Thermal Anisotropy of Polymer Carbon fiber Composites as Revealed by Photodeflection Methods

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1 Abstract

Thermal diffusivity for carbon fiber composites was measured using different fiber types and polymer matrices. Photothermal testing was performed in the various directions parallel and perpendicular to the carbon fiber axis by different photothermal techniques. By focusing the laser beam with a spherical lens local inhomogeneities of the composite surface in the range of $10\mu\text{m}$ are distinguished. When focusing is done with the aid of a cylindrical lens an averaging over larger scales of the photothermal deflected signal takes place. Results for the various carbon fiber materials are discussed in terms of thermal diffusion lengths and thermal diffusivity values. It is shown that the thermal photodeflection method is suitable to measure anisotropy in oriented carbon fiber composites.

2 Introduction

Polymer carbon fiber composites, in which fibers are oriented parallel to the surface, usually exhibit anisotropic electrical [1] and thermal conductivity values. In oriented composites the fibers are drawn in the polymer matrix and heat has to be transferred from one fiber to the next one, resulting in a low thermal conductivity in the direction perpendicular to the fiber axis. Inglehart et al. [4] used the "mirage method" to measure the thermal diffusivity parallel to fiber axes and found that it was twice the diffusivity value in the perpendicular direction. J. Varis et al. [5] studied numerically thermal effects of "line heating" on layered anisotropic carbon fiber composites and also found a clear effect on the surface temperature distributions depending on both, the scanning direction and on the velocity of the line heating.

Photothermal testing methods have proved to be especially suitable for testing of carbon fiber composites [6]. The so-called "flash" technique [7], -heating the sample surface and probing heat flow in the perpendicular direction- only provides an evaluation of thermal conductivity in a direction perpendicular to the sample surface. The photothermal deflection method can be used instead, usefully, to assess the thermal diffusivity in the three directions as we will show here in the case of various carbon fiber composites. The structure of these carbon fiber composites as revealed by X-ray diffraction techniques, the electrical anisotropy study of these systems and the surface mechanical properties determined by microhardness testing has been recently reported [1,2]

3 Experimental

3.1 Techniques

The photothermal set-up that will be used in the present study is the so-called transverse geometry in which the sample is heated with a chopped pump laser beam and the resulting temperature distribution in the air is measured with a second probe laser beam skimmed parallel to the surface in the air [8]. In order to heat the sample surface two different geometries have been used. In the first one, the pump beam was focused with a spherical lens on a small point of the surface. In this disposition the probe was able to detect small inhomogeneities of the surface, heat being given to a region of the dimensions of the pump spot size of about $10\mu m$. This disposition has proven to be very useful in order to "see" the single fiber bundles.

In the second one the pump beam is focused on the sample surface by means of a cylindrical lens along a "line" which can be suitably oriented. In our case it has been chosen perpendicular to the mean direction of the fiber bundles, or perpendicular to them. The "line" disposition is more suitable. If one is interested to measure thermal diffusivity along some direction in the sample,

Finally, to measure the diffusivity in the direction perpendicular to the sample surface, one face of the sample was homogeneously heated and the probe beam analyzed both, the temperature of the heated face and the temperature of the opposite face. The diffusivity values is obtained from the ratio of the two temperatures [9].

The thermal diffusion length has been measured using the phase method [10]

3.2 Materials

The polymer-carbon fiber composites investigated in this work are preimpregnated plies ("prepregs") based on thermoplastic poly(imide) from Mitsui-Toatsu (TPI), poly(ether-ether ketone) from ICI (PEEK) and poly(ether-ketone-keton) from Dupont (PEEK). The carbon fibers used include: T800 from Toray, AS-4 continuous fibers from Hercules and AS4-LDFTM long discontinuous fibers from Hercules. Prepregs 200 μm thick composite systems of TPI/T800, PEEK/AS4 and PEKK/AS4LDFTM were used as supplied by the manufacturers with a composition of about 62 % vol of carbon fibers. Carbon fibers are distributed in a compact manner within the material parallel to the prepreg surface [11,12]. To illustrate this feature SEM micrographies for the different composites are shown in fig. 1. It is interesting to note that for the PEKK/AS4LDF sample a certain degree of fiber interconnection exists.

