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Coefficient of thermal expansion evolution for cryogenic preconditioned hybrid carbon fiber/glass fiber-reinforced polymeric composite materials

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Abstract Polymeric matrix composites are susceptible to degradation and material properties changes if subjected to low-temperature environmental conditions. This paper attempts to present a study on effective coefficient of thermal expansion for various hybrid carbon fibers/glass fibers polymeric composite structures previously subjected to low-temperature environmental conditioning. The hybrid composite architectures were made from various layers of glass mat and/or glass woven embedded along with layers of unidirectional carbon fibers into a polymeric matrix. The samples were preconditioned to a low-temperature environment at a constant temperature of −35 °C for 1-week long, 24 h/day. The instantaneous CTE and thermal strain fields were recorded with a DIL 402 PC/1 dilatometer from Netzsch GmbH (Germany) by setting a monotonically linear rise of temperature from 20 to 250 °C, at a rate of 1 °C min^{-1}. The experimentally retrieved data were compared with the values obtained by running a micromechanical-based approach simulation on a representative volume element.

Keywords Hybrid · Carbon/glass · Composites · Low temperature · Thermal expansion

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List of symbols

Variables

E Elastic (Young's) modulus
ν Poisson ratio
V Volume fraction

Subscripts

c Composite
m Matrix phase
f Fiber

Superscripts

L Longitudinal direction
T Transversal direction

Introduction

Development of new materials in general, and composites in particular, has been always a challenging self-standing research area which addresses several issues that have to be interconnected, interlaced, tailored, optimized, and balanced to provide "a brand new type" that has to be superior or outstanding in terms of properties, characteristics, or behavior.

Many engineering applications from aerospace (e.g., rocket nozzles and fuel tanks), civil engineering (e.g., liquid tanks), electrical (e.g., electrical contacts, electrical shields, and electronic packaging), and automotive (e.g., drive shafts, cylinders, and brake rotors) to manufacturing (e.g., bearings and pistons) industry demand new materials for their structural components to withstand various environmental conditions and/or sudden changes of their loading fields, enlargement of their lifetime and reduced associated costs.

The aforementioned can be met if several requirements are going to be fulfilled starting from the design stage, one of these aiming the control of thermal expansion characteristics to match with those of the other components, the values needed to be as low as possible to assure a good dimensional stability.

The literature is abundant in references approaching the issue of thermal expansion of two phase composite materials, the earliest studies concerning the behavior of metal or ceramic matrix composites reinforced with particles or short fibers, having various distributions of the constitutive, with or without interphase region, subjected to thermal cycling [1–3]. Recently, focused interest was shown to the polymer matrix-reinforced composite materials based on the development of new polymers as well as on woven-reinforced architectures that are still challenging to characterize due to their fiber distribution [4].

Apart from the aforementioned approaches, tailoring concerns and optimization methods were employed to fulfill the dimensional stability issue, many papers being written with respect to the management of thermally induced stresses and thermal distortion. Within these frames, the use of materials exhibiting negative expansion (NTE) behavior proved to be the right choice and one route that were explored during all attempts aiming the understanding of overall material behavior under thermal loading [5–9]. Carbon fibers or silica particles seems to be the favorites among the materials exhibiting a natural NTE behavior and were used in composite structures for tuning their effective coefficient of thermal expansion (CTE) and thus reducing thermally induced stress.

This paper considers the use of unidirectional carbon fibers as the main ingredient in the tailoring process of the overall thermal expansion for several architectures of polymeric composite materials along with the most popular and less costly reinforcement material—E-glass fibers, giving rise to a new class of composites namely multiphase or hybrid ones.

To promote a deeper understanding on the phases' individual material properties and microstructure geometry influences on the overall thermal response of the composite structures several theoretical micromechanics models were derived based on mechanics of materials or energy principles assumptions.

Among these methods are the well known Mori–Tanaka and double inclusion micromechanical procedures [10]. The former is based on the approximate solution provided by Eshelby, whereby each inclusion from the representative volume element (RVE) is behaving as if it was isolated into the real matrix. The assumptions have been made considering the body infinite and subjected to the average matrix strains in the RVE, as the remote strain. The Mori–Tanaka theoretical model, used successfully for predicting the effective properties of composite materials having their inclusion phases <25 % even, proved that it works very well for higher values [11].

