



# Thermal properties comparison of hybrid CF/FF and BF/FF cyanate ester-based composites

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## Abstract

Insights within thermal expansion, conductivity, and decomposition dependencies with temperature on symmetrical and unsymmetrical layered carbon (CF) or basalt (BF) fabrics in combination with flax fibers (FF) were approached. Driven by commercial application and environmental concerns, the paper draws attention on a modified formula of cyanate ester with a common epoxy resin under an optimized ratio of 70:30 (vol%) as well as on the hybrid reinforcements stacking sequences. Synergetic effects were debated in terms of the CF and BF stacking sequences and corresponding volume fraction followed by comparisons with values predicted by the deployment of hybrid mixtures rules (RoHM/iRoHM). CF hybrid architectures revealed enhanced effective thermophysical properties over their BF counterparts and both over the FF-reinforced polymer composite considered as a reference. Thermal conductivities spread between 0.116 and 0.299 W m<sup>-1</sup> K<sup>-1</sup> from room temperature up to 250 °C on all hybrid specimens, giving rise to an insulator character. Concerning the coefficient of thermal expansion, CF hybrid architectures disclosed values of 1.236 10<sup>-6</sup> K<sup>-1</sup> and 3.102 10<sup>-6</sup> K<sup>-1</sup> compared with BF affine exhibiting 4.794 10<sup>-6</sup> K<sup>-1</sup> and 6.245 10<sup>-6</sup> K<sup>-1</sup>, respectively, with an increase in their volume fraction.

**Keywords** Carbon fiber · Basalt fiber · Flax fiber · Hybrid architecture · Cyanate ester resin · Thermal properties

## Introduction

Green composites and natural fibers industry surpassed the limits for threshold attributes on their developed products after decades of focused research work, being on the verge of leveraging their performance attributes, including affordability, wide-range commercial applications, and environmental concerns. The smart combination between natural reinforcements and/or biopolymers, initially intended to address the light-weight and low-cost issues, inherited globally the individual material properties of their constitutive, especially on thermal and acoustic insulation,

or enabled synergetic effects in terms of mechanical and dynamical properties while combined as hybrid composite architectures [1–4]. Thermal degradation and fire-retardant properties of natural reinforcement polymer-based composites captured the researchers' attention over the last decade, mostly due to environmental concerns and safety issues. Alvarez [5], Manfredi [6], Lazko [7], Bar [8], or Kollia [9] and co-authors reported on the changes of aimed material properties for a couple of reinforcements embedded within synthetic resins such as vinyl ester, unsaturated polyester or cyanate ester, in or without surface conditioning by aid of flame retardant agents. Their findings enabled insights into the overall material behavior while establishing new routes for further developments and performance enhancements.

Literature survey allows a comprehensive insight into the world of extensive works on various combinations of materials from renewable resources, more or less environmental friendly and/or fully biodegradable under controlled conditions. Critical reviews covering the encountered challenges, individual material selection

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criteria, compatibility, effective properties, manufacturing and processing techniques, economic and environmental impact, and their ability to meet social and materials need worldwide were kindly provided by several groups of researchers [10–14]. They argued on natural materials' potential benefits despite their inherent hydrophilic nature that prior requires physically or chemically conditioning to improve the fiber/matrix adhesion to limit the penalties of the resulting composite material performances.

In addition, since through hybridization improvements on the combination's effective properties were mostly achieved by individual material selection, both fibers and matrix, by smart reinforcement layering or intimately connecting, predictability about the preferences on the composite architectures adopted by different researchers teams and lately by various industry players worldwide can be easily identified [15–19].

The green polymer-based composites developed hitherto used natural fibers acquired from cellulose/lignocelluloses sources (e.g., jute, flax, hemp, ramie, sisal, wood) embedded mainly within unsaturated polyester resins and epoxies. Attempt on getting an answer to the question regarding the superiority of natural reinforcements over glass fibers from an environmental perspective was given both by Joshi [20] and Wambua [21] and their co-authors using some previous studies based on life cycle assessments (LCA) and several drivers to debate on the tackled issue.

Recently were reported studies on resins developed from renewable resources (e.g., linseed oil, soybean oil) as polymer matrices for natural reinforcements which all showed good mechanical, thermophysical, or dynamical properties in comparison with their counterparts [22–26]. In the paper of Mosiewicki et al. [27] was summarized the main vegetable oil-based composite architectures, covering macro-, micro-, and nanoscale range on the reinforcement dimension and examples in special applications as coatings, adhesives, foams, and shape memory materials. Furthermore, the paper of Lligadas et al. [28] enables the reader to get acquainted with a different perspective on bio-based materials tailored as posing certain material properties, focusing on their biomedical application potential. Further insights on the issue were given by Fombuena et al. [29] with their comprehensive study regarding the mechanical and thermal properties of various protein fillers embedded within an epoxidized soybean oil (ESBO) novel resin combination cured by aid of nadic methyl anhydride. The study revealed enhancement on the properties under the focus with filler mass fraction increase.

