

Thermal stress development in fibrous composites

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Received 11 January 2007; accepted 11 May 2007

Available online 18 May 2007

Abstract

In this work, the thermal stress development in anisotropic fiber-reinforced polymer composites is investigated for temperatures below the glass transition temperature of the resin. By applying two independent experimental methodologies, it was found that the initial thermal (residual) strain in the reinforcing fibers is compressive of about -0.04% at ambient temperatures. This is due to the mismatch of the thermal expansion coefficient between the polymer matrix and fiber, as the material is cooled down from the processing temperature. However, on reheating the composites the compressive stress in the fiber gradually diminishes and becomes zero at $50\text{ }^{\circ}\text{C}$. Further heating to $100\text{ }^{\circ}\text{C}$ introduces tensile strains in the fiber of maximum of 0.13% . The conformity of these results to analytical models that relate the composite thermal strain to the thermal expansion coefficients of fiber and resin, as well as, the fiber volume fraction, is examined. Finally, the possibility of tailoring the sign (positive, negative or, even, zero) of the composite thermal expansion coefficient of certain advanced composites by simply varying the thermal expansion of the polymer matrix, is discussed.

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Keywords: Composite materials; Mechanical properties; Raman spectroscopy; Thermal stresses; Thermal expansion coefficient

1. Introduction

It is now well established that poly (*p*-phenylene terephthalamide) (PPTA) fibers, hereafter referred as aramid, exhibit excellent tensile strength and modulus, but relatively poor axial compressive and flexural strength [1,2]. These disparities can be attributed to the highly anisotropic structure of the fibers that results from nearly perfect orientation of the rigid and extended PPTA chains along the fiber axis. The anisotropy of these fibers is also manifested by a small and negative longitudinal thermal expansion coefficient (CTE) as compared to a relatively large and positive value of CTE in the radial direction [1,3,4] (Table 1). Although the radial CTE of aramid fibers is similar to the CTE of most composite matrix materials [1,4,5], the negative value of CTE in the axial direction causes the fibers to be placed under

axial compression when a composite is cooled from the processing temperature down to room temperature.

Those thermal (residual) stresses/strains are important parameters as they determine the initiation of matrix cracking in fiber-reinforced polymer composites [6,7]. Furthermore, the interface efficiency of fiber polymer composites may also be affected by the presence of residual stresses/strains [6,8]. However, for the present aramid/epoxy composite, the radial thermal expansion coefficient of the fiber is similar to that of the resin so the radial shrinkage stress should be minimal. In our recent work [7], it was found that on the completion of the curing process (0.0% external strain), the epoxy matrix of 4- and 2-ply unidirectional Kevlar[®] 29/epoxy composites was under a residual tensile stress in the axial direction of 45.5 MPa [7,8]. The corresponding residual stress in the fiber was found to be compressive and of magnitude of -40 MPa [8]. Such high internal stresses can affect the integrity of the composite under the application of an external load and are responsible for matrix microcracking and interface failure at high applied strains [6,7,9].

A lot of experimental [6,9,10] and modeling [11–14] work has been carried out over the years to determine the optimal

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temperature profiles during manufacture that are required to minimize the thermal stresses/strains in high volume fraction fiber-reinforced composites. In spite of the significance of the thermal stress/strain development in anisotropic fibrous composites the work reported in this area is rather limited [12–14]. This is mainly attributed to the lack of available experimental techniques for measuring the stress/strain at the fiber level.

In this work, we have employed Raman microscopy as a tool for stress/strain measurement at the microscale. Earlier work has shown that the Raman phonons 1611 cm^{-1} and 1648 cm^{-1} – hereafter referred to as phonon ν_1 and ν_2 , respectively – of aramid fibers (Kevlar® 29) shift linearly to lower values under tension and to higher values under compression, whereas the shift of the ν_1 phonon is twice as large as that of the ν_2 phonon [15–18]. Thus, stress or strain calibration curves (phonon shift vs. axial stress or strain) can be constructed, leading to a potential use of the aramid fibers as stress and/or strain sensors in composite materials [7,19–21]. The dependence of the Raman wave-numbers on temperature for the 1611 and 1648 cm^{-1} bands of the Kevlar® 29 fibers has been firstly determined by Psarras et al. [21] for zero strain/stress and more recently by Bollas et al. [22], for a whole range of applied axial strains. Anagnostopoulos et al. [23,24] have developed a methodology for measuring the fiber stress and strain in a Kevlar® 29/epoxy resin LTM217 composite under an applied tensile load at different elevated temperatures. The effect of temperature upon the stress transfer efficiency or, in other words, the strength of the fiber/matrix interface at a given temperature has also been identified [23].

