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Additional Information

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

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Abstract: Thermo-physical properties of hybrid synthetic/natural reinforcements represent a challenging issue for material designers since several factors have to be accounted in terms of stacking sequence, fibre/matrix interface and individual material properties of constitutive. In this study, a novel cyanate ester resin formula was developed and deployed as a matrix for similar architectures of various stacking sequences of carbon (CF) or basalt fibres (BF) in combination with flax fibers (FF). Coefficients of linear thermal expansion (CTE) and thermal conductivities were debated in terms of CF or BF stacking sequences and volume fraction accounting for the reinforcements' anisotropy behavior with selected temperature range. Further comparison aided by rules of hybrid mixtures (RoHM/iRoHM) enabled a perspective on combinations' synergy, highlighting the insulating character of tailored composites.

Thermo-gravimetric analysis (TGA) supplemented the insights into the temperature dependent properties through information on the decomposition temperatures of constitutive and peaks shift compared to the reference (solely FF) in the DTG curves that can be regarded to the shielding effects caused by synthetic reinforcements (CF or BF).

1. 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 (1-3). 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 (4), Manfredi (5), Lazko (6), Bar (7) or Kollia (8) 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 criteria, compatibility, effective properties, manufacturing and processing techniques, economic and environmental impact as well as their ability to meet social and materials need worldwide were kindly provided by several groups of researchers (9-13). 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 (14-18).

The green polymer based composites developed hitherto used natural fibers acquired from cellulose/lignocelluloses sources (e.g. jute, flax, hemp, ramie, sisal, wood, etc.) 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 (19) and Wambua (20) 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, etc.) as polymer matrices for natural reinforcements which all shown good mechanical, thermo-physical or dynamical properties in comparison with their counterparts (21-23). In the paper of Mosiewicki et al. (24) was summarized the main vegetable oils based composite architectures, covering macro, micro- and nano-scale 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. (25) enables the reader to get acquitting 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. 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 (26). The study revealed enhancement on the properties under the focus with filler weight 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. 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 (27). 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. (28, 29). 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

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4 dielectric constant and dissipation factor, radar transparency, flame retardant, etc.) in high-temperature
5 environments. Moreover, used as a matrix material for carbon fibers, reinforced composites satisfy the low-weight
6 structural material requirements in the aerospace industry. In addition, cyanate ester resin is acknowledged for its
7 recyclable potential under chemical attack or for its self-healing capacity while enhanced with epoxy resin filled
8 micro-capsules, allowing the reuse of reinforcements in remanufacturing processes (30, 31). To the author's
9 knowledge, no systematic study has been carried out on the effect of different stacking sequences and the content of
10 natural reinforcements, especially flax fibers, in combination with carbon fibers or basalt fibers, as hybrid
11 architectures. Further, there are no reports available on natural-fiber reinforced cyanate ester based
12 prepregs/laminates.

13 The present paper explores the feasibility of tailoring hybrid architectures based on flax in combination either with
14 carbon or basalt fibers prepregs. The synergetic effect due to hybridization will be emphasized individually on
15 different stacking sequences by deploying a novel resin system made by cyanate ester and epoxy resins followed by
16 a couple of important material properties' investigation. Debate on effective thermo-physical properties (e.g. thermal
17 expansion and thermal conductivity) and thermal decomposition within selected temperature range of herein
18 samples focuses on the perspective of deploying basalt fibers as potential replacements of carbon reinforcements in
19 applications driven by economic issues (32).
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22 **2. Experimental procedure**

23 **2.1. Material selection and resin blend formulation**

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26 Commercial available plain weave 1/1 flax (n. FF), carbon-fiber (n. CF) and basalt fiber (n. BF) fabrics were
27 selected as reinforcements. The novel resin blend was formulated by intimately mixing dicyanate ester pre-polymer
28 (n. CE - 75% vol.) with methyl ethyl ketone (MEK) solution and further stirring with diglycidyl ether of bisphenol F
29 (n. DGEBF) epoxy resin under a 70:30 (vol.%) ratio in the presence of a bisphenol A hardener. Individual
30 reinforcement properties and resin components are summarized in Table 1 and Table 2, respectively.
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32 **2.2. Sample preparation**

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34 The hybrid composite laminates (dimensions: 310 mm x 310 mm) were produced by stacking individually nine
35 either solely FF and/or combined with CF or BF for the hybrid prepreg sheets. The prepregs were manufactured *in*
36 *situ* after having previously an optimized formula of the novel polymer blend. ISO 15034:1999 standardized
37 procedures were used to determine the resin flow while ISO 15040:1999 was used to evaluate the gel time. A
38 temperature-controlled oven was used to compress (i.e. at 50 kN) and fully cure the composite plates at constant
39 temperature of 180 °C, for one hour. The overall fiber loading fluctuated as shown in Table 3 and an average of 5 %
40 of resin flow was measured, after lamination, for all hybrid composite plates. Solely FF and hybrid FF/CF or FF/BF
41 composite laminates, posing high-quality surfaces, were obtained. Sample thickness ranged from 2.5 to 3 mm
42 depending on the stacking sequence.

43 With respect to the stacking sequence, in the case of the hybrid architectures, the higher strength material (i.e. CF,
44 BF) was layered as the outermost, exterior and exterior/middle layers. Flax fibers were layered in between due to
45 their lower material performance. Table 3 lists the stacking layering codes used to further address the hybrid
46 composite architectures, and their individual and total volume fraction within the final laminate.
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48 **2.3. Material characterization**

49 *Dilatometry (DIL) and laser flash analysis (LFA)*

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52 Expansion in composites were monitored by aid of a push rod dilatometer DIL 402 PC (Netzsch GmbH, D), in
53 controlled atmosphere, within 25 °C – 250 °C temperature range and a 4 K min⁻¹ heating rate, in accordance with
54 ASTM E228:2011 standard procedures. Two successive scans were performed to remove thermal history and to
55 retrieve the aimed thermo-physical property - linear coefficient of thermal expansion (CTE). Thermal conductivities
56 of specimens were retrieved by aid of LFA 447 NanoFlash™ device (Netzsch GmbH, D), within 25 °C – 150 °C
57 temperature range according with the ISO 22007-4:2008 standard procedures. Samples were covered back and forth
58 with a thin layer of graphite to enhance their emission/absorption properties. The density at room temperature was
59 obtained by the buoyancy flotation method. Thermal conductivity data corresponds to the mean value of the
60 recorded values out of 5 single shots on each point considered.
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Thermogravimetric analysis (TGA)

Thermogravimetric analysis on specimens was performed by aid of a STA 449 F3 Jupiter® (Netzsch GmbH, D) at a heating rate of 10 K min⁻¹, in N₂ atmosphere at a 20 mL min⁻¹ flow rate, in accordance with ISO 11358-1:2014. Dynamic mode was deployed in the heating step within the selected 25 °C – 850 °C temperature range. Alumina crucible was used for each individual specimen excerpt. The weight loss was recorded in response to temperature increases.

Scanning electron microscopy (SEM)

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

3. 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_i 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. (33). 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 (34, 35). Nonetheless, more appropriate micromechanical approaches may be deployed to account for the reinforcement characteristics (i.e. anisotropy, orientation, waviness, etc.) but are thought to surpass the purpose of herein contribution and debate.