Alternatively, the double inclusion method proposed by Nemat-Nasser and Hori [12] relays on the following principle: each inclusion having a specific stiffness is surrounded with the real matrix of stiffness, and the outside area is fulfilled by a reference medium with its own stiffness. For linear elastic two-phase composites, the double inclusion model gives a good prediction of the effective material properties no matter the size, volume fraction and individual constitutive material properties of inclusion phase.

Supplementary, other microscale-related theoretical models were emerged and successfully used for the prediction of the effective CTE of either particle or fiber-reinforced composites, more or less popular, in form of upper or lower bounds, for longitudinal or transversal directions accordingly to each case, definitely all using the same dependence on the constitutive volume fraction [13–17].

The use of novel materials in engineering applications often involve monitoring of their structural behavior under various environmental conditions, ranging from extreme low to extreme high temperature, from moisture to hygrothermal, or any other settings resembling their real working conditions. The literature provides references on this issue, especially with respect to the moisture diffusion in several architectures of two-phase polymeric composite materials, the high-temperature conditioning in case of metal matrix composites, the hygrothermal aging of fiber-reinforced polymer composites to quantify the matrix degradation and/or the overall material properties but limited work are provided with respect to the low-temperatures conditioning of the composite materials [18–22]. All the papers were concluding that the temperature and the extreme environmental conditions affect the physical behavior of the composites directly by modifying their structural characteristics.

In a previous study of these hybrid composite samples, the effective CTE was retrieved considering the same thermal loading without preconditioning them to any type of environmental changes; theoretical models used relaying on the homogenization scheme proposed by Mori–Tanaka [23].

In this paper, further experimental work was carried out to assess the changes in the effective CTE material property due to the exposure of these hybrid composites to low-temperature environmental conditions as part of a more comprehensive endeavor to fully characterize and tailor the material properties of these novel hybrid composite architectures. With respect to the theoretical predictions, other micromechanics approaches were exploited and used to assess the overall CTE of the hybrid composite architectures considered herein, based on a multi-step homogenization procedure.

Table 1 Hybrid composites samples' layer architecture

Samples	Layer sequence	No. of layers
1	1GF/1GF/1GF/1GF/1GF	5
2	1GF/1GF/1CF/1GF/1GF	5
3	1GF/1CF/1GF/1CF/1GF	5
4	1GF/1GF/1GF/1CF/1GF/1GF/1GF	7
5	1GF/1GF/1WR/1GF/1CF/1GF/1WR/1GF/ 1GF	9

Experimental research

Material description

The hybrid polymeric composite samples have been manufactured as a layered structure using three distinct phases—chopped strand mat (n. GF; MultiStrat™ Mat ES 33-0-25 from Johns Manville, USA), woven roving (n. WR) E-glass fibers, and unidirectional (n. CF; Panex® 35 from Zoltek Co., USA) carbon fibers—embedded into a polymeric matrix under different layers architecture. The matrix material is commercially known as SYNOLITE 8388 P2 from DSM Composite Resins (Switzerland), a polyester resin type. The manufacturing technology used was a vacuum-assisted resin transfer molding process.

In Table 1 are being given the layer sequences and the layer numbers for the hybrid composite structures under the study.

Testing procedure

Low-temperature samples preconditioning

The samples were conditioned within a temperature-controlled climatic chamber from FEUTRON (Germany) by subjecting them to a low-temperature environment of −35 °C, 7 days long, 24 h/day, and relative humidity of 45 %. The relative humidity and temperature within the conditioning inside were maintained constantly during the scheduled time range.

CTE measurements

The effective CTE measurements were performed using a DIL 420 PC/1 differential dilatometer from NETZSCH GmbH (Germany). The composite samples were shaped into rectangular bars of 25 mm in length and 5-mm wide, the transversal external surfaces being polished to guarantee plan-parallel surfaces for precise positioning within the measuring head. For systems' error elimination, the dilatometer has been calibrated by measuring a standard SiO_2 specimen under the same conditions.

Each sample was subjected to two successive heating stages to size one of the influencing factors on the samples' CTE variation and to get a general overview on the composite phases' behavior with temperature variation. This can be viewed in Fig. 1 while the discussion in the subsequent chapter.