Flax and hemp fibers classified as favorites among the preferences while selecting the reinforcements for this composite class. A recent paper of Pil et al. [30] attempted to provide a large spectrum of facts and data while arguing

positively the question used as title regarding the fascination of designers for these types of natural materials. They succeeded to capture the substantial spectrum of applications deploying these materials due to their intrinsic property of having a high vibration damping capacity in addition to the excellent mechanical properties and lower environmental impact compared with the glass and carbon-reinforced composites.

In addition, the nature and individual features of the polymer matrix strongly influence mechanical and temperature-dependent properties, like storage modulus or damping factor. Subsequently, matrix-material selection must be tackled as sharing the same importance in the composite design. For example, epoxy resin was preferred in the early stages of advanced composite development and has maintained its position, even following extensive research into new blend formulas to transcend the drawbacks encountered with respect to transition temperature, moisture control, toxicity, polymer viscosity, etc. [31, 32]. Next, epoxy resin was used to enhance the individual processing properties of other polymer resins through novel blend synthesis. Special attention was given to the synthesis with cyanate ester thermosetting resin. The latter is particularly preferred for its material performance (e.g., high strength, low dielectric constant and dissipation factor, radar transparency, flame retardant) in high-temperature environments. Moreover, used as a matrix material for carbon fibers, reinforced composites satisfy the low-weight structural material requirements in the aerospace industry. In addition, cyanate ester resin is acknowledged for its recyclable potential under chemical attack or for its self-healing capacity while enhanced with epoxy resin filled microcapsules, allowing the reuse of reinforcements in remanufacturing processes [33, 34]. To the author's knowledge, no systematic study has been carried out on the effect of different stacking sequences and the content of natural reinforcements, especially flax fibers, in combination with carbon fibers or basalt fibers, as hybrid architectures. Further, there are no reports available on natural-fiber-reinforced cyanate ester-based prepregs/laminates.

The present paper explores the feasibility of tailoring hybrid architectures based on flax in combination either with carbon or basalt fibers prepregs. The synergetic effect due to hybridization will be emphasized individually on different stacking sequences by deploying a novel resin system made by cyanate ester and epoxy resins followed by a couple of important material properties' investigation. Debate on effective thermophysical properties (e.g., thermal expansion and thermal conductivity) and thermal decomposition within selected temperature range of herein samples focuses on the perspective of deploying basalt fibers as potential replacements of carbon reinforcements in applications driven by economic issues [35].

## Experimental

### Material selection and resin blend formulation

Commercial available plain weave 1/1 flax (n. FF), carbon-fiber (n. CF), and basalt fiber (n. BF) fabrics were selected as reinforcements. The novel resin blend was formulated by intimately mixing dicyanate ester pre-polymer (n. CE—75 vol%) with methyl ethyl ketone (MEK) solution and further stirring with diglycidyl ether of bisphenol F (n. DGEBF) epoxy resin under a 70:30 (vol%) ratio in the presence of a bisphenol A hardener. Individual reinforcement properties and resin components are summarized in Tables 1 and 2, respectively.

### Sample preparation

The hybrid composite laminates (dimensions: 310 mm × 310 mm) were produced by stacking individually nine either solely FF and/or combined with CF or BF for the hybrid prepreg sheets. The prepregs were manufactured in situ by exposing individual resin impregnated fabrics to 80 °C for about 5 min within a temperature-controlled oven. ISO 15,034:1999 standardized procedures were used to determine the resin flow while ISO 15,040:1999 was used to evaluate the gel time. A temperature-controlled press was used to compress (i.e., at 50 kN) and fully cure the composite plates at constant temperature of 180 °C, for 1 h. The overall fiber loading fluctuated as shown in Table 3 and an average of 5% of resin flow was measured, after lamination, for all hybrid composite plates. Solely FF and hybrid FF/CF or FF/BF composite laminates, posing high-quality surfaces, were obtained. Sample thickness ranged from 2.5 to 3 mm depending on the stacking sequence.

With respect to the stacking sequence, in the case of the hybrid architectures, the higher strength material (i.e., CF, BF) was layered as the outermost, exterior, and exterior/middle layers. Flax fibers were layered in between due to

their lower material performance. Table 3 lists the stacking layering codes used to further address the hybrid composite architectures, and their individual and total volume fraction within the final laminate.

