composite architectures were developed by layering the synthetic reinforcements (i.e. CF, BF) as the outermost, either as exterior and exterior/middle layers owing to their improved fire reaction characteristics. Table 1 lists the individual and total volume fraction of reference and hybrid composites along with the identification codes provided accounting on the stacking sequences as previously reported [33].

Composite samples characterization

Cone calorimetry (CC)

Fire tests were conducted according to ISO 5660-1:2015 standard procedures using a cone calorimeter from Fire Testing Ltd. (UK) under an incident heat flux of 50 kW m^{-2} corresponding to a fully developed fire. From each panel, $100 \times 100 \times 3 \text{ mm}^3$ samples were cut with a water-cooled

Table 1 Composite identification codes, stacking sequences and reinforcements' volume fractions

Stacking sequence	Laminate codes	Reinforcements volume fraction/vol%			Total fibre loading/vol%
		nf	sf		
□□□□□□□□	9FF	45	–	45	
■□□□□□□■	CF/7FF/CF	18	17	35	
■□□□□□□■	BF/7FF/BF	21	14	35	
■□□■□□□■	BF/3FF/BF/3FF/BF	13	17	30	
■□□■□□□■	CF/3FF/CF/3FF/CF	19	11	30	

■ synthetic reinforcement (sf); □ natural reinforcement (nf)

diamond wheel saw and wrapped with aluminium foil prior heat exposure. Both fire risks parameters, such as heat release rate (HRR), total heat release (THR) and time to ignition (TTI) and fire hazards, like fire load, flame spread, smoke and CO production, were measured. Additionally, parameters like peak of heat release rate (pHRR), fire growth rate (FIGRA) or maximum average of heat emission (MAHRE) were determined. Three replicated samples were tested for every composite architecture, followed by statistical analysis on reaction-to-fire parameters for further data reporting (Origin® 2018).

Results and discussion

Cone calorimetric tests were performed to provide further insights to the CF/FF and BF/FF hybrid cyanate ester/epoxy blends behaviour with the temperature increase, as part of a comprehensive thermal analysis approach, including dynamic mechanical and expansion, degradation and conduction, respectively, etc.

The main cone calorimeter results are summarized in Table 2, whereas in Fig. 1 it shows excerpts from char formation of CF/7FF/CF hybrid composite specimen ($100 \times 100 \times 3.15 \text{ mm}^3$) during exposure to the 50 kW m^{-2} heat flux. In all hybrid composite specimens, the synthetic outermost layer, either CF or BF, acts as a heat-insulating protective barrier at the solid surface along with the char deposited upon during exposure to the radiation heat. This is confirmed by the experimental values reported hereinafter and HRR curves of the reference and selected hybrid composites with less synthetic reinforcement content as plotted in Fig. 2a–d.

Heat release

It is acknowledged that the amount of heat released by fibre-reinforced polymer composites during fire comes from the balance between the heat generated by the combustion of flammable volatiles, and the heat absorbed by

Table 2 Cone calorimeter data summary for reference FF, CF/FF and BF/FF hybrid composites

Specimen	pHRR/kW m ⁻²	t-pHRR/s	THR/MJ m ⁻²	MAHRE/kW m ⁻²	FIGRA/kW m ⁻² s ⁻¹
9FF-epoxy	736.70 ± 8.93	100.33 ± 2.43	63.00 ± 1.01	393.33 ± 3.02	6.24 ± 0.41
9FF	611.66 ± 3.28	133.00 ± 6.11	56.03 ± 0.21	316.33 ± 3.38	4.61 ± 0.21
CF/7FF/CF	357.00 ± 5.80	93.00 ± 1.90	47.23 ± 1.20	246.33 ± 3.81	7.86 ± 1.67
BF/7FF/BF	517.33 ± 3.9	76.00 ± 6.25	55.76 ± 1.25	226.66 ± 2.96	7.55 ± 0.72
CF/3FF/CF/3FF/CF	372.00 ± 4.00	115.67 ± 1.30	47.03 ± 1.95	264.33 ± 2.80	9.40 ± 1.24
BF/3FF/BF/3FF/BF	509.00 ± 2.9	123.67 ± 2.87	55.16 ± 1.73	256.00 ± 2.00	9.18 ± 0.60

pHRR peak heat release rate, t-pHRR time to peak heat release rate, THR total heat release, FIGRA fire growth rate index, MAHRE maximum average rate of heat emitted