The temperature variation was set up having a linear trend from 20 to 250 °C, at a relatively low heating rate of 1 °C min^{-1}, into a static air atmosphere, giving rise to a time consuming experimental set up. The change in the specimen length based on temperature raise, $\Delta L/\Delta T$, was the measured value, allowing thus the overall instantaneous CTE retrieval as a ratio to the initial sample length L.

Micromechanical-based theoretical approach

The mean field homogenization schemes have been already implemented in specialized modeling computer software, the micromechanical concepts being developed around a RVE containing single or multiple inclusions. Defining a proper RVE depends on several factors that influence the effective material property under the study, including the fillers' orientation, shape factor, volume fraction, etc.

Figure 2 shows a RVE corresponding to an interface of fiber–fiber-reinforced hybrid polymeric composite sample

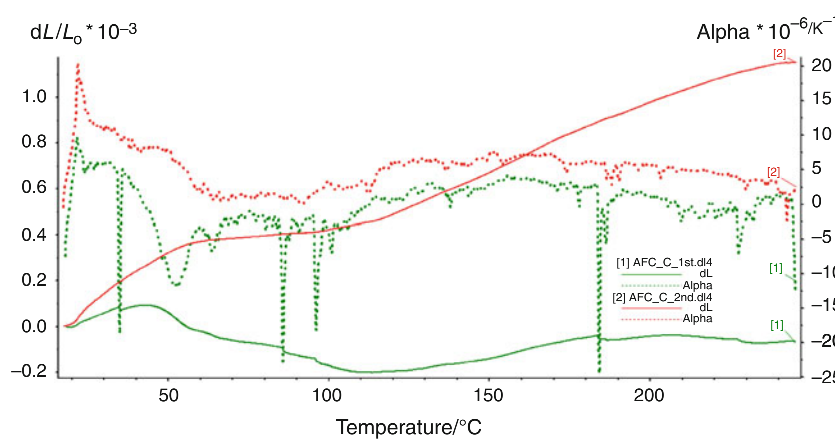

Fig. 1 Thermal strain and instantaneous CTE for sample 1 hybrid architecture preconditioned at low-temperature environment and subjected to two successive heating cycles

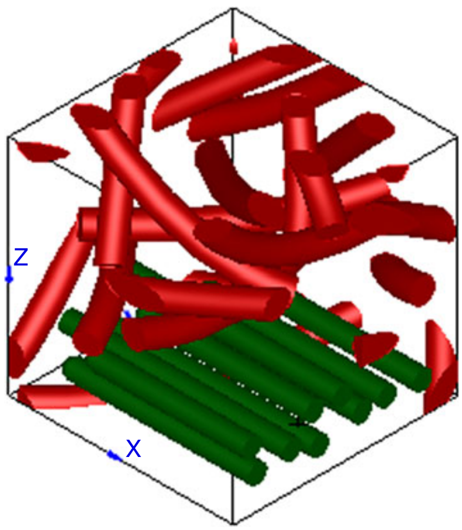

Fig. 2 RVE associated to the fiber–fiber interface of the hybrid composite architecture of samples

Table 2 Material properties of the matrix and the phases used in the numerical prediction [13, 23]

Material	Density/ kg m^{-3}	Elasticity modulus/GPa		Linear CTE/ $\times 10^{-6}$ °C^{-1}		Poisson ratio	
Matrix	1,140	4		50		0.36	
Carbon	1,800	Axial	303	Axial	0	Axial	0.2
		In-plane	15.2	In-plane	83	In-plane	0.2
Glass	2,600	0.74		5		0.25	

(e.g., E-glass fibers and carbon fibers). The RVE has been generated using the computer software called DIGIMAT (from X-stream Engineering Inc., Luxembourg), and the predicted effective CTE values have been retrieved based on the *Mori–Tanaka* scheme in two homogenization steps. The data used in the numerical predictions are provided in Table 2.

For this hybrid configuration, the computer-generated RVE was possible only if penetration between phases were allowed. This does not have to be seen as a drawback and often happens during the composites manufacturing stage. The RVE associated to the woven roving-random, long glass fibers failed to be generated using this computer software and could not be taken into account for the effective property of sample 5.