### Material characterization

#### Dilatometry (DIL) and laser flash analysis (LFA)

Expansion in composites were monitored by aid of a push rod dilatometer DIL 402 PC (Netzsch GmbH, D), in controlled atmosphere, within 25–250 °C temperature range and a 4 K min<sup>−1</sup> heating rate, in accordance with ASTM E228:2011 standard procedures. Sample dimensions were set as 25 mm × 5 mm in length and width, respectively. Two successive scans were performed to remove thermal history and to retrieve the aimed thermophysical property—linear coefficient of thermal expansion (CTE). Thermal conductivities of specimens were retrieved by aid of LFA 447 NanoFlash<sup>TM</sup> device (Netzsch GmbH, D), within 25–150 °C temperature range according to the ISO 22007-4:2008 standard procedures. Samples (8 mm × 8 mm) were covered back and forth with a thin layer of graphite to enhance their emission/absorption properties. The density at room temperature was obtained by the buoyancy flotation method. Thermal conductivity data correspond to the mean value of the recorded values out of five single shots on each point considered.

#### Thermogravimetric analysis (TGA)

Thermogravimetric analysis on specimens was performed by aid of a STA 449 F3 Jupiter<sup>®</sup> (Netzsch GmbH, D) at a heating rate of 10 K min<sup>−1</sup>, in N<sub>2</sub> atmosphere at a 20 mL min<sup>−1</sup> flow rate, in accordance with ISO 11,358-1:2014. Dynamic mode was deployed in the heating step within the selected 25–850 °C temperature range. Alumina crucible was used for each individual specimen excerpt.

**Table 1** Material data of the present reinforcements

	Carbon fiber/n. CF/(KDK 8003)	Basalt fiber/n. BF	Flax fiber/n. FF
Fabric areal mass/g m <sup>−2</sup>	200 ± 10	475 ± 10	175 ± 10
Fabric thickness/mm	0.30 ± 0.05	0.35 ± 0.05	0.400 ± 0.05
Commercial trade name	SIGRATEX <sup>®</sup>	—	—
Supplier	SGL Technologies GmbH	DBF Deutsche Basalt Faser GmbH	Leinenweberei Hoffmann GmbH
Thermal expansion/μstrain °C <sup>−1</sup> *	0.2	3.5	30
Thermal conductivity/ W m <sup>−1</sup> °C <sup>−1</sup> *	80	0.038	0.3

\* CES EduPack 2016 (Granta Design Limited)

**Table 2** Individual physical properties of polymer system

	Cyanate ester resin (Primaset™ BA 230 S)	DGEGBF epoxy resin (Epikote™ 862)
Glass transition temperature/°C	320 (by DMA)	270 (by DSC)
Viscosity @ 25 °C/mPa s	450 ± 100	740 ± 150
Density @ 20 °C/g cm <sup>-3</sup>		1.18 ± 0.02
Curing agent	Bisphenol A (BA)	
Supplier	Lonza Ltd	Momentive

**Table 3** Details on hybrid composites stacking sequences, assigned codes and volume fractions

Stacking sequence	Laminate codes	Reinforcements volume fraction/vol%		Total fiber loading/vol%
		<i>Nf</i>	<i>sf</i>	
□□□□□□□□	9FF	45	—	45
■□□□□□□■	BF/7FF/BF	21	14	35
■□□■□□□■	BF/3FF/BF/3FF/BF	13	17	30
■□□□□□□■	CF/7FF/CF	18	17	35
■□□■□□□■	CF/3FF/CF/3FF/CF	19	11	30

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

The mass loss was recorded in response to temperature increases.

### Scanning electron microscopy (SEM)

Specimens' morphology was examined by aid scanning electron microscopy (SEM) on an EVO MA 25 (Zeiss, D) at room temperature, deploying different magnification modes—500 × and 2.0 K ×, respectively. The prevailing images, after sputtering the samples with a gold thin layer, were closely investigated to qualitatively characterize the fiber–matrix interfaces.

### Micromechanical approaches: RoM/iRoM and RoHM/iRoHM

Effective thermal properties of individual laminate (i.e., FF, BF or CF) and correspondingly tailored composite architectures were predicted deploying rules of mixtures and inverse mixtures (RoM/iRoM) as well as rules of hybrid mixtures and inverse hybrid mixtures (RoHM), respectively, as delivered in Table 4. In the expressions of addressed thermal properties, the following hold for the fiber loadings— $V_{nf}$  and  $V_{sf}$ , either natural or synthetic, while  $V_t$  is the total reinforcement volume fraction.

Deviation from the reference (i.e., 9FF architecture) of the experimental values reveals the hybrid effects, which can be ranked as positive or negative according to

Marom et al. [36]. These hybrid effects highlight the influence of stacking sequences and synthetic reinforcement's nature upon addressed thermal properties being indicators for the synergetic behavior of the combinations. On the other hand, since the retrieved thermal conductivity values represent through thickness measurements, RoM and RoHM must be replaced with their correspondingly inverse expressions accounting for the applied external load and fibers' orientation. This series model provides the lowest values of the composites' equivalent thermal conductivity [37, 38]. Nonetheless, more appropriate micromechanical approaches may be deployed to account for the reinforcement characteristics (i.e., anisotropy, orientation, waviness) but are thought to surpass the purpose of herein contribution and debate.