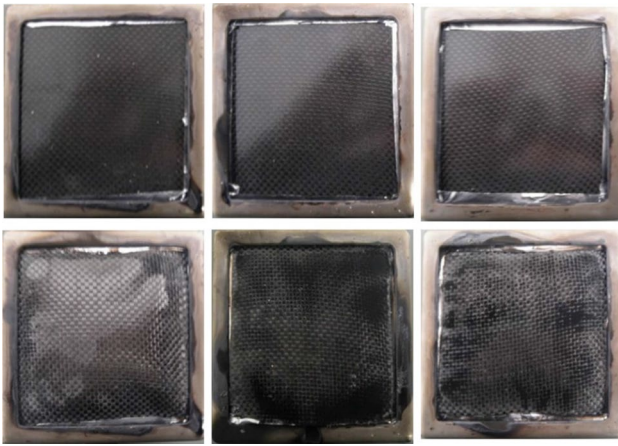


Fig. 1 Char formation for CF/7FF/CF hybrid composite subjected to an incident heat flux of 50 kW m^{-2}

the endothermic decomposition of the polymeric matrix [2, 34, 35]. As it can be seen in the excerpts of Fig. 2a–d, the heat released rate (HRR) of these composite specimens is influenced both by the resin and fibre architecture.

Initial combustion of the cyanate ester/epoxy resin from the specimens' surface establishes the first peak in less than 1 min (about 50 s) of heat flux exposure. This first sharp step rise in the HRR curves results from the ignition of the flammable volatiles followed by a decrease in the heat release from the consumption of the resin blend. The latter is a complex process, proven the combination between two resins that behave differently under a fire scenario. The epoxy resin is more flammable than the cyanate ester resin due to the increased aliphatic content in the reacted network. This can be quantified accounting on the pHRR values in Table 2 or visual inspection of Fig. 2a–b.

A second peak occurs prior to flameout in the FF composite as the pyrolysis zone approaches the specimens' backside and heat accumulation causes an abrupt rise in the HRR (see Fig. 2b). On the other hand, in the hybrid composites, the flax fibre layers embedded between outermost CF and BF reinforced layers are responsible for the change in curve shape from 2 peaks to 1 peak corresponding to medium fire and thermally thick charring (i.e. residue forming) samples according to Schartel and Hull [36].

The prolonged decrease in the HRR curves experienced after 150 s can be assigned to resin degradation towards its full consumption, by this stage the composite specimens being deteriorated extensively. This behaviour can be viewed as a shielding effect for resin combustion from both fibre plies and char on top, respectively, the first being resin-depleted and delaminated.

Further insights into the time evolution of HRR recorded values for time instants are listed in Table 3. These are useful in simulation and modelling approaches and not

tackled herein as it goes beyond the main purpose of this contribution.

The reduction of pHRR is the most important reaction-to-fire parameter since it provides an indication of the size of the fire and its propagation [36]. As it can be observed, with the increase in CF or BF content within the hybrid structure, the pHRR decreases about 45% and 15%, respectively, compared with the FF reference. There are little discrepancies between the values on each natural/synthetic reinforcement combination irrespective on their stacking sequences. Further, the same tendency holds on THR average values as listed in Table 2 and their time evolution as represented in Fig. 3, the CF/FF combinations revealing small values compared with the reference (approx. 15.75% on both layered combinations) and their counterparts, that can be assigned to the fire-resistant behaviour of CF.

The MAHRE parameter (maximum rate of heat emission) represents a good estimator on the propensity towards the fire development in composite structures in real situations [37]. The decreasing tendency for the pHRR values by the addition of synthetic reinforcements, CF and BF, can be identified as the MAHRE values, indicating the performance in fire of hybrid composites. The parameter depends upon the stacking sequence and volume fraction of reinforcements, the smaller values encountered in the reduced number of synthetic layers' architectures.

Furthermore, the effective heat of combustion (EHC), as listed supplementary in Table 4, represents the measure of the amount of heat released from the burning of composite samples per unit of sample burned during combustion in the cone calorimeter test [7]. Average EHC values computed for the composite samples herein reveal small discrepancies by switching between synthetic reinforcement types and a slight increase with the increase in their content. Specifically, the values are in line with increased mass loss rate in the absence of synthetic reinforcement as the outermost layers acting as a protective barrier.