In all previous work [23,24] the fiber stress under a combined thermal and mechanical field was examined. In this letter, we make an attempt to assess the development of thermal stresses/strains in the fibers under no external mechanical load. Raman microscopy and electrical resistance strain gages are employed for measuring the strain in the fibers and resin, respectively. The results are compared with calculations based on the relative thermal expansion coefficients of fiber and polymer resin and useful conclusions are drawn about the usefulness of existing predictive models.

2. Experimental

In general, for fibrous composites the recorded total Raman wave-number shift $\Delta\nu_{\text{tot}}$ can be interpreted as the sum of three terms [21,22]:

$$\Delta\nu_{\text{tot}} = \Delta\nu_{\text{M}} + \Delta\nu_{\text{T}} + \Delta\nu_{\text{R}} \quad (1)$$

where $\Delta\nu_{\text{M}}$ is the Raman wave-number shift due to external applied mechanical stress, σ ($\Delta\nu_{\text{M}} = k \cdot \sigma$, where k is the stress/strain sensitivity coefficient of each phonon (ν_1 and ν_2)) [21,22], $\Delta\nu_{\text{T}}$ is the corresponding Raman wave-number shift due to temperature for the free Kevlar® 29 fibers ($\Delta\nu_{\text{T}} = k_{\text{T}} \cdot \Delta T$, where k_{T} is the sensitivity to temperature of each phonon (ν_1 and ν_2), and $\Delta T = T - T_0$ is the difference between the applied and the ambient temperatures ($25\text{ }^\circ\text{C}$)). $\Delta\nu_{\text{R}}$ is a constant term and reflects the mismatch of the thermal expansion coefficient between the fiber and the matrix [1,3,4,17,25] (Table 1) that

Table 1

The coefficient of thermal expansion of the LTM217 epoxy resin and Kevlar® 29 aramid fiber, respectively [1–3,21]

CTE epoxy resin LTM217 ($10^{-6}/^\circ\text{C}$)	CTE aramid fiber Kevlar® 29 ($10^{-6}/^\circ\text{C}$)	
	Axial	Transverse
87.3	– 3.76	66

The value for the resin was determined experimentally in this work by means of thermo-mechanical analysis.

brings about the development of internal–residual-stresses as the composite is cooled from the curing temperature down to ambient temperature. In the absence of an external mechanical field, Eq. (1) becomes:

$$\Delta\nu_{\text{tot}} = \Delta\nu_{\text{M}} + \Delta\nu_{\text{T}} + \Delta\nu_{\text{R}} \Rightarrow \Delta\nu_{\text{tot}} = \Delta\nu_{\text{T}} + \Delta\nu_{\text{R}} \quad (2)$$

From previous works, when aramid/epoxy resin composite materials are examined under elevated temperature ($T > 25\text{ }^\circ\text{C}$), the axial stress, σ , on the aramid fibers is evaluated via ν_2 phonon (1648 cm^{-1}), since its peak position is practically temperature insensitive, $\Delta\nu_{\text{T}} \approx 0$ [19]. Thus, the corresponding wave-number component of thermal field at high temperature, $\Delta\nu_{2,\text{R}}|_{T>25\text{ }^\circ\text{C}}$, can be estimated by:

$$\begin{aligned} (2) \Rightarrow \Delta\nu_{2,\text{tot}} &= 0 + \Delta\nu_{2,\text{R}} \Rightarrow \Delta\nu_{2,\text{tot}} \\ &= (\Delta\nu_{2,\text{R}}|_{T>25\text{ }^\circ\text{C}} + \Delta\nu_{2,\text{R}}|_{T=25\text{ }^\circ\text{C}}) \Rightarrow \Delta\nu_{2,\text{R}}|_{T>25\text{ }^\circ\text{C}} \\ &= \Delta\nu_{2,\text{tot}} - \Delta\nu_{2,\text{R}}|_{T=25\text{ }^\circ\text{C}} \end{aligned} \quad (3)$$

For the case of $25\text{ }^\circ\text{C}$, the recorded total wave-number shift of ν_2 phonon is equal with the corresponding shift due to thermal field, $\Delta\nu_{2,\text{R}}|_{T=25\text{ }^\circ\text{C}}$ [21,22]. As a result, we can extract the values of thermal stress/strain at high temperatures ($60, 80, 100\text{ }^\circ\text{C}$), using the appropriate stress/strain sensitivity coefficients of ν_2 phonon [22].