4. Results and discussion

Effect of structure on the effective thermal properties

SEM images from Fig. 1, (a) and (b) were collected for the FF specimens and the highest number of layers of BF reinforcements in the hybrid composite samples to reveal the synergetic effects on their morphology. Images clearly evidence the weak adhesion between the CE&DGEBF resin and BF fibers due to the high sensitivity of CE resin to -OH groups and other volatiles present in the 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 (36). In addition, Fig. 1(b) 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, exception the behavior shown between 100 to 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 that react with the resin as the temperature increase. Novel CE&DGEBF resin has a complicated structure and prone to be highly sensitive to the moisture. Thermal

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4 history cannot be accounted with the responsible mechanisms to the overall expansion behavior since the second
5 runs were reported.

6 The increase in the rigid phase content with the hybrid architectures influences the amplitude of recorded data such
7 there is a direct connection irrespective of the reinforcement deployed, CF or BF. On the other hand, the CF hybrid
8 composites, either symmetrical or unsymmetrical stacked, reveal an opposite behavior to their BF counterparts,
9 especially on the alpha curves variation as the temperature increases. This overall lowering effect can be assigned to
10 the extremely low or negative thermal expansion of CF with temperature increases as widely acknowledged or
11 shown by herein authors into a previous contribution (37). Moreover, the higher the CF content the more
12 pronounced is the decrease on the overall linear coefficient of thermal expansion values, especially within 150 °C to
13 250 °C temperature range.

14 A theoretical predicted vs. experimentally retrieved values' (see values listed in Table 5) comparison, in terms of
15 relative error (see Fig. 4, square symbol), reveal high discrepancies up to 95% in case of 9FF architecture and
16 approximately 60% to 92% for the hybrid combinations, irrespective of the synthetic reinforcement. These values
17 have to be viewed in accordance to their significance as long as the theoretically values belong to the upper limit
18 predicted by micromechanical expressions within literature (34).

19 With respect to the hybrid effects, accounting for the relative differences between the experimentally retrieved
20 values from either CF/FF or BF/FF combinations and 9FF reference specimen (see Fig. 4, triangle symbol), positive
21 departures were recorded in all cases. Thereof, irrespective of the stacking sequence, the presence of synthetic fibers
22 (i.e. CF or BF) within the composite architecture enables a synergetic behavior at the overall assembly level from a
23 thermal expansion perspective.
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25 *Effect of hybridization on the thermal conductivity*

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27 Figure 5 depicts the thermal conductivity curves of the analyzed polymer composite specimens, between 0.116 and
28 0.299 W m⁻¹K⁻¹ within selected temperature range. As it can be seen, thermal conductivity values of the hybrid
29 composites, irrespective of the synthetic reinforcement, are in the same order of magnitude and can be ranked as
30 thermal insulators despite the presence of a thermal conductivity phase. Moreover, a slight difference on thermal
31 conductivity values retrieved from the CF and BF hybrid architectures is present within temperature range.

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

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

46 On the other hand, the relative error values unveil relatively small differences among the predicted and
47 experimentally retrieved values on FF and CF/FF hybrid architectures (between 45% up to 60%) in comparison with
48 the BF reinforced architectures (up to 200%). The latter should be assigned to the individual thermal conductivity
49 values of BF fabrics reported with literature (38).
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51 *Thermal decomposition of hybrid composites*

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53 In order to provide an extended perspective on other temperature related properties on herein hybrid CF and BF
54 reinforced composites, a systematical study was carried out by means of thermogravimetric analysis (TGA) under
55 controlled nitrogen atmosphere. Weight losses vs. temperature together with their derivatives are being delivered in
56 Figs. 7 and 8. Additionally, relative mass losses and residues as well as peak values from both curves were extracted
57 and listed in Table 6 to aid thermal degradation characterization in inert atmosphere (i.e. pyrolysis).

58 As it can be seen, both neat CE&DGEBF resin and either FF or CF/BF hybrid reinforced composites revealed two
59 peaks in the DTG curves. With a single exception, the unsymmetrical CF stacked layers composite, in all fiber
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4 reinforced specimens, the first DTG peaks can be identified around 320 °C and further attributed to the
5 decomposition of the primary and secondary walls of flax fibers, especially to cellulose micro fibrils (10, 39). With
6 the exception, there was encountered a shift toward 365 °C that can be attributed to the shielding effect caused by
7 the presence of CF fibers. TGA curves are shifted to lowering temperatures showing a decrease in thermal stability
8 of all hybrid composites. This could be the result of degradation of both natural/synthetic fibers and fibers/matrix
9 interfacial bonding. Furthermore, the stacking layer number and reinforcement type seems to influence the
10 magnitude of the decomposition peaks, too. Thus, from the plotting can be identified a decreasing tendency of the
11 first peaks with the addition of synthetic reinforcements, both CF and BF, with smaller values for the latter
12 architectures.

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

16 The less pronounced deflections within 100 °C up to 200 °C temperature range encountered in the DTG curves can
17 be regarded to decomposition of hemicelluloses micro fibrils from the composition of flax fibers, whereas the lignin
18 component of the flax fibers is decomposing near 400 °C (10). The latter cannot be separated from decomposition of
19 the polymer resin that further holds within 350 °C and 450 °C temperature range, revealing a second shoulder
20 around the same temperature point. This temperature range corresponds to a 50% weight loss for all composite
21 excerpts and more pronounced shifts to lowering temperatures in the second peaks recorded with hybrid specimens
22 can be seen comparatively with the pure resin system. These shifts can be regarded to a char layer formation from
23 the CF or BF layers that decompose with temperature increases. This char layer inhibits the heat and mass transfer
24 from the inner layers of flax fibers and/or synthetic fibers and the melting resin toward the surface, thus affecting the
25 thermal stability of correspondingly composites.

26 Finally, comments on residues may further aid the thermal decomposition processes analysis of herein composite
27 architectures. Correspondingly values listed in Table 6 highlights the amount of char assumed mainly from synthetic
28 fibers that were not decomposed near 850 °C, the temperature end considered for the experimental recordings. Thus,
29 at this temperature value, it seems that BF reinforced hybrid excerpts are decomposing slower compared with their
30 counterparts, the shielding effect due to the presence of the former synthetic reinforcement being increasingly
31 pronounced.
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34 35 **5. Conclusions**

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

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

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

52 Inverse RoM and RoHM formula were accounted in the effective thermal conductivity predictions proven the
53 experimental setup enabling through thickness measurements. Comparisons revealed the anisotropic behavior
54 particular about the CF reinforcements that are impeding heat dissipation from these panels and thereby their overall
55 performances.
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57 Furthermore, if cost issues become stringent with respect to the individual material selection of the hybrid composite
58 constituents with the aim of similar thermo-physical effective properties, decision making can focus on the less-
59 expensive reinforcements herein, namely basalt fibers, which have proven to be highly competitive and less
60 anisotropic along all directions.
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4 The conclusions from this study can be thought to apply to a broad range of lignocellulosic reinforcements (e.g.
5 kenaf, ramie, hemp, coir, jute, etc.) by stacking similarly in combination to carbon or basalt fibers or accounted for
6 other hybrid composite architectures.
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13 formula and access to the composite manufacturing technology.
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18 **References**