Flame spread

Flame spread is not measured directly in a cone calorimeter. A fire growth rate index (FIGRA) and fire growth index can be used as estimators to the flame spread [38]. The fire growth rate index was estimated from the HRR curves on each particular sample as the maximum value of the heat release rate to the time of peak, and their mean value listed in Table 2 as resulted from individual estimation on measured triplicates. Both fibre reinforcement type and content pose their influence on the flame spread rate. As it can be seen, there are small discrepancies between the values computed for identical stacking sequence, especially on higher contents of synthetic

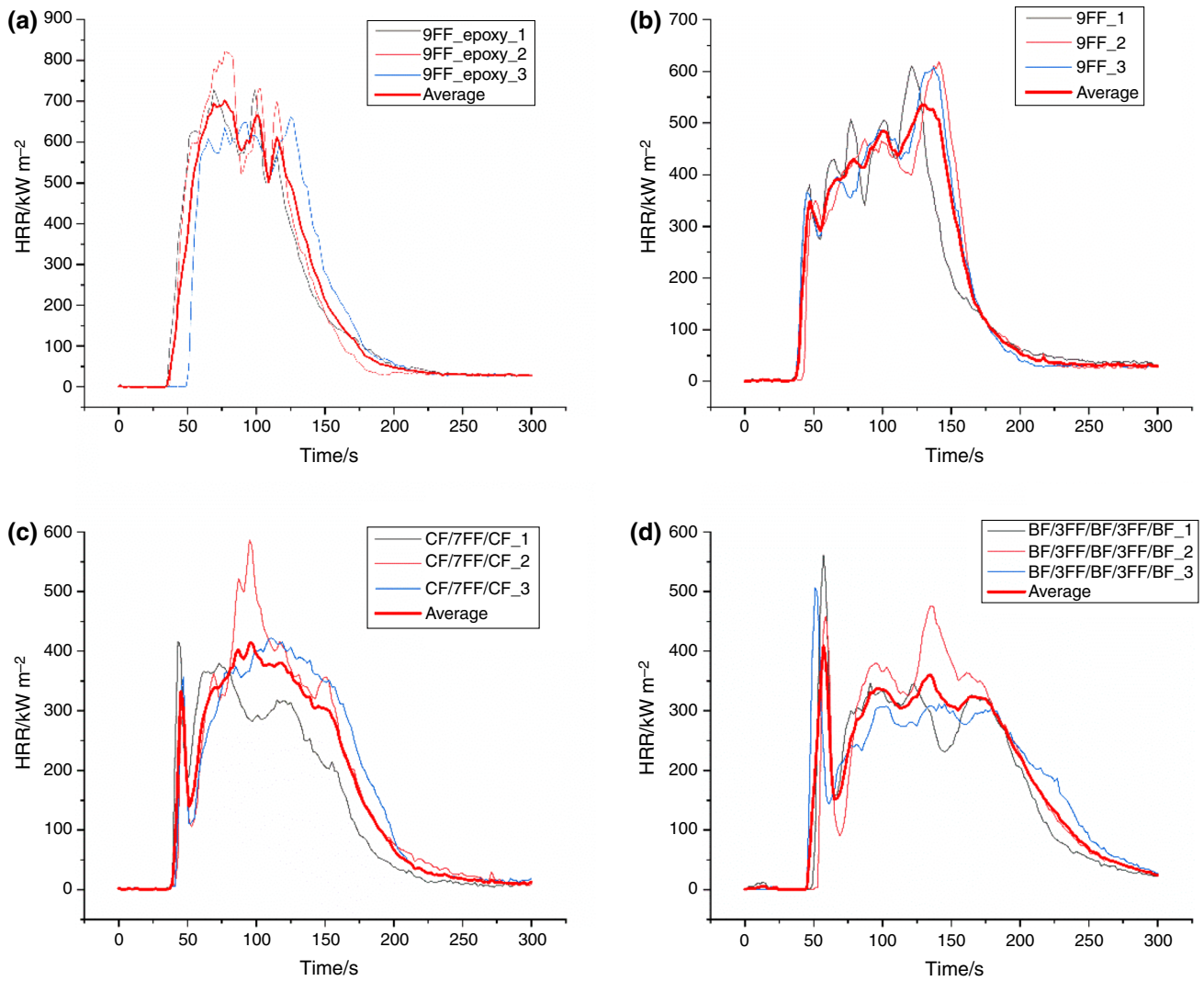


Fig. 2 Heat release rate (HRR) curves of excerpts **a** 9FF-epoxy **b** 9FF, **c** CF/7FF/CF and **d** BF/7FF/BF hybrid composite specimens (triplicates and average curves)