$$\varepsilon_{\text{thermal}} = \frac{\Delta\nu_{2,\text{R}}|_{T>25\text{ }^\circ\text{C}}}{k_{2,\varepsilon}} \quad (4)$$

and

$$\sigma_{\text{thermal}} = \frac{\Delta\nu_{2,\text{R}}|_{T>25\text{ }^\circ\text{C}}}{k_{2,\sigma}} \quad (5)$$

where $\varepsilon_{\text{thermal}}$, σ_{thermal} is the thermal strain and stress at higher temperatures, respectively and $k_{2,\varepsilon}$, $k_{2,\sigma}$ are the corresponding strain and stress sensitivity factors of ν_2 phonon at $T > 25\text{ }^\circ\text{C}$ [22].

As explained recently [23,24], when the stress measurements are conducted via the ν_2 phonon, which is practically insensitive to thermal effects, the obtained experimental data are highly scattered, especially at low applied strain levels ($\varepsilon_{\text{applied}} < 0.5\%$) and elevated temperatures ($T > 100\text{ }^\circ\text{C}$). As postulated elsewhere [22], the ν_2 phonon can be employed with a confidence of 90%, as a stress sensor only at moderately elevated temperatures for stress gradients of more than 100 MPa. In order to avoid these problems, we apply the same methodology to ν_1 phonon, which has been found to exhibit much greater

stress and strain sensitivity than its adjacent ν_2 phonon [22]. However, since the ν_1 phonon is both stress and temperature, the latter must be known in order to determine the stress distribution [22]. By assuming that the temperature on the composite is the same with the applied one, we can estimate the corresponding Raman wave-number shift due to temperature for ν_1 phonon, $\Delta\nu_{1,T}$ according to the following equation:

$$\Delta\nu_{1,T} = k_T^1 \cdot \Delta T \quad (6)$$

where k_T^1 is the temperature sensitivity of phonon ν_1 ($k_T^1 = -0.014 \text{ cm}^{-1}/^\circ\text{C}$) and $\Delta T = T - T_0$ is the difference between the elevated and the ambient temperature [21,22].

Therefore, we can estimate the corresponding wave-number component of thermal field at high temperatures, $\Delta\nu_{1,R}|_{T>25^\circ\text{C}}$.

$$\begin{aligned} (2) \Rightarrow \Delta\nu_{1,\text{tot}} &= \Delta\nu_{1,T} + \Delta\nu_{1,R} \Rightarrow \Delta\nu_{2,\text{tot}} = \Delta\nu_{1,T} \\ &+ (\Delta\nu_{2,R}|_{T>25^\circ\text{C}} + \Delta\nu_{2,R}|_{T=25^\circ\text{C}}) \Rightarrow \Delta\nu_{1,R}|_{T>25^\circ\text{C}} \\ &= \Delta\nu_{1,\text{tot}} - \Delta\nu_{1,T} - \Delta\nu_{1,R}|_{T=25^\circ\text{C}} \end{aligned} \quad (7)$$

In the case of 25°C , the recorded total wave-number shift of ν_1 phonon is equal with the corresponding shift due to thermal field, $\Delta\nu_{1,R}|_{T=25^\circ\text{C}}$, while $\Delta\nu_{1,T} = 0$ [21,22]. As a result, we can extract the values of the fiber thermal stress/strain at high temperatures (60, 80, 100°C), using the appropriate stress/strain sensitivity coefficients of ν_2 phonon [22].

$$\varepsilon_{\text{thermal}} = \frac{\Delta\nu_{1,R}|_{T>25^\circ\text{C}}}{k_{T,\varepsilon}^1} \quad (8)$$

and

$$\sigma_{\text{thermal}} = \frac{\Delta\nu_{1,R}|_{T>25^\circ\text{C}}}{k_{T,\sigma}^1} \quad (9)$$

where $\varepsilon_{\text{thermal}}$, σ_{thermal} is the thermal strain and stress at higher temperatures, respectively and $k_{T,\varepsilon}^1$, $k_{T,\sigma}^1$ are the strain and stress sensitivity factors of ν_1 phonon at $T > 25^\circ\text{C}$ [22].