- 19
- 20
- 21 1. Assarar M, Zouari W, Sabhi H, Ayad R, Berthelot J-M. Evaluation of the damping of hybrid carbon–flax
22 reinforced composites. *Composite Structures*. 2015;132:148-54.
23
- 24 2. Duc F, Bourban PE, Plummer CJG, Månson JAE. Damping of thermoset and thermoplastic flax fibre
25 composites. *Composites Part A: Applied Science and Manufacturing*. 2014;64:115-23.
26
- 27 3. Saba N, Jawaid M, Alothman OY, Paridah MT. A review on dynamic mechanical properties of natural fibre
28 reinforced polymer composites. *Construction and Building Materials*. 2016;106:149-59.
29
- 30 4. Alvarez V, Rodriguez E, Vázquez A. Thermal degradation and decomposition of jute/vinylester composites.
31 *Journal of Thermal Analysis and Calorimetry*. 2006;85(2):383-9.
32
- 33 5. Manfredi LB, Rodríguez ES, Wladyka-Przybylak M, Vázquez A. Thermal degradation and fire resistance of
34 unsaturated polyester, modified acrylic resins and their composites with natural fibres. *Polymer Degradation and
35 Stability*. 2006;91(2):255-61.
36
- 37 6. Lazko J, Landercy N, Laoutid F, Dangreau L, Huguet MH, Talon O. Flame retardant treatments of insulating
38 agro-materials from flax short fibres. *Polymer Degradation and Stability*. 2013;98(5):1043-51.
39
- 40 7. Bar M, Alagirusamy R, Das A. Flame retardant polymer composites. *Fibers and Polymers*. 2015;16(4):705-17.
41
- 42 8. Kollia E, Loutas T, Fiamegkou E, Vavouliotis A, Kostopoulos V. Degradation behavior of glass fiber reinforced
43 cyanate ester composites under hydrothermal ageing. *Polymer Degradation and Stability*. 2015;121:200-7.
44
- 45 9. Jawaid M, Abdul Khalil HPS. Cellulosic/synthetic fibre reinforced polymer hybrid composites: A review.
46 *Carbohydrate Polymers*. 2011;86(1):1-18.
47
- 48 10. Azwa ZN, Yousif BF, Manalo AC, Karunasena W. A review on the degradability of polymeric composites based
49 on natural fibres. *Materials & Design*. 2013;47:424-42.
50
- 51 11. Cheung H-y, Ho M-p, Lau K-t, Cardona F, Hui D. Natural fibre-reinforced composites for bioengineering and
52 environmental engineering applications. *Composites Part B: Engineering*. 2009;40(7):655-63.
53
- 54 12. Dittenber DB, GangaRao HVS. Critical review of recent publications on use of natural composites in
55 infrastructure. *Composites Part A: Applied Science and Manufacturing*. 2012;43(8):1419-29.
56
- 57 13. Faruk O, Bledzki AK, Fink H-P, Sain M. Biocomposites reinforced with natural fibers: 2000–2010. *Progress in
58 Polymer Science*. 2012;37(11):1552-96.
59
60
61
62
63
64
65

14. Praveen RS, Jacob S, Murthy CRL, Balachandran P, Rao YVKS. Hybridization of carbon–glass epoxy composites: An approach to achieve low coefficient of thermal expansion at cryogenic temperatures. *Cryogenics*. 2011;51(2):95-104.
15. Jawaid M, Abdul Khalil HPS, Alattas OS. Woven hybrid biocomposites: Dynamic mechanical and thermal properties. *Composites Part A: Applied Science and Manufacturing*. 2012;43(2):288-93.
16. Swolfs Y, Gorbatikh L, Verpoest I. Fibre hybridisation in polymer composites: A review. *Composites Part A: Applied Science and Manufacturing*. 2014;67:181-200.
17. Rojo E, Alonso MV, Oliet M, Del Saz-Orozco B, Rodriguez F. Effect of fiber loading on the properties of treated cellulose fiber-reinforced phenolic composites. *Composites Part B: Engineering*. 2015;68:185-92.
18. LeGault M. Natural fiber composites: market share, one part at the time *Composites World*. 2016:68-75.
19. Joshi SV, Drzal LT, Mohanty AK, Arora S. Are natural fiber composites environmentally superior to glass fiber reinforced composites? *Composites Part A: Applied Science and Manufacturing*. 2004;35(3):371-6.
20. Wambua P, Ivens J, Verpoest I. Natural fibres: can they replace glass in fibre reinforced plastics? *Composites Science and Technology*. 2003;63(9):1259-64.
21. Bertomeu D, García-Sanoguera D, Fenollar O, Boronat T, Balart R. Use of eco-friendly epoxy resins from renewable resources as potential substitutes of petrochemical epoxy resins for ambient cured composites with flax reinforcements. *Polymer Composites*. 2012;33(5):683-92.
22. Alam M, Akram D, Sharmin E, Zafar F, Ahmad S. Vegetable oil based eco-friendly coating materials: A review article. *Arabian Journal of Chemistry*. 2014;7(4):469-79.
23. Bakare FO, Ramamoorthy SK, Åkesson D, Skrifvars M. Thermomechanical properties of bio-based composites made from a lactic acid thermoset resin and flax and flax/basalt fibre reinforcements. *Composites Part A: Applied Science and Manufacturing*. 2016;83:176-84.
24. Mosiewicki MA, Aranguren MI. A short review on novel biocomposites based on plant oil precursors. *European Polymer Journal*. 2013;49(6):1243-56.
25. Lligadas G, Ronda JC, Galià M, Cádiz V. Renewable polymeric materials from vegetable oils: a perspective. *Materials Today*. 2013;16(9):337-43.
26. Fombuena V, L S-N, MD S, D J, R B. Study of the Properties of Thermoset Materials Derived from Epoxidized Soybean Oil and Protein Fillers. *Journal of the American Oil Chemists' Society*. 2013;90(3):449-57.
27. Pil L, Bensadoun F, Pariset J, Verpoest I. Why are designers fascinated by flax and hemp fibre composites? *Composites Part A: Applied Science and Manufacturing*. 2016;83:193-205.
28. Wooster TJ, Abrol S, Hey JM, MacFarlane DR. Thermal, mechanical, and conductivity properties of cyanate ester composites. *Composites Part A: Applied Science and Manufacturing*. 2004;35(1):75-82.
29. Mallarino S, Chailan JF, Vernet JL. Glass fibre sizing effect on dynamic mechanical properties of cyanate ester composites I. Single frequency investigations. *European Polymer Journal*. 2005;41(8):1804-11.
30. Sothje D, Dreyer C, Bauer M, editors. Advanced possibilities in thermoset recycling. The 3rd International Conference on Thermosets; 2013; Berlin, Germany, .
31. Yuan L, Huang S, Gu A, Liang G, Chen F, Hu Y, et al. A cyanate ester/microcapsule system with low cure temperature and self-healing capacity. *Composites Science and Technology*. 2013;87(0):111-7.