Table 3 Average HRR values at time instants of all composite specimens

Specimen	HRR1 min/ kW m ⁻²	HRR2 min/ kW m ⁻²	HRR3 min/ kW m ⁻²	HRR4 min/ kW m ⁻²	HRR5 min/ kW m ⁻²	HRR6 min/kW m ⁻²
9FF-epoxy	561.7 ± 26.4	488.3 ± 16.9	349.0 ± 6.1	269.3 ± 4.2	221.3 ± 3.2	202.7 ± 13.3
9FF	373.7 ± 21.5	412.3 ± 15.1	305.3 ± 9.9	237.3 ± 6.4	195.7 ± 4.2	167.3 ± 3.1
CF/7FF/CF	314.00 ± 27.5	326.33 ± 31.9	255.00 ± 31.1	196.00 ± 25.1	159.00 ± 20.7	134.67 ± 17.9
BF/7FF/BF	340.00 ± 9.6	350.00 ± 32.0	292.67 ± 14.0	229.00 ± 8.72	186.33 ± 7.23	157.67 ± 6.66
CF/3FF/CF/3FF/ CF	301.33 ± 19.01	336.33 ± 8.33	251.67 ± 6.51	193.67 ± 6.03	158.33 ± 5.13	139.00 ± 4.58
BF/3FF/BF/3FF/ BF	282.67 ± 25.01	302.33 ± 33.3	276.33 ± 17.9	223.67 ± 12.5	183.00 ± 9.54	154.67 ± 8.02

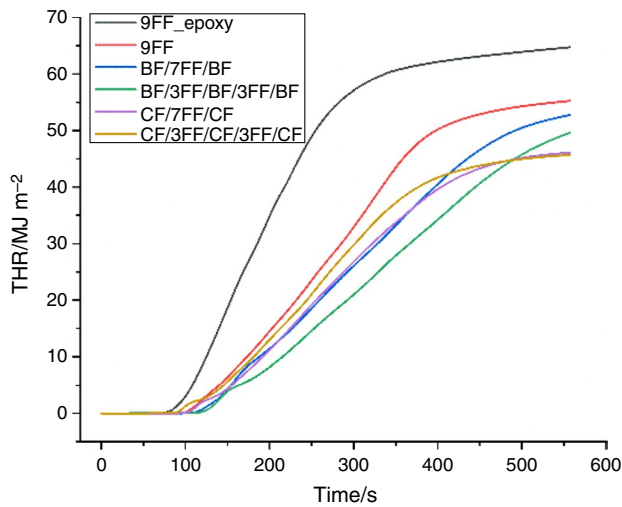


Fig. 3 Time evolution of average total heat release (THR) of FF and CF/FF, BF/FF hybrid composite specimens

reinforcements (approx. 9.40 and $9.15 \text{ kW m}^{-2} \text{ s}^{-1}$ for the CF and BF, respectively) but relatively consistent while comparing with the reference.

Time to ignition

Fire hazard of composite materials can be assessed accounting on their ignition. It is acknowledged that polymer resins used in composites can ignite in short time since exposing to the heat flux and the increased the reinforcement content the higher values of ignition time [2, 39]. This is consistent with the recorded data on benchmark, FF, CF/FF and BF/FF reinforced cyanate ester/epoxy composites under scrutiny as listed in Table 4. Since there are no significant differences in the specimens' thickness or changes on applied cone irradiance, time to achieve sustained flaming conditions (TTI) is relatively the same in all specimens, within 38 to 48 s range. Small discrepancies can be referred to the resin type, resin non-uniformity and volatiles content of the outermost layers. This is consistent with other findings as concluded by Mouritz and Gibson [39].