4 Results

4.1 Thermal Diffusion Parallel to the Sample Surface

4.1.1 Spherical lens focusing

The set up utilized to measure the local thermal response on the sample using a spherical lens to focus the pump beam on the sample is shown in fig. 2. The sample was shifted parallel to itself along a given direction, x , by maintaining the pump and probe relative positions fixed in such a way that the distance between the beam axis (offset x) was zero.

Results of the obtained results are shown in figs. 3 which give the amplitude (modulus) of the signal as a function of the position x in the sample for TPI-T800 and PEKK-AS4LDF samples (fig. 3a) and both, amplitude and phase for

the PEEK-AS4 sample (fig. 3b). In all cases the specimens were moved parallel (x-direction) or perpendicular(y-direction) to the main axis of the carbon fibers. One can easily see that when the translation direction was parallel to the fiber bundles the signal is more stable, whilst when it is moved normally to the fiber bundles, large variations in the signal are seen which are reminiscent of the dimensions of the bundles. In this case one obtains bundles dimensions which range between $30\text{ }\mu\text{m}$ for PEEK-AS4 to $150\text{ }\mu\text{m}$ for TPI-T800. Since the fiber dimensions are of about $5\text{ }\mu\text{m}$, this method is capable to reveal the existence of a bigger structure formed by fiber bundles in which thermal resistivity among fibers is expected to be low. In the case of PEKK/AS4LDF, the signal exhibits variations in both directions suggesting a smaller degree of fiber alignment than in the other two investigated cases.

4.1.2 Phase method

The phase method employed to measure the thermal diffusivity of glasses has been described in reference [10]. In this method the probe beam is kept fixed in some region of the sample, and the pump is shifted parallel to itself along the plane. The phase of the signal is plotted as a function of the relative offset between the two beams.

If the method is applied using a spherical lens to focus the pump beam a very fluctuating phase signal is obtained when the pump beam is shifted perpendicularly to the axis of the fibers. However, when the beam is shifted in the parallel direction to the fibers a more stable signal is obtained as shown in Fig. 4a for a TPI-T800 sample. In the case of PEKK-AS4LDF sample, in which the fiber are less aligned, very fluctuating signals are obtained in both directions (fig. 4b).

4.1.3 Cylindrical lens focusing

The set up in which the pump beam is focalized on a line on the sample is shown in fig. 5. In this case the probe beam is made to skim on the surface along a direction parallel to the pump line. The measurements are made here by changing the distance x between the two lines in stationary conditions. This means that each measurement is done when the temperature distribution has reached its steady state and no dynamical problems arise. In this case one can assume that the temperature on a line at distance x from the pump line is related to the temperature $T(x=0)$ by:

$$T(x) = T(0)\exp(-x/l_t) \quad (1)$$

where l_t is the thermal diffusion length. The ratio of the two moduli M taken along the lines at $x=0$ and X is:

$$\frac{M(x)}{M(0)} = 2\exp(-x/l_t) \quad (2)$$

or

$$\ln \frac{M(x)}{M(0)} = \ln 2 - x(\pi f/D)^{1/2} \quad (3)$$

and the phase ϕ of the photothermal signal on the line at a distance x is:

$$\phi = -x(\pi f/D)^{1/2} \quad (4)$$

where f is the frequency of the modulation of the pump intensity and D is the thermal diffusivity.

Examples of the obtained results are shown in figs. 6 and 7. In fig. 6 the phase and the amplitude (modulus) of the signal for a TPI/T800 sample are shown as a function of the offset different chopper frequencies in the

parallel configuration. In fig. 7 the phase and amplitude of the signal at a fixed frequency (400 Hz) are given for the three samples for, both, parallel and perpendicular configuration.

First of all, results indicate that the phase signal in the case of the line pumping has a smooth behaviour which shows that an averaging over a large dimension of the sample has been performed. In contrast the results obtained in the case of a spherical lens are strongly inhomogeneous (see figs.4). Secondly the slope of the phase signal is different depending on which direction is chosen, either perpendicular or parallel to the fiber bundles. From these measurements a marked anisotropy results as shown in table I. The thermal diffusivity length l_{eq} derived from the slope of the phase curve (see ref. [10]) is given in this table for the different samples in the parallel and perpendicular directions respectively for different frequencies.