- 1
2
3
4 32. Czigány T. Special manufacturing and characteristics of basalt fiber reinforced hybrid polypropylene
5 composites: Mechanical properties and acoustic emission study. *Composites Science and Technology*.
6 2006;66(16):3210-20.
7
8 33. Marom G, Fischer S, Tuler FR, Wagner HD. Hybrid effects in composites: conditions for positive or negative
9 effects versus rule-of-mixtures behaviour. *J Mater Sci*. 1978;13(7):1419-26.
10
11 34. Torquato S. *Random heterogeneous materials : microstructure and macroscopic properties*. New York, NY
12 Springer; 2002.
13
14 35. Cherki A-b, Remy B, Khabbazi A, Jannot Y, Baillis D. Experimental thermal properties characterization of
15 insulating cork–gypsum composite. *Construction and Building Materials*. 2014;54:202-9.
16
17 36. Bismarck A, Aranberri-Askargorta I, Springer J, Lampke T, Wielage B, Stamboulis A, et al. Surface
18 characterization of flax, hemp and cellulose fibers; Surface properties and the water uptake behavior. *Polymer*
19 *Composites*. 2002;23(5):872-94.
20
21 37. Motoc Luca D, Ferrandiz Bou S, Balart Gimeno R. Effects of fibre orientation and content on the mechanical,
22 dynamic mechanical and thermal expansion properties of multi-layered glass/carbon fibre-reinforced polymer
23 composites. *Journal of Composite Materials*. 2014.
24
25 38. CES EduPack. Granta Design; 2013.
26
27 39. Monteiro SN, Calado V, Rodriguez RJS, Margem FM. Thermogravimetric behavior of natural fibers reinforced
28 polymer composites—An overview. *Materials Science and Engineering: A*. 2012;557:17-28.
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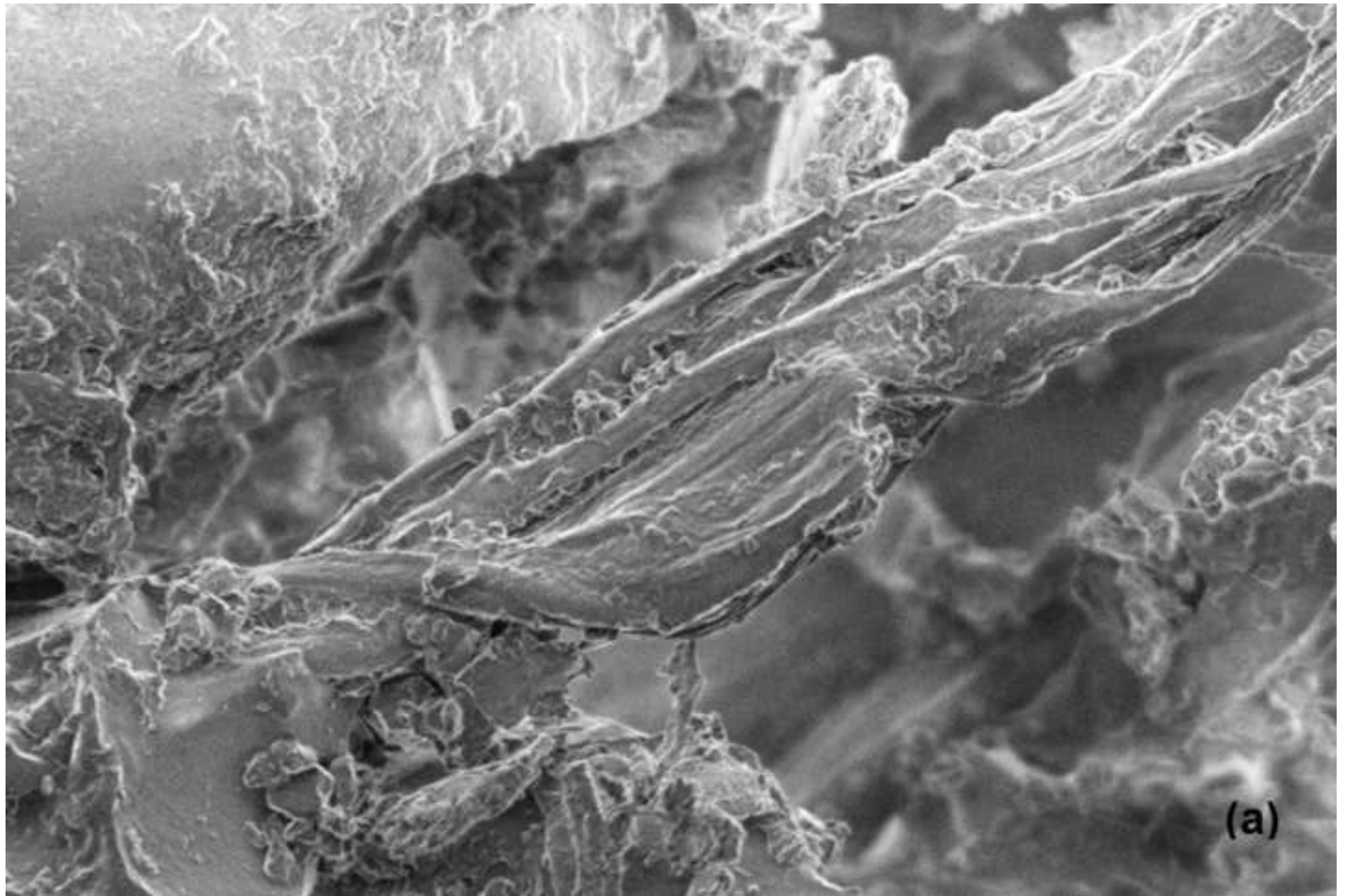
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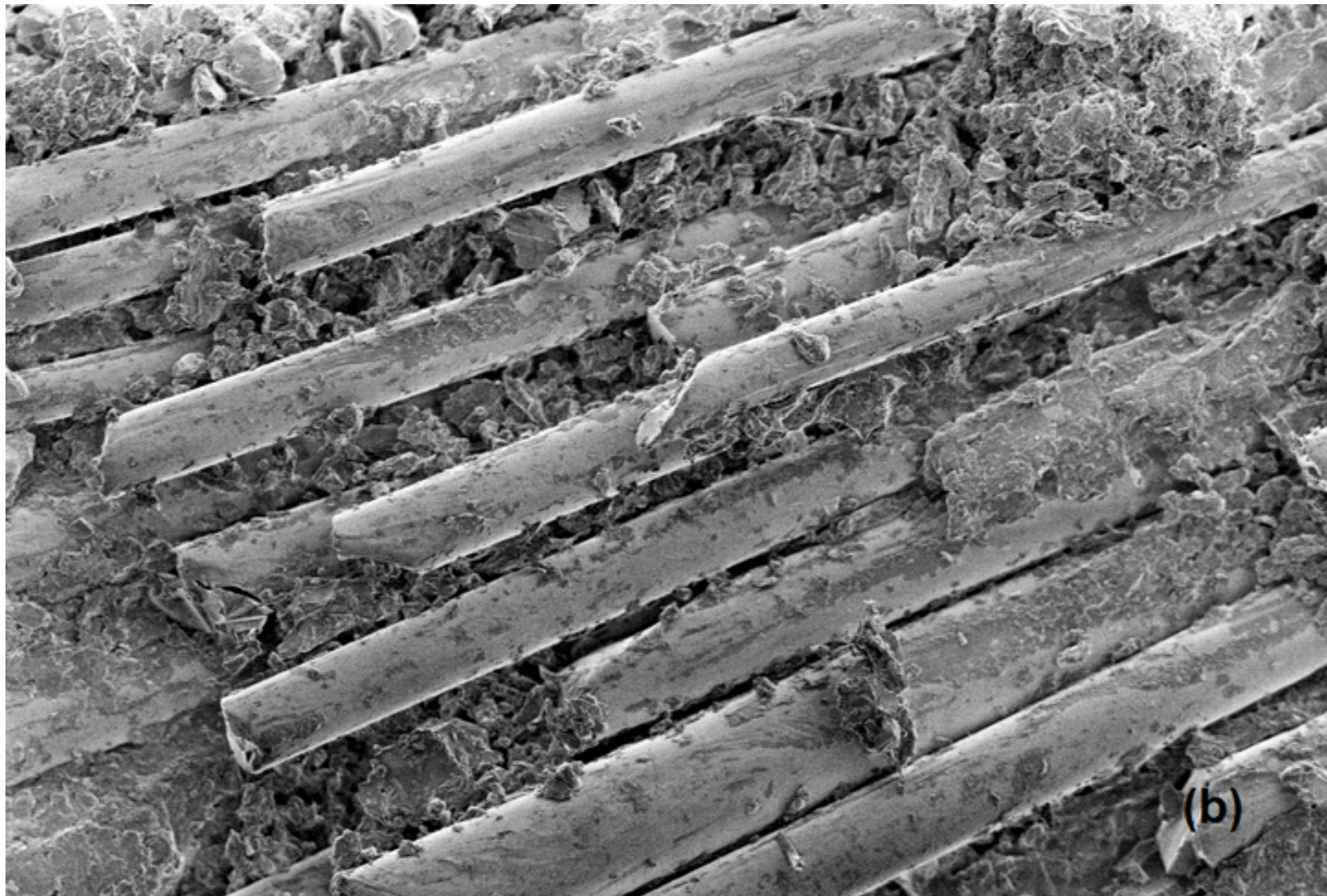
Figures