In addition to the t-pHRR and TTI, there is another timing parameter associated with the flame extinction—time to flameout (TFO), whose average values are provided in Table 4 for all natural and natural/synthetic hybrid composites herein. It can be seen that BF/FF reinforced samples show prolonged times between initiation of sustained flaming to cessation of the flaming activity compared with their counterpart CF/FF specimens (approx. 15 and 20%) and reference (approx. 25 and 30%).

Smoke release and smoke toxicity

Smoke production expressed by the specific extinction area (SEA) of cyanate ester-based composite herein is being plotted in Fig. 4. Average values of total smoke (TSR) released during testing corresponding to each composite architecture are provided in Table 4 along with resulted standard deviation values (SD), while in Fig. 5, the evolution in time is being illustrated. Experimental data reveal relatively high SD values that are not necessarily unusual since cone calorimeter fire scenario, generally, resembles with real material combustion. In relation with other reaction-to-fire parameters from above, TSR depends on the fibre reinforcement type. It is evident in the data provided that CF/FF composites, about approx. $1400 \text{ m}^2 \text{ m}^{-2}$, correspond to diminished smoke production compared with their counterparts and reference that are consistent with the findings on HRR for identical specimens. The strong correlation between these two fire reaction properties should be recalled or/and acknowledged.

Fire hazard properties include information on the toxic gases released during combustion, mainly carbon monoxide (CO) and carbon dioxide (CO_2). Figure 6 illustrates the CO_2 yield curves, whereas Fig. 7 illustrates the rate CO production from cyanate ester/epoxy-based specimens and selected benchmark. These curves are closely connected with the HRR curves as resulted from thermal decomposition of the polymer blend-based specimens. Both CO and smoke production provide further insights into specimens' reaction to fire. As it can be seen, after ignition (approx. 150 s), both yield curves exhibit sharp peaks followed by appreciatively a constant evolution in time. Further, prior

Table 4 Cone calorimeter data summary for supplementary fire risk and hazard parameters

Specimen	TTI/s	TFO/s	TSR/ $\text{m}^2 \text{ m}^{-2}$	EHC/ MJ kg^{-1}	Char/mass%
9FF-epoxy	40.33 ± 8.50	226.3 ± 35.0	1457.3 ± 48.00	19.00 ± 0.00	7.70 ± 0.58
9FF	39.33 ± 13.51	244 ± 12.03	1625 ± 82.21	16.67 ± 0.58	12.33 ± 1.15
CF/7FF/CF	38.33 ± 12.08	288.00 ± 12.96	1419.33 ± 35.79	16.00 ± 1.00	25.33 ± 3.21
BF/7FF/BF	46.33 ± 13.50	329.33 ± 12.82	1819 ± 41.07	16.67 ± 0.58	31.67 ± 0.58
CF/3FF/CF/3FF/CF	40.66 ± 11.52	292.33 ± 12.51	1402 ± 69.75	17.33 ± 0.58	30.00 ± 1.00
BF/3FF/BF/3FF/BF	48.66 ± 12.50	369.66 ± 11.93	1771.66 ± 84.73	17.33 ± 0.58	40.66 ± 2.08

TTI time to ignition, TFO time to flameout, TSR total smoke, EHC effective heat of combustion

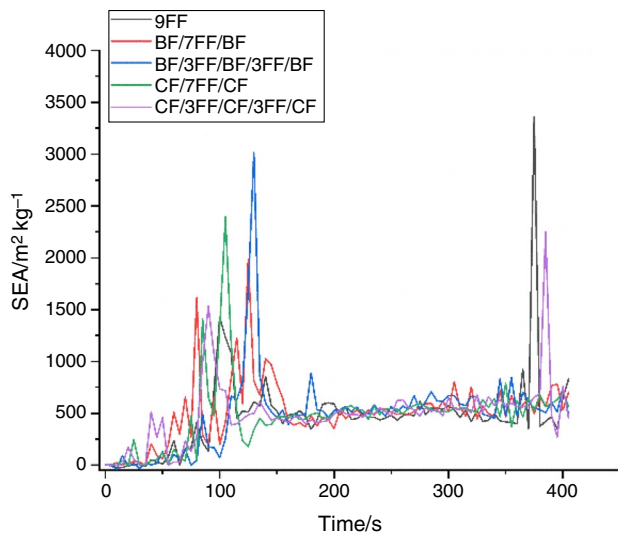


Fig. 4 Specific extinction area (SEA) of FF and CF/FF, BF/FF hybrid composite specimens