## Results and discussion

### Effect of structure on the effective thermal properties

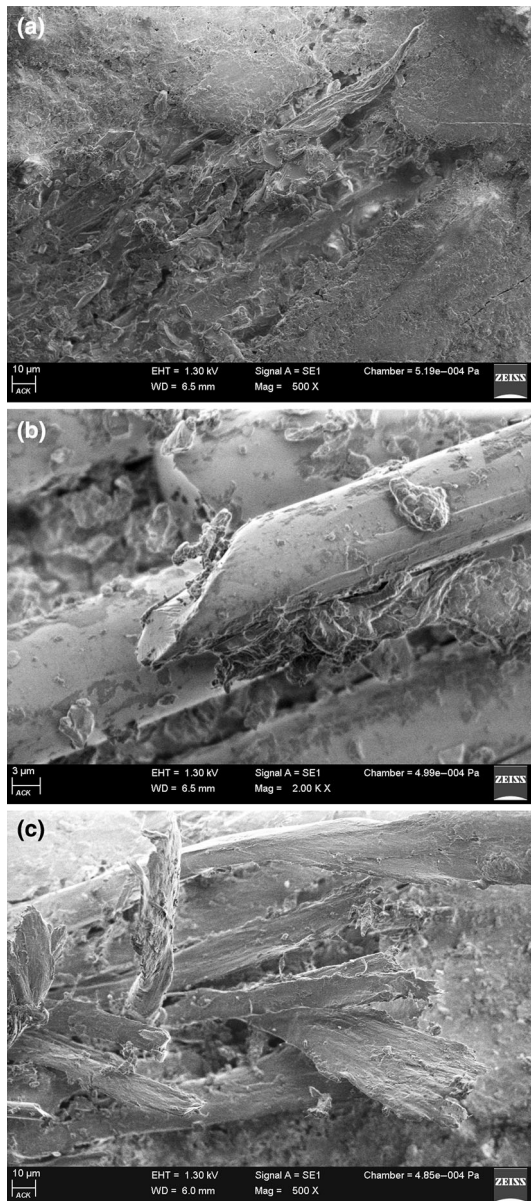
SEM images from Fig. 1a–c were collected for the FF specimens, and the highest number of layers of BF and CF reinforcements in the hybrid composite samples reveal the synergetic effects on their morphology. Images clearly evidence the weak adhesion between the CE&DGEGBF resin and BF or CF fibers due to the high sensitivity of CE resin to –OH groups and other volatiles present in the



**Table 4** RoM and RoHM expressions of thermophysical properties

Thermal property	RoM/iRoM		RoHM/iRoHM
	Natural fiber-based composites	Synthetic fiber-reinforced composites	
Linear coefficient of thermal expansion	$\alpha_{nfc} = \alpha_{nf} V_{nf} + \alpha_m (1 - V_{nf})$	$\alpha_{sfc} = \alpha_{sf} V_{sf} + \alpha_m (1 - V_{sf})$	$\alpha_c = \alpha_{nfc} V_{cnf} + \alpha_{sfc} V_{scf}^*$
Thermal conductivity	$\frac{1}{k_{nfc}} = \frac{V_{nf}}{k_{nf}} + \frac{(1-V_{nf})}{k_m}$	$\frac{1}{k_{sfc}} = \frac{V_{sf}}{k_{sf}} + \frac{(1-V_{sf})}{k_m}$	$\frac{1}{k_c} = \frac{V_{cnf}}{k_{nfc}} + \frac{V_{scf}^*}{k_{sfc}}$

\*  $V_{cnf} = \frac{V_{nf}}{V_t}$ ,  $V_{scf} = \frac{V_{sf}}{V_t}$ ,  $V_t = V_{nf} + V_{sf}$

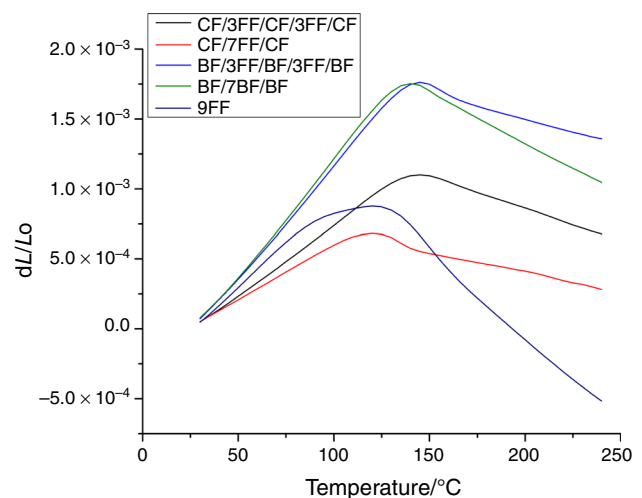
**Fig. 1** SEM images of the side views for **a** 9FF, **b** BF/3FF/BF/3FF/BF and **c** CF/3FF/CF/3FF/CF composites