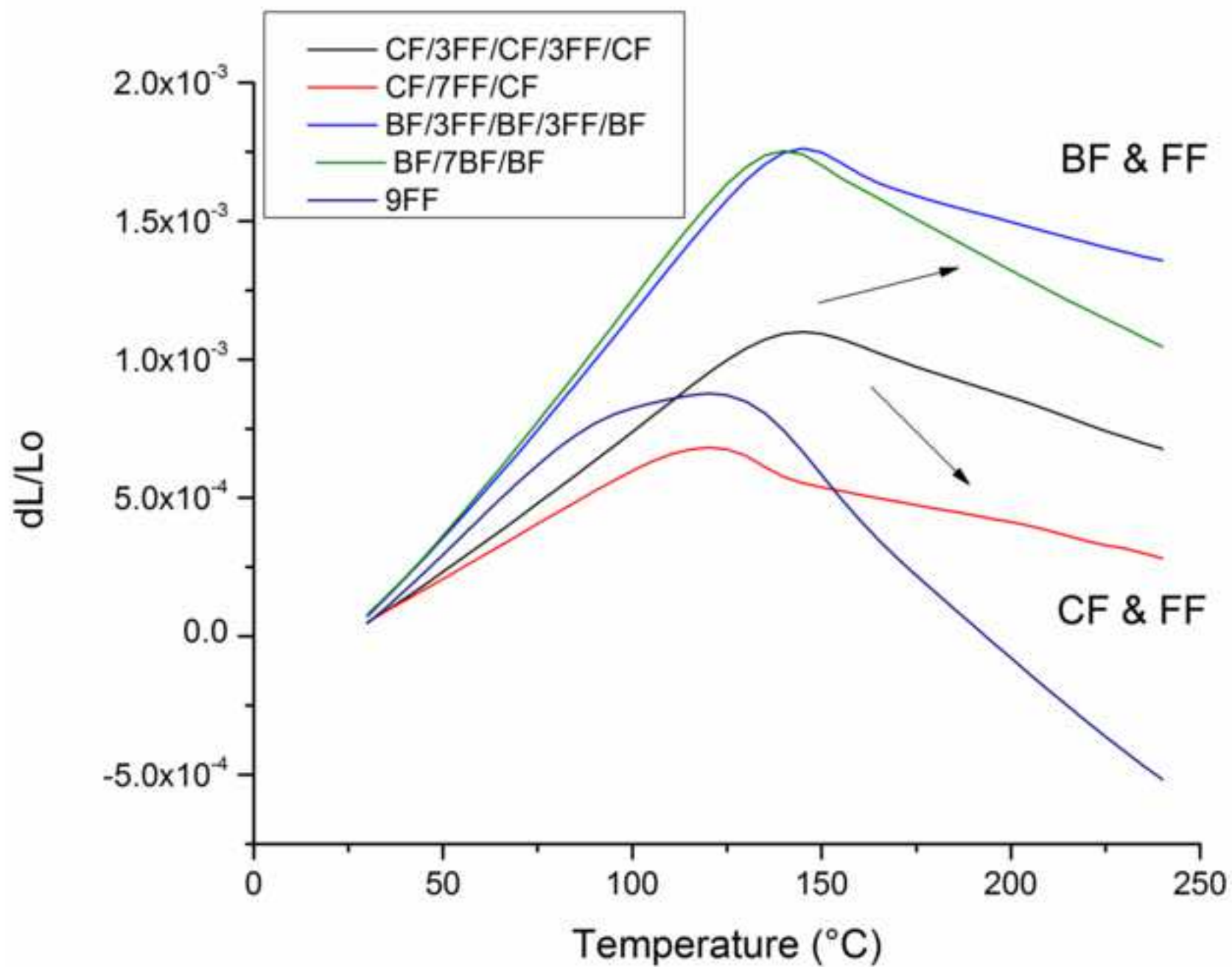
- Fig. 1** - SEM images of the side views for (a) 9FF and (b) BF/3FF/BF/3FF/BF composites
- Fig. 2** – Thermal strain within various stacking sequences of CF and BF reinforced composites
- Fig. 3** – Technical alpha at different temperatures from DIL measurements
- Fig. 4** – Hybrid effects and relative errors on CTE values with herein composites
- Fig. 5** – Thermal conductivity variations at different temperature values from LFA measurements
- Fig. 6** – Hybrid effects on thermal conductivity and TCEF values comparison with herein composites
- Fig. 7** – TGA mass loss-temperature profiles of FF and CF/BF reinforced hybrid composite architectures
- Fig. 8** – DTG profiles of FF and CF/BF reinforced hybrid composite architectures