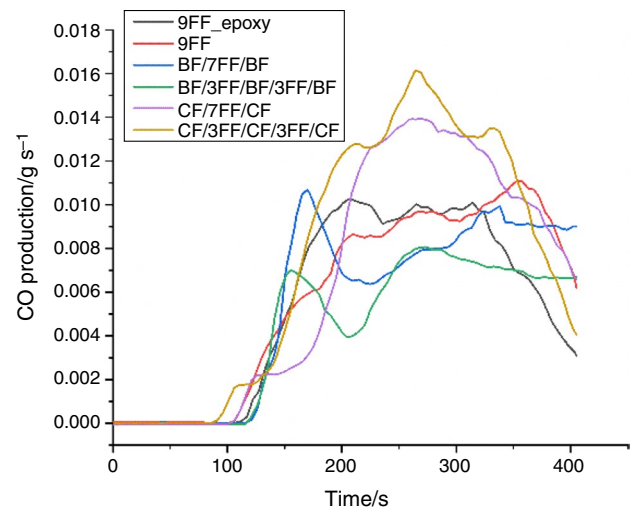


Fig. 6 Time evolution of average CO production of FF and CF/FF, BF/FF hybrid composite specimens

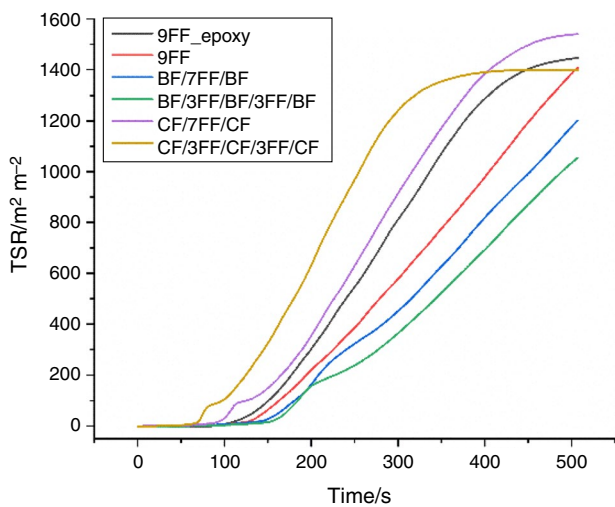


Fig. 5 Time evolution of average total smoke released (TSR) of FF and CF/FF, BF/FF hybrid composite specimens

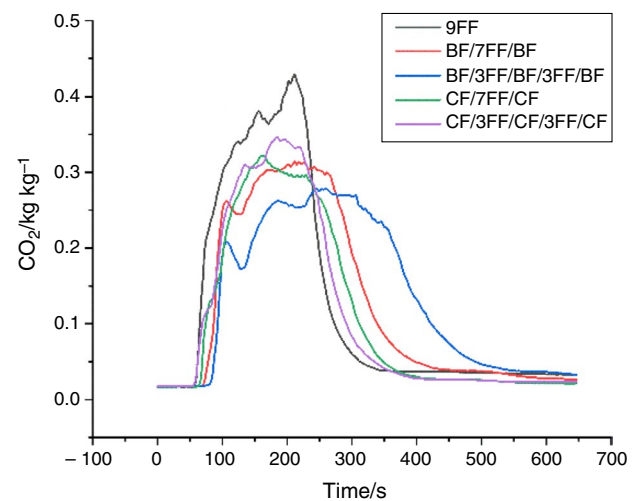


Fig. 7 Time evolution of average CO₂ yield of FF and CF/FF, BF/FF hybrid composite specimens

flame extinction, the CO production curves reveal another sharp peak when HRR and CO₂ decrease substantially, being almost negligible. This behaviour can be regarded to the completeness of the combustion reactions.

Conclusions

This study emphasized the inherent fire retardant of cyanate ester polymer blends, and its composites compared with a selected benchmark under identical manufacturing conditions and cone calorimetry set-up. In the absence of

any fire-retardant modifier for the polymer matrix and/or reinforcements, the influence of synthetic (e.g. carbon, basalt) or natural (e.g. flax) fibres, content and layering sequences upon the common reaction-to-fire parameters was investigated. Specimen thickness was not accounted on proven small discrepancies.