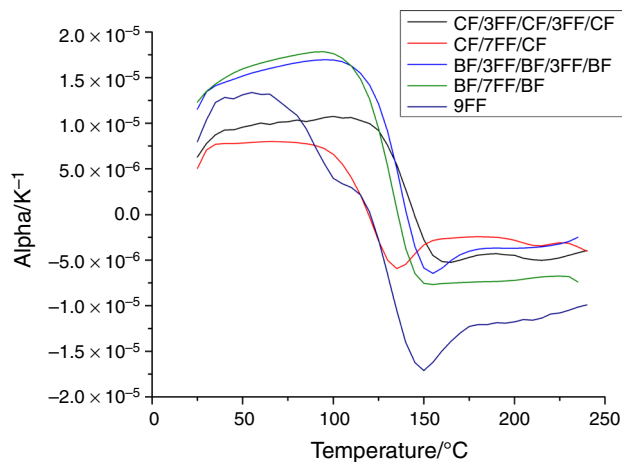
untreated fibers. Moreover, different types of interactions can be outlined in these composites function of fiber types.

These are interactions between the fiber bundles and interactions between the cells of natural fiber. The latter is of particular importance because it can cause inter-fibrillar failure and uncoiling of the helical fibrils, and thus diffuse matrix cracking in practical applications [39]. In addition, Fig. 1b, c reveals both fiber/matrix adhesion and the beauty of the fiber orientation. The latter can be considered to be in favor of BF while the replacements of CF with these are becoming an issue.

### Effect of hybridization on the expansion behavior

Thermal strain fields with FF and either CF/FF or BF/FF-reinforced novel cyanate ester-based composites experience the same tendency over the temperature range (Fig. 2), such as a linear increase before a peak value, followed by a similar decrease toward the final value. Furthermore, physical alpha curves (Fig. 3) reveal approximately linear variation with temperature increases, except the behavior shown between 100 and 150 °C associated with an abrupt decrease. This behavior can be regarded mainly to the hydrophilic nature of FF fibers, namely the aforementioned –OH groups and other volatiles

**Fig. 2** Thermal strain within various stacking sequences of CF and BF-reinforced composites



**Fig. 3** Technical alpha at different temperatures from DIL measurements

that react with the resin as the temperature increase. Novel CE&DGE BF resin has a complicated structure and prone to be highly sensitive to the moisture. Thermal history cannot be accounted with the responsible mechanisms to the overall expansion behavior since the second runs were reported.

The increase in the rigid phase content with the hybrid architectures influences the amplitude of recorded data such there is a direct connection irrespective of the reinforcement deployed, CF or BF. On the other hand, the CF hybrid composites, either symmetrical or unsymmetrical stacked, reveal an opposite behavior to their BF counterparts, especially on the alpha curves variation as the temperature increases. This overall lowering effect can be assigned to the extremely low or negative thermal expansion of CF with temperature increases as widely acknowledged or shown by herein authors into a previous contribution [40]. Moreover, the higher the CF content the more pronounced is the decrease on the overall linear coefficient of thermal expansion values, especially within 150–250 °C temperature range.

A theoretical predicted versus experimentally retrieved values' (see values listed in Table 5) comparison, in terms of relative error (see Fig. 4, square symbol), reveal high discrepancies up to 95% in case of 9FF architecture and approximately 60% to 92% for the hybrid combinations, irrespective of the synthetic reinforcement. These values have to be viewed in accordance with their significance as long as the theoretically values belong to the upper limit predicted by micromechanical expressions within literature [37].

With respect to the hybrid effects, accounting for the relative differences between the experimentally retrieved values from either CF/FF or BF/FF combinations and 9FF reference specimen (see Fig. 4, triangle symbol), positive departures were recorded in all cases. Thereof, irrespective

of the stacking sequence, the presence of synthetic fibers (i.e., CF or BF) within the composite architecture enables a synergetic behavior at the overall assembly level from a thermal expansion perspective.