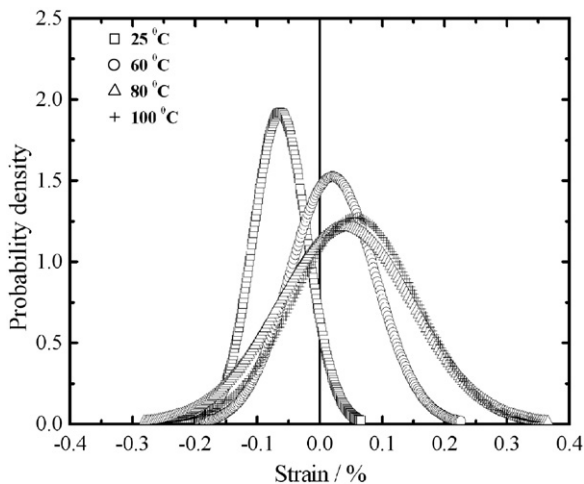


Fig. 1. The resulting normalized distributions of fiber strain at different applied temperatures (25°C (\square), 60°C (\circ), 80°C (\triangle), 100°C (+)). Each distribution corresponds to 200 data points.

Table 2

The calculated from Eq. (10) coefficient of thermal expansion of LTM217 epoxy resin/Kevlar[®] 29 aramid fiber composite

T ($^\circ\text{C}$)	E_f (GPa)	E_m (GPa)	$a_{\text{composite}}$ ($10^{-6}/^\circ\text{C}$)
25	71.3	4.1	0.70
60	71.3	3.7	0.29
80	67	3.4	0.20
100	60.5	3.1	0.24

The experimental values of fiber and resin moduli at various temperatures are also given.

The test specimens were 2-ply unidirectional Kevlar[®]29/LTM217 composites of approximately 53.5% in fiber volume fraction. A more detailed description of specimen production is presented elsewhere [20]. The gage length of the specimen was 40 mm and the specimen width was 12 mm [7,20,24]. The specimen was carefully mounted on an appropriate in-house set-up and was heated underneath by the use of a Peltier element [24]. Two thermo-sensitive strain gages were attached to the top and bottom surfaces of the specimen [24] and instant reading of the resistance was carried out by means of a digital multimeter. Finally, two high precision wire thermocouples were also attached to the top and bottom surfaces of the specimen and the values of temperature were provided by means of digital thermometers.

We have conducted experiments at elevated temperatures of 60, 80, 100°C on Kevlar[®] 29/LTM217 composites, by Raman sampling at random points (200 measurements) along the gage length of the specimens, and have derived both the average fiber thermal strain and stress using: (a) the stress/strain sensitivity of the ν_1 phonon (Eqs. (8) and (9)) and, also for comparison purposes, through (b) the stress/strain sensitivity of ν_2 phonon (Eqs. (4) and (5)).

3. Results and discussion

In Fig. 1, the overall mechanical integrity of the composites to the application of external thermal field is presented. Raman sampling has been performed at random points within the effective length of the examined specimens. The resulted distributions, presented in Fig. 1, were derived from a set of 200 measurements. The results, obtained via ν_1 phonon methodology, are fitted with Gaussian functions as described elsewhere [20,25]. As can be seen, at the onset of the experiment (ambient temperature) the average fiber strain is compressive for reasons explained earlier [20,25,26]. However, as the temperature increased (60, 80, 100°C) those thermal strains are relieved and then become tensile.

Similar results, concerning the average fiber strain, were obtained also via ν_2 phonon. However, those strain values have high standard deviations owing to lower confidence of ν_2 phonon as a stress sensor [22]. Furthermore, as is shown in Fig. 1, the fiber strain distributions become significantly broader as the external temperature increases, which indicate the presence of a gradient of stress in the embedded fibers. This gradient can be attributed to the internal stresses that are developed inside the composite due to the expansion of the matrix in tandem with the simultaneous axial contraction of the fibers.

When a unidirectional composite is heated up from an ambient temperature, then at equilibrium, the developing strains in the direction of the fiber and the matrix should be the same. Hence, in this work we

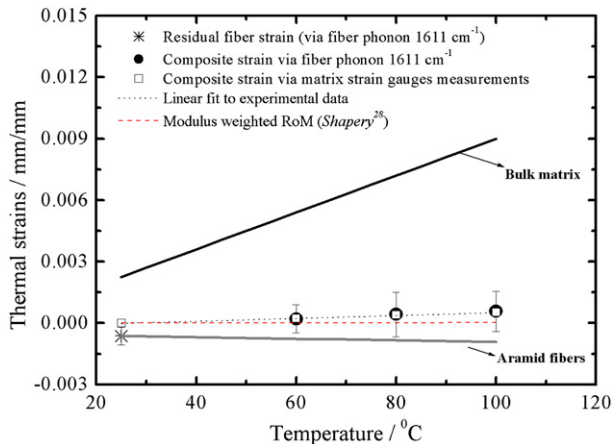


Fig. 2. The thermal strains vs. the applied temperature for the epoxy matrix (black solid line), Kevlar® 29 aramid fibers (grey solid line) are plotted. As for the composite material the dash line represents the predicted value of a modulus-weighted rule of mixture. Also, the experimental data of composite thermal strains vs. temperature obtained via aramid fibers phonon ν_1 (●) and via matrix strain-gage measurements (□) are presented. Finally, a linear fit on the experimental data is also presented.