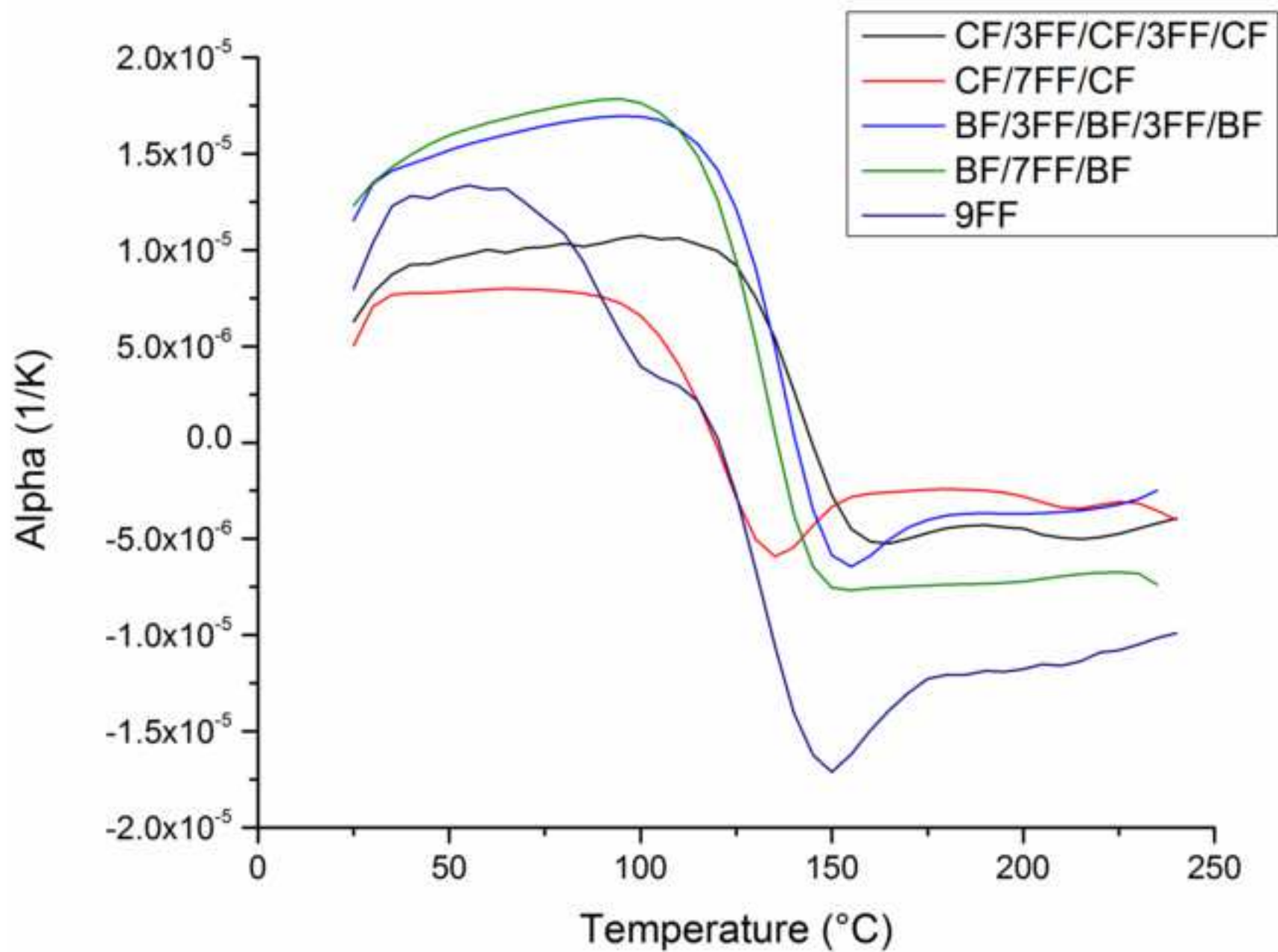
Tables

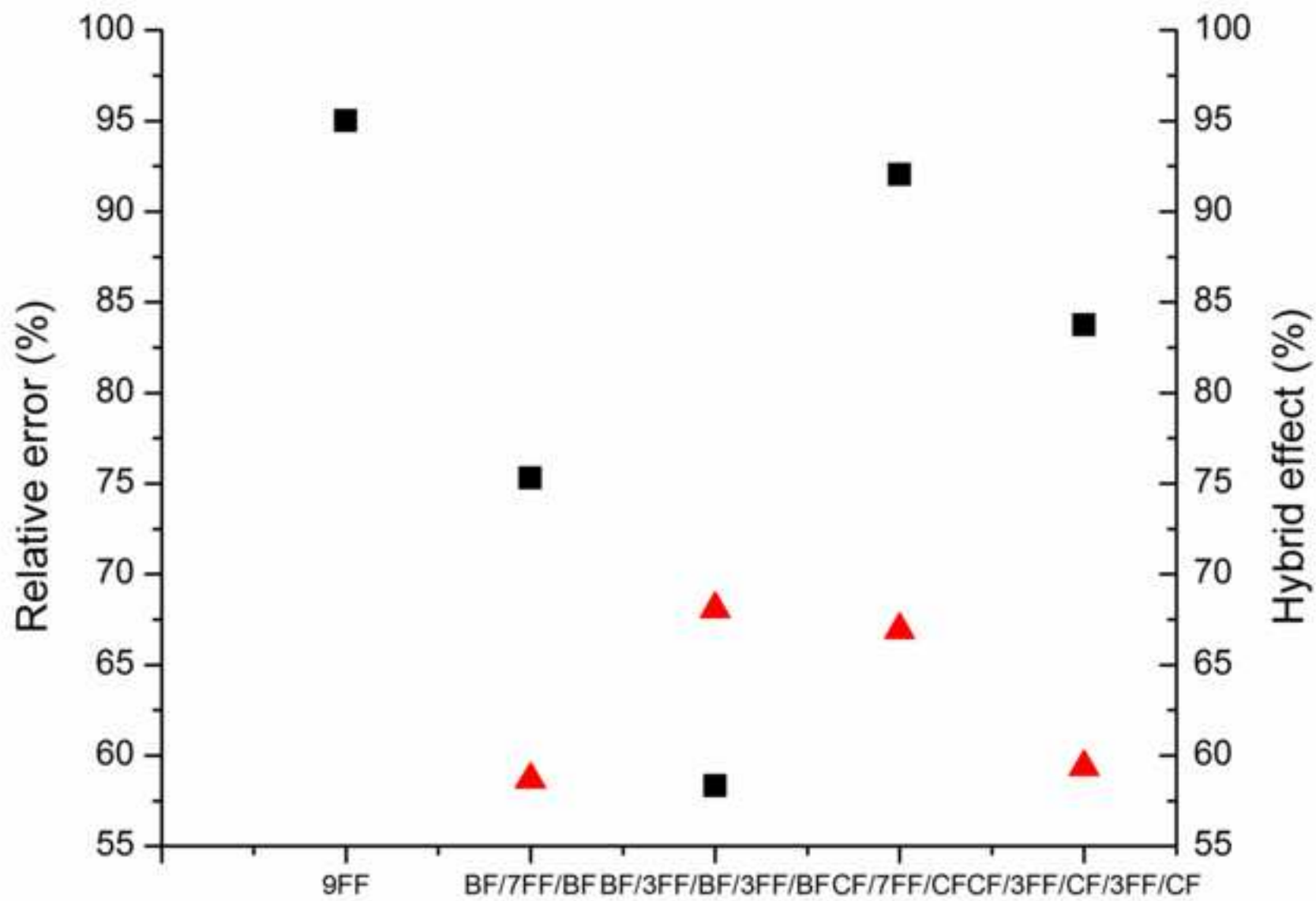
- Table 1** – Material data of the present reinforcements
- Table 2** – Individual physical properties of polymer system
- Table 3** - Details on hybrid composites stacking sequences, assigned codes and volume fractions
- Table 4** - RoM and RoHM expressions of thermo-physical properties
- Table 5** – Experimental CTE values, curve peaks and associated temperatures
- Table 6** – Thermogravimetric parameters and degradation temperatures at different levels of TG weight loss