### Effect of hybridization on the thermal conductivity

Figure 5 depicts the thermal conductivity curves of the analyzed polymer composite specimens, between 0.116 and 0.299 W m<sup>-1</sup> K<sup>-1</sup> within selected temperature range. As it can be seen, thermal conductivity values of the hybrid composites, irrespective of the synthetic reinforcement, are in the same order of magnitude and can be ranked as thermal insulators despite the presence of a thermal conductivity phase. Moreover, a slight difference on thermal conductivity values retrieved from the CF and BF hybrid architectures is present within temperature range.

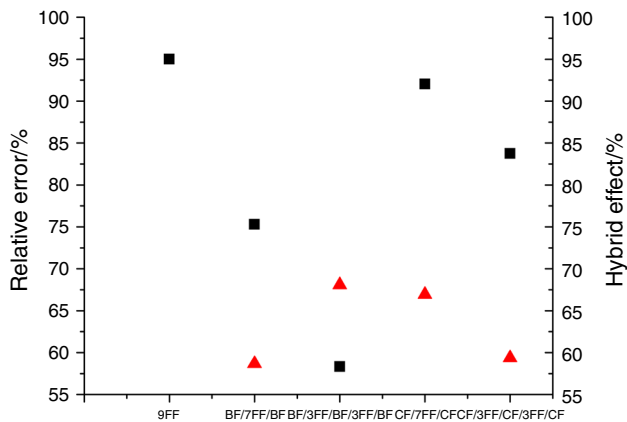
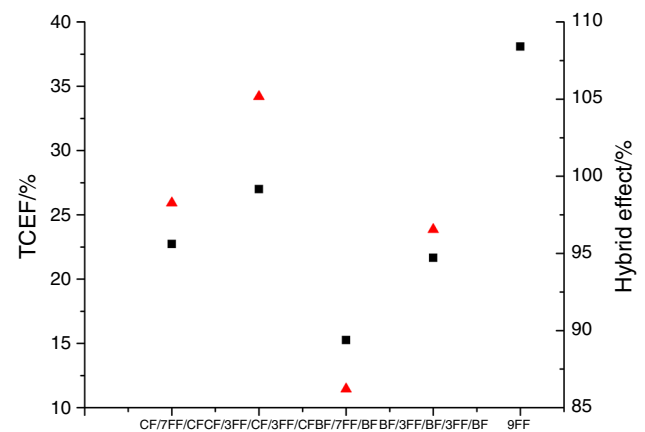
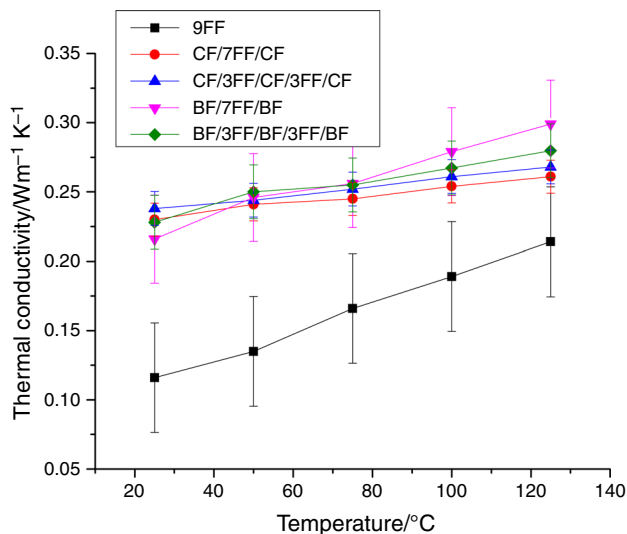
In particular, it seems that BF-reinforced hybrid composite specimens are exhibiting enhanced thermal conductivities compared both with the reference and CF architectures. Indeed, sudden changes in thermal conductivity between 75 and 125 °C with BF hybrid architectures can be observed in the above graphical representation. These changes can be related both to the glass transitions and synergetic behavior while combined with FF reinforcements, being consistent with the thermal expansion behavior of the similar architectures.

Supplementary, due to the relatively small values of the through-thickness thermal conductivities, heat dissipations from panels made from these materials are limited, restricting thus their potential applications. Indirectly, the heat dissipation issue can be tackled based on the hybrid effect reflecting the synergy due to sequencing and individual reinforcement selection compared with the reference. The results are presented in Fig. 6 and seem to be more pronounced for CF hybrid specimens accounting the thermal conductivities values recorded at room temperatures. A conductivity enhancement factor (n. TCEF, in %), defined as the relative error between the retrieved hybrid composite architectures and matrix thermal conductivities at 25 °C, can be used further to debate on the heat dissipation within the specimens (see Fig. 6). The values vary from 15 up to 38% showing an increasing tendency in terms of efficiency due to hybridization and deployment of more synthetic layers within the composites.

On the other hand, the relative error values unveil relatively small differences among the predicted and experimentally retrieved values on FF and CF/FF hybrid architectures (between 45 up to 60%) in comparison with the BF-reinforced architectures (up to 200%). The latter should be assigned to the individual thermal conductivity values of BF fabrics reported with literature [41].