The simulations were carried out using the thermo-mechanical loading module where a negligible amount of uniaxial strain was imposed, the temperature field considered as having a monotonically rise from 20 to 250 °C. The predicted data using this model will be shown in comparison to the experimental data in the following chapter.

In addition, a multi-step homogenization scheme based on several theoretical micromechanical-based models from the literature was employed to aid the analysis. The multi-step scheme was developed using the same expressions in all the homogenization steps for each individual case considered, for the combination herein being needed only two steps to fulfill the requirement of overall CTE prediction. The theoretical models were developed solely for the fiber-reinforced composite materials, either their random or unidirectional distribution, being provided in Table 3.

With respect to the previous, the first homogenization step was carried out by considering the polymer matrix and carbon fibers as phases for giving rise to the so-called *equivalent matrix* that will take the roll of the matrix in the next homogenization step along with the second phase of random glass fibers.

Owing to the different expansion behavior of the carbon fibers, the overall CTE of composites reinforced with such fiber types has to be considered as a contribution in the longitudinal, transversal, and normal directions. The later usually provide small values ($\cong 10^{-15}$) that are negligible in terms of effects on the overall composite material expansion, the other previous remaining under discussion. With respect to the expansion coefficients in the longitudinal and transversal directions, the later hold the highest percentage in the overall CTE of the composite structure for filler volume fraction <50 % and approximately equally for values >60 %, as revealed by the predicted values.

As it can be seen in the mathematical formulation of the micromechanical models, Eqs. (1–5), the composite's CTE in longitudinal direction hold for all the theoretical models approaches while the one in the transversal direction take different formulation in terms of individual material properties and volume fraction of the constitutive. These micromechanical models are not the most popular ones but proved to be more appropriate and comprehensive to be

Table 3 Theoretical micromechanics-based models for the overall CTE predictions [13]

Theoretical model	Mathematical expression
Schapery	$\alpha_c^L = \frac{\alpha_f^L E_m V_f + \alpha_m E_m (1 - V_f)}{E_f V_f + E_m (1 - V_f)}$ (1)
	$\alpha_c^T = (1 + \nu_f)\alpha_f^L V_f + (1 + \nu_m)\alpha_m (1 - V_f) - \alpha_c^L \nu_c$ (2)
Hopkins–Chamis	$\alpha_c^T = \frac{E_m}{E_c^T}\left[(1 - V_f)\alpha_m + \frac{\alpha_m \sqrt{V_f} - V_f\left(\alpha_m - \alpha_f^T\right)}{1 - \sqrt{V_f}\left(1 - \frac{E_m}{E_f}\right)}\right]$ (3)
	where $E_c^T = (1 - V_f) + \frac{\sqrt{V_f}}{1 - \sqrt{V_f}\left(1 - \frac{E_m}{E_f}\right)}$ (4)
Geier	$\alpha_c^T = \alpha_f^T V_f + (1 - V_f) \left[\alpha_m + \left(\alpha_m - \alpha_f^L\right) \frac{\nu_m + \nu_f \frac{E_m}{E_f^T}}{V_f + (1 - V_f)\frac{E_m}{E_f^L}} V_f\right]$ (5)

used in the characterization of the overall expansion behavior of the fiber-reinforced composites.

The variation with the constitutive volume fraction of the CTE predicted values in longitudinal and transversal directions using the aforementioned theoretical models is shown in Fig. 3. As it is generally acknowledged in the literature for two-phase composites, the CTE predicted values decrease with increase of the constitutive volume fraction. This affirmation holds in case of this multi-step procedure.

In addition, the effective CTE values predicted based on the *Mori–Tanaka* homogenization scheme for all the hybrid composite samples under the study are represented in Fig. 4. As it can be seen, the more E-glass fiber layers, either random or woven distributed, the higher the CTE predicted values comparatively with the hybrid composite structures encompassing one or more carbon fiber layers.