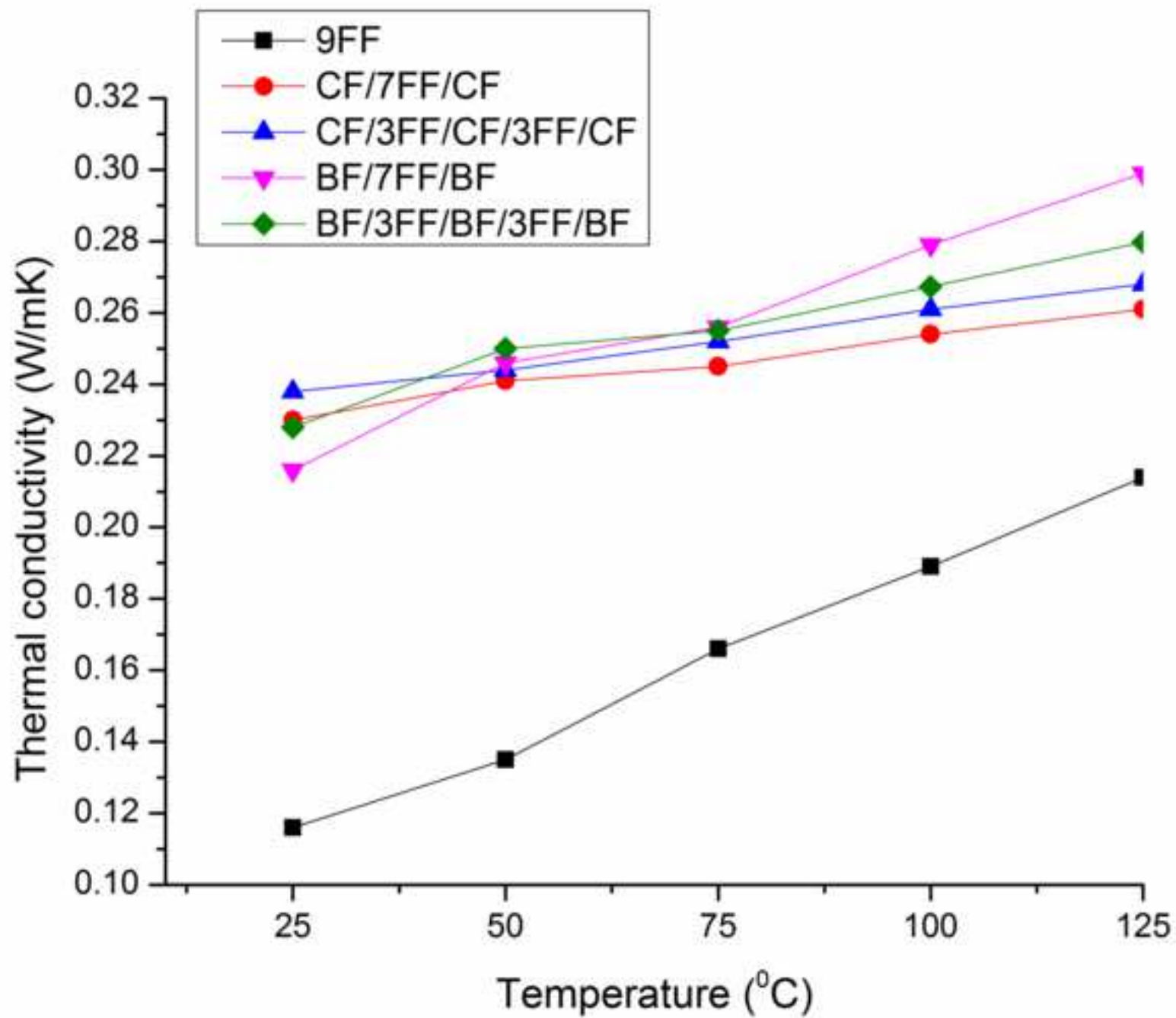


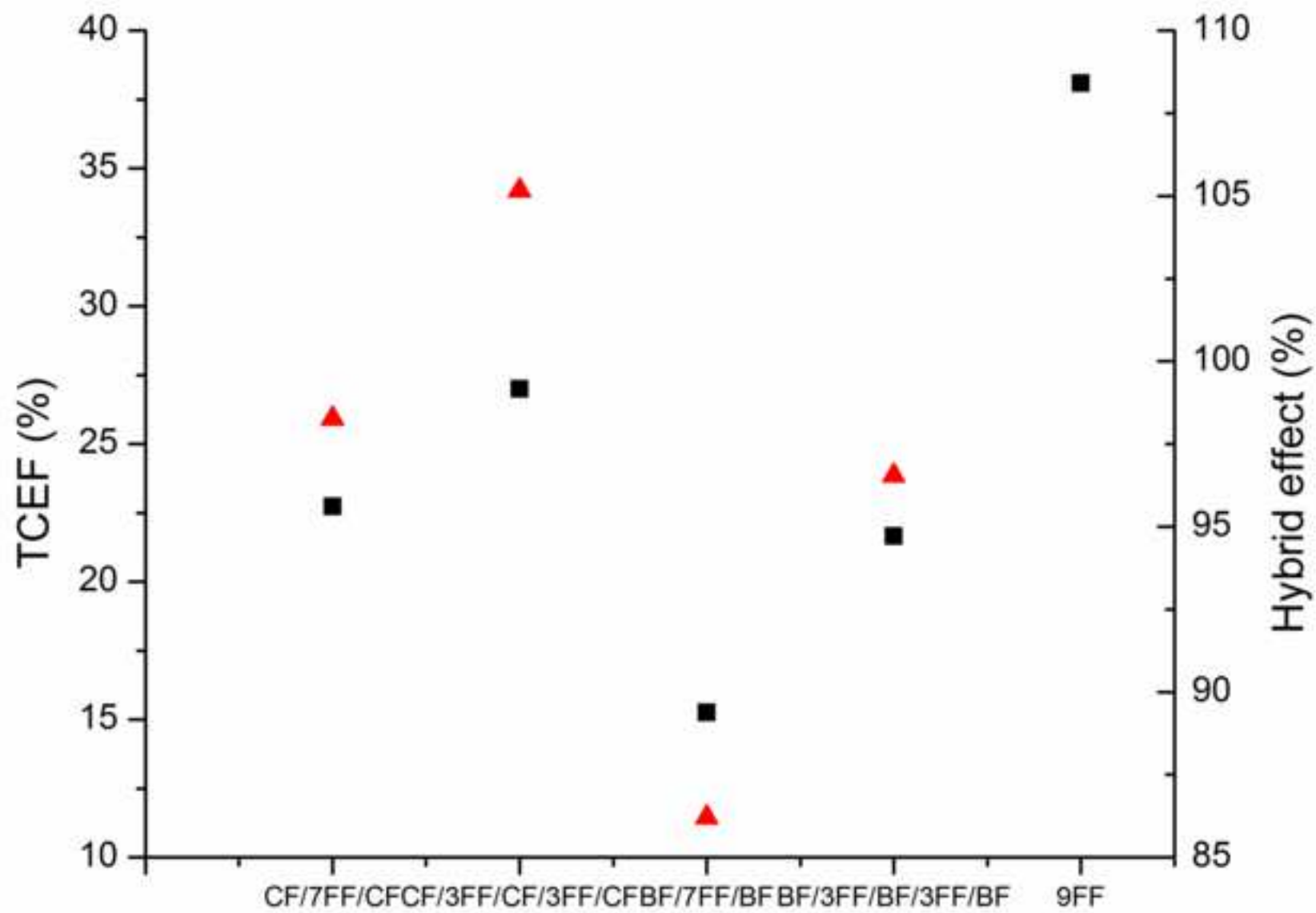


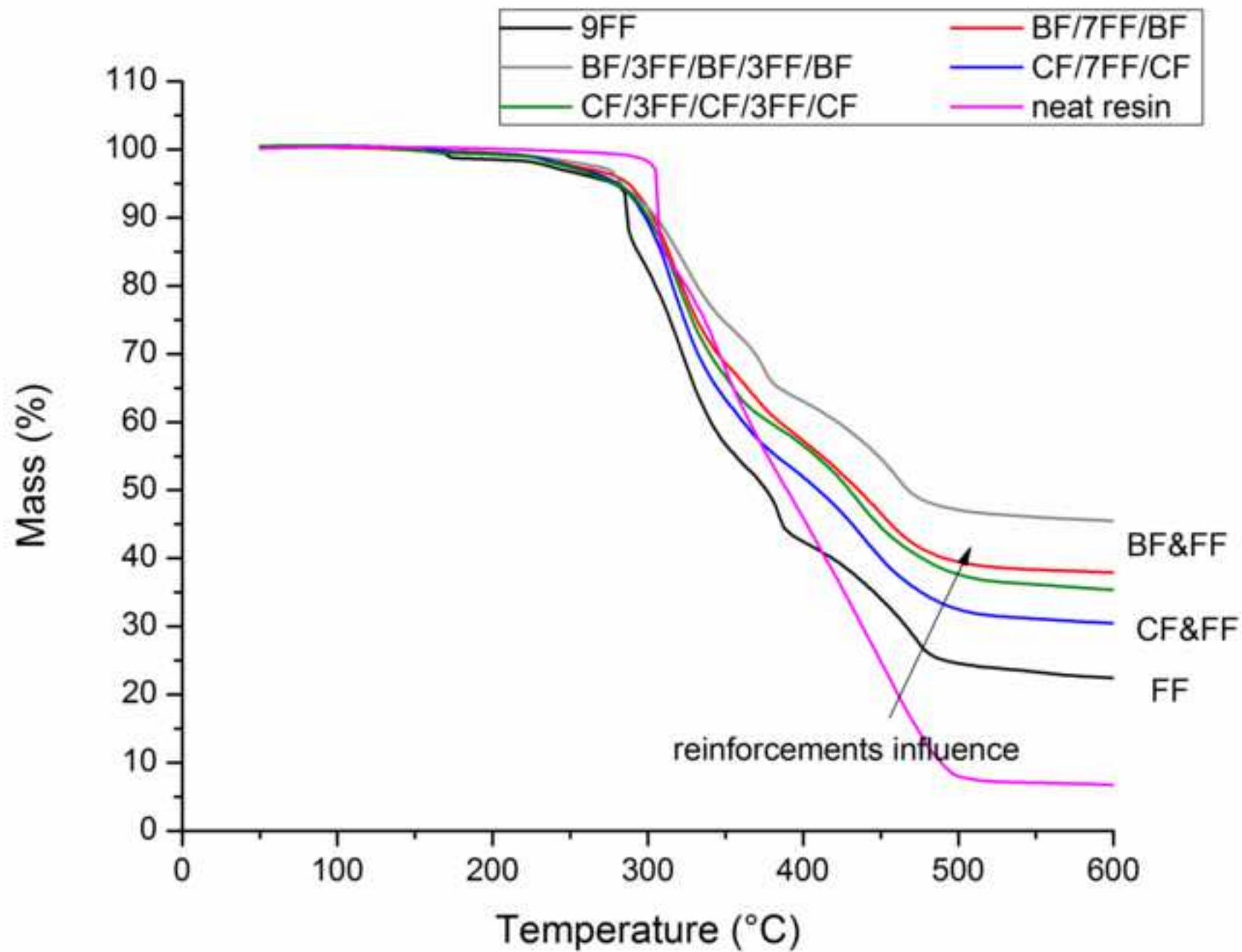


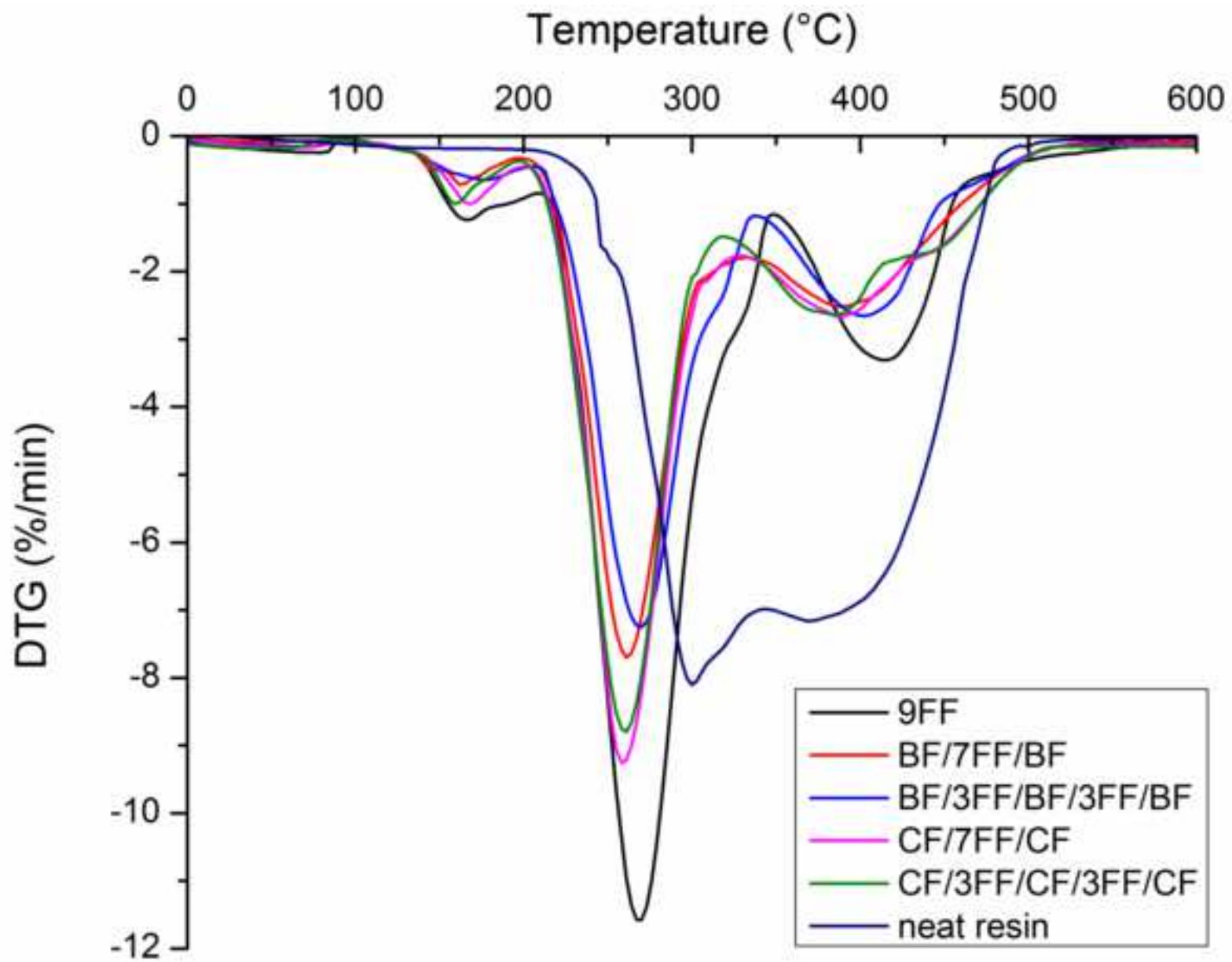












Table_1

	Carbon fiber (n. CF) (KDK 8003)	Basalt fiber (n. BF)	Flax fiber (n. FF)
Fabric areal weight (g/m ²)	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®	-	-
Supplier	SGL Technologies GmbH	DBF Deutsche Basalt Faser GmbH	Leinenweberei Hoffmann GmbH
Thermal expansion (μstrain/°C)*	0.2	3.5	30
Thermal conductivity (W/m°C)*	80	0.038	0.3

*CES EduPack 2016 (Granta Design Limited)

Table_2

	Cyanate ester resin (Primaset™ BA 230 S)	DGEBF 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 ³)		1.18 ± 0.02
Curing agent	bisphenol A (BA)	
Supplier	Lonza Ltd	Momentive

Table_3

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).

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	$\frac{1}{k_{nfc}} = \frac{V_{nf}}{k_{nf}} + \frac{(1 - V_{nf})}{k_m}$	$\frac{1}{k_{sfc}} = \frac{V_{sf}}{k_{sf}} + \frac{(1 - V_{sf})}{k_m}$	$\frac{1}{k_c} = \frac{V_{cnf}}{k_{nfc}} + \frac{V_{scf}}{k_{sfc}} *$

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

Table_5

Composite architectures	CTE ($\times 10^{-6}$ K)	Peak values	
		CTE _{max} ($\times 10^{-3}$ K)	Temperature ($^{\circ}$ 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

Table_6

Composite architectures	Onset (°C)	Temperatures at different weight loss (°C)				1 st DTG peak (°C)	2 nd 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&DGEBF resin	378.4	-	398.2	420.8	618.9	347.5	410.0	0.05