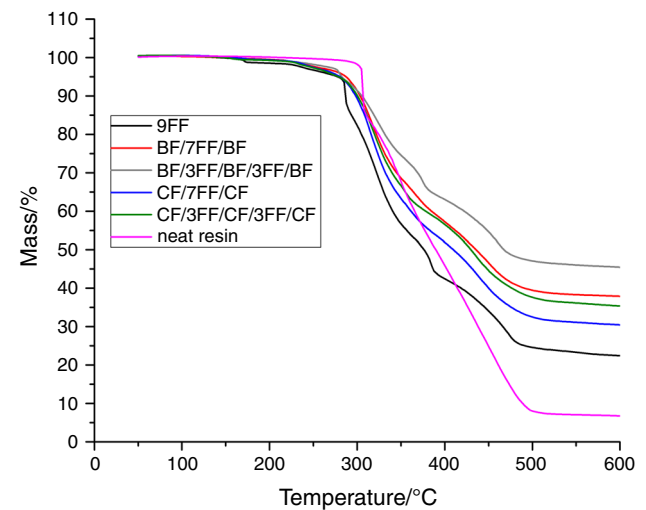
**Table 5** Experimental CTE values, curve peaks and associated temperatures

Composite architectures	CTE/ $10^{-6} \text{ K}^{-1}$	Peak values	
		CTE <sub>max</sub> / $10^{-3} \text{ K}^{-1}$	Temperature/ $^{\circ}\text{C}$
9FF	2.346	0.8904	121.9
BF/7FF/BF	4.794	1.7543	140.3
BF/3FF/BF/3FF/BF	6.245	1.7622	145.2
CF/7FF/CF	1.236	0.6821	120.7
CF/3FF/CF/3FF/CF	3.102	1.1155	144.1

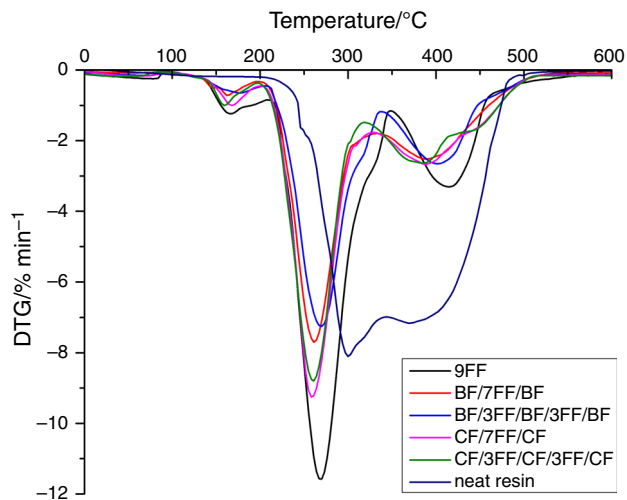
**Fig. 4** Hybrid effects and relative errors on CTE values with herein composites**Fig. 6** Hybrid effects on thermal conductivity and TCEF values comparison with herein composites**Fig. 5** Thermal conductivity variations at different temperature values from LFA measurements

### Thermal decomposition of hybrid composites

In order to provide an extended perspective on other temperature related properties on herein hybrid CF and BF-reinforced composites, a systematical study was carried out by means of thermogravimetric analysis (TGA) under

**Fig. 7** TGA mass loss-temperature profiles of FF and CF/BF-reinforced hybrid composite architectures

controlled nitrogen atmosphere. Mass losses versus temperature together with their derivatives are being delivered in Figs. 7 and 8. Additionally, relative mass losses and residues as well as peak values from both curves were extracted and listed in Table 6 to aid thermal degradation characterization in inert atmosphere (i.e., pyrolysis).



**Fig. 8** DTG profiles of FF and CF/BF-reinforced hybrid composite architectures

As it can be seen, both neat CE&DGE BF resin and either FF or CF/BF hybrid-reinforced composites revealed two peaks in the DTG curves. With a single exception, the unsymmetrical CF stacked layers composite, in all fiber-reinforced specimens, the first DTG peaks can be identified around 320 °C and further attributed to the decomposition of the primary and secondary walls of flax fibers, especially to cellulose microfibrils [11, 42]. With the exception, there was encountered a shift toward 365 °C that can be attributed to the shielding effect caused by the presence of CF fibers. TGA curves are shifted to lowering temperatures showing a decrease in thermal stability of all hybrid composites. This could be the result of degradation of both natural/synthetic fibers and fibers/matrix interfacial bonding. Furthermore, the stacking layer number and reinforcement type seem to influence the magnitude of the decomposition peaks, too. Thus, from the plotting can be identified a decreasing tendency of the first peaks with the

addition of synthetic reinforcements, both CF and BF, with smaller values for the latter architectures.