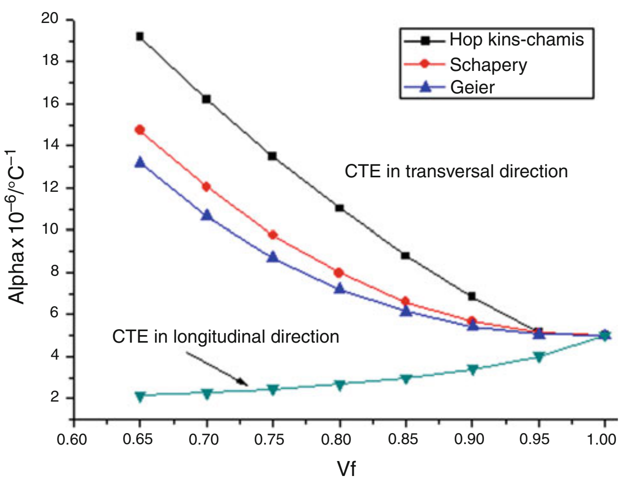

Fig. 3 Comparative effective CTE values predicted for all the hybrid composite samples using the Mori–Tanaka scheme

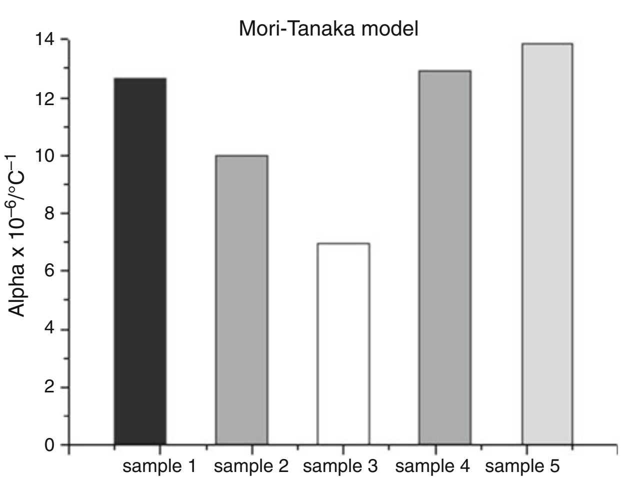

Fig. 4 Effective CTE values variation with constitutive volume fraction predicted based on a multi-step procedure using the Hopkins–Chamis, Schapery and Geier homogenization models

Results and discussion

The experimental research conducted on hybrid polymer composite materials manufactured by embedding negative coefficient of dilatation materials like carbon fibers were revealing different behavior associated not only to the type and characteristics particular to the fillers and/or polymeric matrix but to their structural interdependencies and architecture.

The experiments were conducted by applying successive thermal conditioning cycles upon to the low-temperature preconditioned hybrid composite samples developed in this study. From all the experimental data the ones retrieved from the second thermal conditioning has to be hold as being relevant to this assessment because the first thermal conditioning regime can be considered as a thermal treatment applied upon the samples with the purpose of finishing the matrix's polymerization process. In addition, as it can be seen from Fig. 5a, b, the low-temperature preconditioning regime induces the occurrence of more peaks in the instantaneous overall CTE field over the temperature range, having a highly departure from the linear variation up to temperatures corresponding to the glass transition temperature of the polymer matrix (around 95 °C). These can be associated to the micro-cracks induced during the low-temperature environmental conditioning and polymer thermal conditioning during the temperature rise. Matrix degradation proceeds gradually in the first thermal cycling and then more rapidly in the second thermal cycle.

Figure 6 shows the strain fields experimentally recorded for all the hybrid architectures under this study in the second thermal cycle. The variations reveal the influence of adding negative CTE carbon fibers as well as the different layers architecture. Increasing the number of glass fibers layers, either in their random or woven distribution, the closer the strain variation fields and more clustered (see the plotted data of the samples 1 and 3–5). On the other side, keeping the same number of layer (e.g., 5) but starting to replace one of them with a layer exhibiting a negative coefficient of expansion (see architecture of sample 2), the effective CTE as well as the associated thermal strain field lowers abruptly over the temperature range.

The mean values of the effective CTE based on statistical manipulation of the experimental recorded data for all the thermal cycles applied upon the hybrid composites analyzed, with or without preconditioning to a low-temperature environment are plotted in Fig. 7. As it can be seen, the previous remarks hold and are more clearly seen in the plotting; the lower effective mean CTE being retrieved for the sample 3 architecture that was manufactured as having 2 layers of carbon fibers out of the overall hybrid architecture made from 5 layers.