Consequently, all specimens were forming a char layer at the end of cone calorimeter tests with consequence on pHRR values. The addition of carbon and basalt reinforcements was drastically reducing these values compared with

flax sample. Further, for similar reinforcement type but different resin system, the novel polymer blend introduced proved to be more performant. Although time-to-ignition values recorded on all specimens were revealing small discrepancies, there are relatively significant differences in the total smoke released that is about 8% and 12% higher in the BF reinforced architectures compared with their FF counterpart. By disposing the synthetic fibres as the outermost layers, the emissions of toxic gases during combustion are diminished compared with the FF specimen. This has consequences when used in engineering applications, where the addition of protective layer (e.g. gel coat) may further enhance the fire performance of these hybrid architectures.

Acknowledgements The corresponding author gratefully acknowledges the financial assistance of German Academic Exchange Service—DAAD that enabled and supported the internship with Fraunhofer Research Institution for Polymeric Materials and Composites—PYCO, Germany.

References

- Brown JR, Fawell PD, Mathys Z. Fire-hazard assessment of extended-chain polyethylene and aramid composites by cone calorimetry. *Fire Mater.* 1994;18(3):167–72.
- Correia JR, Bai Y, Keller T. A review of the fire behaviour of pultruded GFRP structural profiles for civil engineering applications. *Compos Struct.* 2015;127:267–87.
- Avila MB, Dembsey NA, Dore C. Effect of resin type and glass content on the reaction to fire characteristics of typical FRP composites. *Compos Part A Appl Sci Manuf.* 2008;39:1503–11.
- Chapple S, Anandjiwala R. Flammability of natural fiber-reinforced composites and strategies for fire retardancy: a review. *J Thermoplast Compos Mater.* 2010;23(6):871–93.
- ISO 3795. Road vehicles and tractors and machinery for agriculture and forestry—determination of burning behaviour of interior materials 1989. (R 2013, R 2019).
- EN 2825. Aerospace series. Burning behaviour of non metallic materials under the influence of radiating heat and flames. Determination of smoke density 2011.
- ISO 5660-1. Reaction-to-fire tests—heat release, smoke production and mass loss rate—part 1: heat release rate (cone calorimeter method) and smoke production rate (dynamic measurement) 2015.
- Colectiv nightclub fire. 2019. [Available from: https://en.wikipedia.org/wiki/Colectiv_nightclub_fire. Accessed 15 June 2019.
- Martin FJ, Price KR. Flammability of epoxy resins. *J Appl Polym Sci.* 1968;12(1):143–58.
- Rallini M, Natali M, Kenny JM, Torre L. Effect of boron carbide nanoparticles on the fire reaction and fire resistance of carbon fiber/epoxy composites. *Polymer.* 2013;54(19):5154–65.
- Saba N, Jawaid M, Paridah MT, Al-othman OY. A review on flammability of epoxy polymer, cellulosic and non-cellulosic fiber reinforced epoxy composites. *Polym Adv Technol.* 2016;27(5):577–90.
- Hamerton I. Chemistry and technology of cyanate ester resins. Berlin: Springer; 2012.
- Walters RN, Lyon RE. Fire-resistant cyanate ester–epoxy blends. *Fire Mater.* 2003;27(4):183–94.
- Chen X, Liang G, Gu A, Yuan L. 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 boards. *Ind Eng Chem Res.* 2015;54(6):1806–15.
- Chen X, Wang J, Huo S, Yang S, Zhang B, Cai H. Preparation of flame-retardant cyanate ester with low dielectric constants and dissipation factors modified with novel phosphorus-contained Schiff base. *J Therm Anal Calorim.* 2019;135(6):3153–64.
- Delfa G, Voigt W, Abgottspon M. High temperature and flame retardant cyanate ester resins for aerospace applications. In: SETEC 10 - SAMPE Conference, Europe, Brindisi, Sept. 16–17, 2010.
- Dreyer CJ, Bauer M, Bauer J, Keil N, Yao H, Zawadzki C. Polycyanurate ester resins with low loss and low birefringence for use in integrated optics. In: SPIE 2001.
- Bauer M, Decker D, Richter F, Gwiazda M, inventors. Hybrid polymers made of cyanates and silazanes, method for the production and use thereof. Germany patent EP2408846B1 2010.
- Dreyer C, Sothje D, Bauer M. Progress in recycling of composites with polycyanurate matrix. *Adv Chem Eng Sci.* 2014;4:167–83.
- Toldy A, Szolnoki B, Marosi G. Flame retardancy of fibre-reinforced epoxy resin composites for aerospace applications. *Polym Degrad Stab.* 2011;96(3):371–6.
- Toldy A, Szlancsik Á, Szolnoki B. Reactive flame retardancy of cyanate ester/epoxy resin blends and their carbon fibre reinforced composites. *Polym Degrad Stab.* 2016;128:29–38.
- Wang X, Kalali EN, Wan J-T, Wang D-Y. Carbon-family materials for flame retardant polymeric materials. *Prog Polym Sci.* 2017;69:22–46.
- Zhang J, Delichatsios MA, Fateh T, Suzanne M, Ukleja S. Characterization of flammability and fire resistance of carbon fibre reinforced thermoset and thermoplastic composite materials. *J Loss Prev Process Ind.* 2017;50:275–82.
- Yang F. Fire-retardant carbon-fiber-reinforced thermoset composites. In: Wang D-Y, editor. Novel fire retardant polymers and composite materials. Sawston: Woodhead Publishing; 2017. p. 271–93.
- Eibl S. Influence of carbon fibre orientation on reaction-to-fire properties of polymer matrix composites. *Fire Mater.* 2012;36(4):309–24.
- Eibl S, Swanson D. Influence of out-of-plane fiber orientation on reaction-to-fire properties of carbon fiber reinforced polymer matrix composites. *Fire Mater.* 2018;42(2):234–43.
- Grigoriou K, Mouritz AP. Influence of ply stacking pattern on the structural properties of quasi-isotropic carbon-epoxy laminates in fire. *Compos A Appl Sci Manuf.* 2017;99:113–20.
- Mngomezulu ME, John MJ, Jacobs V, Luyt AS. Review on flammability of biofibres and biocomposites. *Carbohydr Polym.* 2014;111:149–82.
- Marosi G, Szolnoki B, Boczk K, Toldy A. Fire-retardant recyclable and biobased polymer composites. In: Wang D-Y, editor. Novel fire retardant polymers and composite materials. Sawston: Woodhead Publishing; 2017. p. 117–46.
- Kim NK, Dutta S, Bhattacharyya D. A review of flammability of natural fibre reinforced polymeric composites. *Compos Sci Technol.* 2018;162:64–78.
- Fan M, Naughton A, Bregulla J. 14 - Fire performance of natural fibre composites in construction. In: Fan M, Fu F, editors. Advanced high strength natural fibre composites in construction. Woodhead Publishing; 2017. p. 375–404.
- Das O, Kim NK, Hedenqvist MS, Bhattacharyya D. 15 - The flammability of biocomposites. In: Jawaid M, Thariq M, Saba N, editors. Durability and Life Prediction in Biocomposites, Fibre-Reinforced Composites and Hybrid Composites. Woodhead Publishing; 2019. p. 335–65.