4.2 Thermal Diffusion Perpendicular to the Sample Surface

To measure the thermal diffusion perpendicular to the sample surface, the sample was heated by the pump beam from one side. The probe beam skims parallel to the sample surface on both the pump or the opposite side (see fig. 8). By making the pump spot dimension much greater than the sample surface size, the solution of the heat diffusion equation in this case, for a thermally thick sample (i.e. l_t larger than the sample thickness) gives for the ratio of the signal when heating from the back to the signal when heating from the front [10]:

$$Ln \frac{M(L)}{M(0)} = Ln 2 - \left(\frac{\omega}{2D}\right)^{1/2} L \quad (5)$$

and :

$$\phi = -(\omega/2D)^{1/2}L \quad (6)$$

where $\omega=2\pi f$ is the angular frequency of the chopper, and L is the sample thickness. From these expressions the thermal diffusivity can be obtained, as shown in table II (Third column).

The values of l_{eq} given in table I are shown in figs.9 as a function of the reciprocal square root of the frequency for the three samples measured in the parallel and the perpendicular direction respectively with respect to the fibers.

To obtain the correct value of the thermal diffusivity D , the technique described in ref [8] has been used. In this case:

$$D = \pi K^2 = \pi f l_t^2 \quad (7)$$

where l_t is the diffusion length and:

$$K = [l_{eq}(f_1) - l_{eq}(f_2)] / [(1/f_1)^{1/2} - (1/f_2)^{1/2}] \quad (8)$$

has been derived from figs. 9.

By a simple inspection of figs. 9, the equivalent value of the diffusion length l_{eq} can be derived:

$$l_{eq} = l_t + C \quad (9)$$

where C is a constant that depends on the distance z of the probe beam from the surface (vertical offset). In our case C depends from the state of the surface. In ref [10] it has been shown that for an homogeneous sample with flat surface it has positive values. From the results presented in figs. 9 one sees that when heat propagates in the direction perpendicular to the fibers direction (curve 2) the value of C is always negative and high (about $50\mu\text{m}$); on the contrary for

heat propagating parallel to the fibers direction the C value is practically equal to zero. At the moment we have no reasonable explanation for this behaviour.

From equations 7,8 and 9 the thermal diffusivity can be obtained as shown in table II, where the results for the thermal diffusivity are given in the three directions. Sample TPI-T800 was too thin to apply the reported method and it was nor possible to determine the diffusivity perpendicular to the sample surface.

5 Discussion

The obtained results appear to be in contrast with what one could in principle expect, owing to the fact that carbon fibers show a much higher thermal conductivity than the polymer matrix. In other words, thermal diffusivity in the surface plane is larger in the perpendicular than in the parallel direction to the fiber bundles. On the other hand, as expected, the diffusivity value perpendicular to the sample surface is very low being nearly given by the polymer matrix (whose diffusivity is about $6 \cdot 10^{-3} \text{ cm}^2/\text{s}$). Furthermore, the thermal conductivity of the composites is expected to be larger along the fiber axis than perpendicular to it in analogy with electrical conductivity measurements [1]. The thermal conductivity behaviour can be qualitatively evaluated by measuring the width of the maximum amplitude of the photothermal signals (see figs 7). For the same frequency the width is larger for the measurements parallel to the fiber than for those normal to the fiber direction. This means that the thermal flux is larger in the parallel direction to the fiber. One has, therefore, the unexpected result that $K_{\perp} < K_{\parallel}$ and $D_{\parallel} > D_{\perp}$. One way to explain the obtained observations would be to consider that during the formation phase of the composite, when heat treatment is applied, spherulites are formed in the

matrix between fibers [13]. However, as shown in a previous work [1], the polymeric matrices investigated in this work are amorphous. Unless heat treatment at about $T > \approx 150^{\circ}\text{C}$ would be applied no crystallinity development should be expected. Therefore, a tentative explanation of the observed experimental features can be given by considering the following geometrical factors. If we consider that, after a heating pulse reaches the sample surface the carbon fiber acts as a heat emitting source then, the heat propagation perpendicular to the fiber direction will be admittedly larger than in the parallel direction. In this way, the relation of heat emitting surface(carbon fiber) to inert surface (polymer) is enhanced in the perpendicular direction to the fiber as schematically shown in fig.. Finally, the lower values of thermal diffusivity in the z direction as compared with the values in the plane (see table II) may be due to the existence of additional absorption effects due to inhomogeneities across the sample.

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