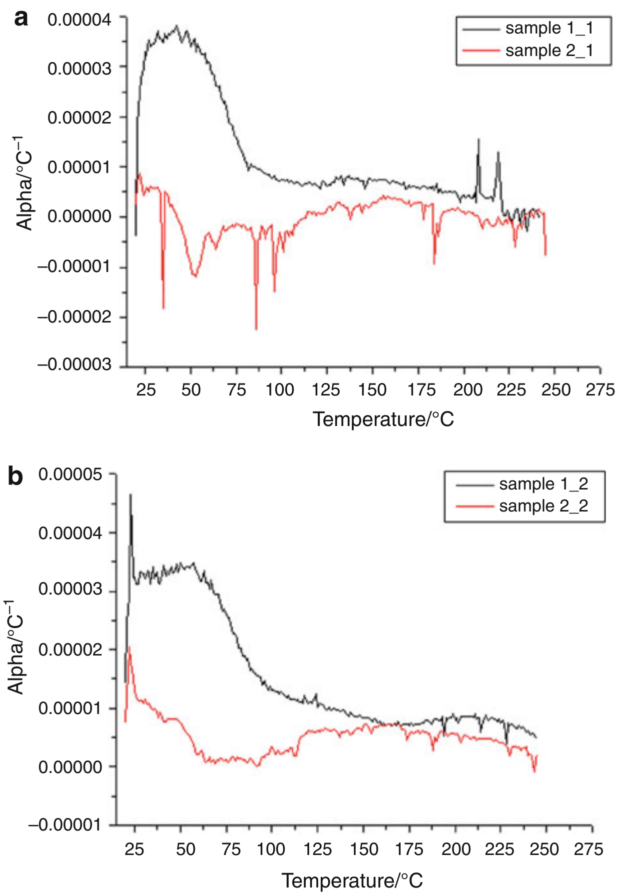

Fig. 5 **a** Comparative instantaneous overall CTE temperature variations experimentally recorded during the 1st heating cycle applied upon to samples 1 and 2. **b** Comparative instantaneous overall CTE temperature variations experimentally recorded during the 2nd heating cycle applied upon to samples 1 and 2

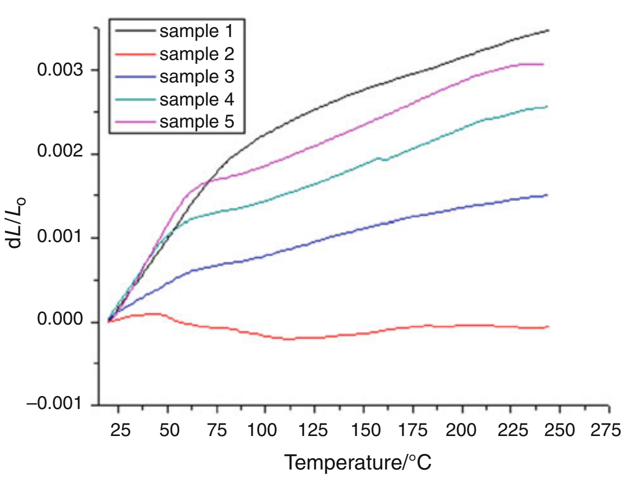

Fig. 6 Comparative thermal strain fields over the temperature range recorded in the 2nd thermal cycling for all the composite samples

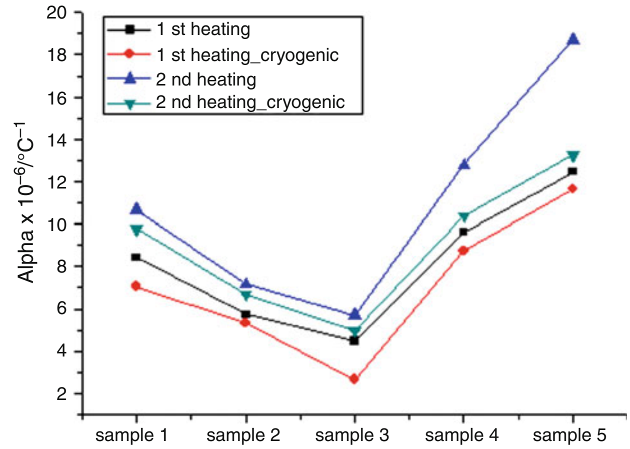

Fig. 7 Mean effective CTE experimentally retrieved values for the hybrid composite samples associated to each applied thermal cycle, with and without low-temperature preconditioning