33. Luca Motoc D, Ferrandiz Bou S, Balart R. Thermal properties comparison of hybrid CF/FF and BF/FF cyanate ester-based composites. *J Therm Anal Calorim*. 2018;133(1):509–18.
34. Redfern JP. Rate of heat release measurement using the Cone Calorimeter. *J Therm Anal*. 1989;35(6):1861–77.
35. Ding Y, Stoliarov SI, Kraemer RH. Pyrolysis model development for a polymeric material containing multiple flame retardants: relationship between heat release rate and material composition. *Combust Flame*. 2019;202:43–57.
36. Scharrel B, Hull R. Development of fire-retarded materials—interpretation of cone calorimeter data. *Int J*. 2007;31:327–54.
37. Dorez G, Taguet A, Ferry L, Lopez-Cuesta JM. Thermal and fire behavior of natural fibers/PBS biocomposites. *Polym Degrad Stab*. 2013;98(1):87–95.
38. Kruger HJ, Focke WW, Mhike W, Taute A, Roberson A, Ofosu O. Cone calorimeter study of polyethylene flame retarded with expandable graphite and intumescent fire-retardant additives. *J Fire Sci*. 2014;32(6):498–517.
39. Mouritz AP, Gibson AG. Fire properties of polymer composite materials. Berlin: Springer; 2007.

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.