Moreover, the TG/DTG curves of the novel formula of neat polymer resin reveal a beginning of thermal decomposition near 350 °C that will be present further in the decomposition process of the natural/synthetic-reinforced composites in their second peaks.

The less pronounced deflections within 100 up to 200 °C temperature range encountered in the DTG curves can be regarded to decomposition of hemicelluloses microfibrils from the composition of flax fibers, whereas the lignin component of the flax fibers is decomposing near 400 °C [11]. The latter cannot be separated from decomposition of the polymer resin that further holds within 350 and 450 °C temperature range, revealing a second shoulder around the same temperature point. This temperature range corresponds to a 50% mass loss for all composite excerpts and more pronounced shifts to lowering temperatures in the second peaks recorded with hybrid specimens can be seen comparatively with the pure resin system. These shifts can be regarded to a char layer formation from the CF or BF layers that decompose with temperature increases. This char layer inhibits the heat and mass transfer from the inner layers of flax fibers and/or synthetic fibers and the melting resin toward the surface, thus affecting the thermal stability of correspondingly composites.

Finally, comments on residues may further aid the thermal decomposition processes analysis of herein composite architectures. Correspondingly values listed in Table 6 highlights the amount of char assumed mainly from synthetic fibers that were not decomposed near 850 °C, the temperature end considered for the experimental recordings. Thus, at this temperature value, it seems that BF-reinforced hybrid excerpts are decomposing slower compared with their counterparts, the shielding effect due to the presence of the former synthetic reinforcement being increasingly pronounced.

**Table 6** Thermogravimetric parameters and degradation temperatures at different levels of TG mass loss

Composite architectures	Onset/°C	Temperatures at different mass loss/°C				1st DTG peak/°C	2nd DTG peak/°C	Residue/%
		5%	25%	50%	75%			
9FF	276.2	277.7	314.2	376.3	491.6	323.8	–	19.55
BF/7FF/BF	289.0	–	331.5	435.8	–	318.0	–	35.67
BF/3FF/BF/3FF/BF	281.9	282.2	348.2	467.6	–	324.4	434.9	41.46
CF/7FF/CF	289.3	280.2	323.4	410.0	–	315.7	423.3	29.94
CF/3FF/CF/3FF/CF	333.2	–	350.1	372.6	–	367.6	641.8	30.06
CE&DGE BF resin	378.4	–	398.2	420.8	618.9	347.5	410.0	0.05



## Conclusions

The paper aimed to develop, investigate, and debate the overall temperature related behavior of differently stacked sequences of synthetic- (i.e., CF/BF) and natural- (i.e., FF) fiber-reinforced laminates. The novel thermosetting cyanate ester formula proved to fulfill adhesion criterion and easiness during handling while deployed as the matrix for the laminates, spawning high-quality surface samples. The synergetic effects, due to individual synthetic or natural reinforcements and various stacking sequences, were debated accounting on the effective thermophysical properties (i.e., thermal expansion, thermal conductivity) and thermal decomposition processes.

Thus, from the previous findings, improvements in the coefficients of thermal expansion and thermal conductivity values can be noticed for all hybrid composite architectures herein, irrespective of the constitutive stacking sequence and reinforcement material compared with the reference (9FF). Furthermore, CF-reinforced hybrids revealed poor performances both in thermal expansion and thermal conductivity values in comparison with BF-reinforced hybrids for the same stacking sequence. These effects are not necessarily negative in terms of overall thermophysical properties and should be assigned to the transversal anisotropy particular about the CF reinforcements.

Positive and negative hybrid effects were accounted for while comparing the predicted values with the experimental data. As expected, and consistent with reported values within the literature, the RoM-based predictions reveal the highest values since they represent the upper bounds on the CTE values. On the other hand, RoHM predicted values are closer to the experimental data, and thus a better predictor model for the hybrid composite architectures.

Inverse RoM and RoHM formula were accounted in the effective thermal conductivity predictions proven the experimental setup enabling through thickness measurements. Comparisons revealed the anisotropic behavior particular about the CF reinforcements that are impeding heat dissipation from these panels and thereby their overall performances.

Furthermore, if cost issues become stringent with respect to the individual material selection of the hybrid composite constituents with the aim of similar thermophysical effective properties, decision making can focus on the less-expensive reinforcements herein, namely basalt fibers, which have proven to be highly competitive and less anisotropic along all directions.

The conclusions from this study can be thought to apply to a broad range of lignocellulosic reinforcements (e.g., kenaf, ramie, hemp, coir, jute) by stacking similarly in

combination to carbon or basalt fibers or accounted for other hybrid composite architectures.

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