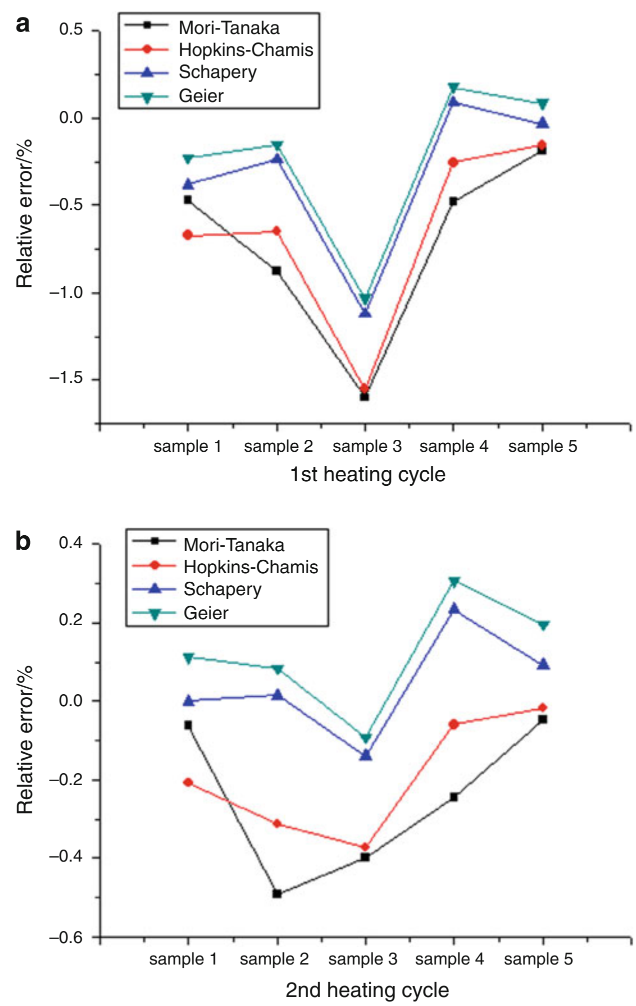

Fig. 8 **a** Relative errors (%) between the samples' effective CTE retrieved in the 1st heating cycle and theoretically predicted values. **b** Relative errors (%) between the samples' effective CTE retrieved in the 2nd heating cycle and theoretically predicted values

With respect to the relative error, defined as the ratio between the measured and predicted effective CTE values over the measured value of the effective CTE in %, estimated individually for each composite sample, the highest differences hold for the values retrieved by applying the so-called polymerization, ending thermal cycle, whereas the second thermal regime provides closer values to the theoretically predicted data. Thus, it can be seen in Fig. 8a, b for all the theoretical models considered herein.

Nonetheless, these discrepancies can be further associated to the RVE used in the predictions, ideal material properties and behavior used in the numerical simulations, to the lack of influence due to the preconditioning at a low-temperature regime, and to the real interface imperfections and polymer kinematics that were not encompassed in the modeling.

Conclusions

Heterogeneous structural architectures and low-temperatures preconditioning of this hybrid polymer-based composite materials are the major influencing internal/external related factors on the variation of their effective CTE and its departure from the invariant occurrence. Adding phases exhibiting a negative CTE such are the carbon fibers one can tailor the overall composite thermal property and design material suited to a particular engineering application and working environments, including low-temperature conditions. As has been shown, the higher the volume fraction of the later, the higher the probability of retrieving a near zero effective coefficient of dilatation for the overall composite structure.

The polymer matrix contributes significantly to dimensional stability of the heterogeneous structures in terms of the changes induced in the internal stress and strain fields by temperature rising and cycling, as well as low-temperature environmental conditionings.

Further works aims experimental related developments by conditioning these hybrid polymer-based composites to other types of environmental changes (e.g., temperate or high extreme climates) according to their further application areas, to further characterize by monitoring their hygroscopic behavior or weathering under imposed temperature regimes. Nonetheless, residual thermal stress and thermal conductivity assessment are the other major concerns in this endeavor of hybrid polymer composite structures development and characterization.

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