have measured the strains in the embedded aramid fibers by means of Raman spectroscopy and the strain in the matrix by employing electrical resistance strain gages attached to the surface of the specimens. As it seems (Fig. 1), by increasing the external temperature, the thermal stress/strain field becomes tensile.

At this point, it is worthwhile here to compare our experimental results with calculations based on the relative thermal expansion coefficients of fiber and polymer resin and useful conclusions are drawn about the usefulness of existing predictive models. According to Shapery [8,27,28], by assuming equal strain conditions for the matrix and the fibers ($\epsilon_{\text{fiber}} = \epsilon_{\text{matrix}} = \epsilon_{\text{composite}}$) and zero total stress, it is easy to derive the composite CTE as:

$$a_{\text{composite}} = \frac{a_f \cdot E_f \cdot V_f + a_m \cdot E_m \cdot V_m}{E_f \cdot V_f + E_m \cdot V_m} \quad (10)$$

where E_f , E_m are the tensile moduli of fiber and matrix at each examined temperature, respectively. The calculated coefficients of thermal expansion of the composite at each examined temperature are presented in Table 2.

By using the above coefficients, the thermal strains on the composite under moderately elevated temperatures can be predicted. In Fig. 2, a plot of the thermal strains vs. temperature is presented. The black solid line represents the thermal strains of the bulk epoxy resin (LTM217) [29] and the corresponding grey solid line the thermal strains of aramid fibers (Kevlar® 29) [1]. The abscissas of both lines correspond to their respective residual strains at ambient temperature that have been obtained experimentally [7].

According to earlier work [1,3,4,29], the CTE values for both fibers and resin do not seem to change within the 25–100 °C temperature range. As is evident from Fig. 2, the composite strain measured either in the fiber by laser Raman spectroscopy (full circles) or in the resin by strain-gage measurements (open squares), yields identical results, confirming the prevalence of the equal strain condition under thermal strain development. Moreover, the experimental CTE data (Fig. 2) are positive and lie just above the analytical treatment proposed by Shapery [8,27,28]. It is worth adding, however, that the linear relationship between the developed thermal composite strain and the applied temperature is retained. Closer examination of Eq. (10) indicates that, for high volume fraction com-

mercial composites, such as aramid or carbon, the high fiber modulus should offset the effect of matrix modulus and the composite should be biased towards the fiber and, therefore, exhibit a negative CTE.

However, the recently developed RFI (resin film infusion) or RTM (resin transfer molding) epoxy resins have much greater – positive – values of CTE [30] than conventional epoxies and hence the composite CTE can be shifted, in certain cases, to zero or to positive values at ambient or moderate temperatures. This is an interesting result because it allows future material developers particularly aerospace companies to tailor the thermal expansion of even polymer composites to zero in the axial direction or to any value they desire – positive or negative – provided a choice for the desirable matrix CTE is made prior to composite manufacturing. The critical value of matrix CTE for zero axial thermal expansion has been estimated to be $75E-06/^\circ\text{C}$. Values above or below this threshold should yield to expansion or contraction of the composite, respectively. Finally, it is worth adding that for elevated temperatures to obtain zero CTE for the composite then apart from the matrix CTE, the ratio of the fiber to matrix moduli should be considered as well (see Eq. (10)).

4. Conclusions

The thermal stress development in anisotropic fiber-reinforced polymer composites is investigated for temperatures below the glass transition temperature of the resin. The composite strain with temperature was measured either via the fiber by means of laser Raman spectroscopy or through the matrix by means of strain-gage measurements. The results were compared with a well established analytical model that relates the composite thermal strain to the thermal expansion coefficients of fiber and resin, as well as, the fiber volume fraction. The conditions for which a polymer composite that incorporates aramid or carbon fibers can have positive, negative or, even, zero thermal expansion coefficient have been defined.

Acknowledgements

The authors would like to acknowledge the General Secretariat of Research & Technology of Greece for funding and supporting Dr. George Anagnostopoulos, and also the Nanofun-Poly Network of Excellence of the European Communities for supporting the research group.

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