Thermal anisotropy of polymer carbon fiber composites as revealed by photodeflection methods

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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 configurations. By focusing the laser beam with a spherical lens, local inhomogeneities of the composite surface in the range of 10 μm 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. The results for 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 for measuring anisotropy in oriented carbon fiber composites. © *1995 American Institute of Physics.*

I. INTRODUCTION

Polymer carbon fiber composites, in which fibers are oriented parallel to the surface, usually exhibit anisotropic electrical[1-3] and thermal conductivity values.[3] 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 the fiber axis and found that it was twice the diffusivity value in the perpendicular direction. Varis *et al.*[5] studied the numerically thermal effect 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 the testing of carbon fiber composites.[6] The so-called "*flash*" technique,[7] which involves heating the sample surface and probing the heat flow in the perpendicular direction, only provides an evaluation of thermal conductivity in a direction perpendicular to the sample surface. By contrast, the photothermal deflection method can be used to assess the thermal diffusivity in three directions. Thus we will use this method for various carbon fiber composites. The structure of these carbon fiber composites as revealed by x-ray diffraction techniques, electrical anisotropy studies, and surface mechanical properties determined by microhardness testing has recently been reported.[1,2]

II. EXPERIMENTAL

A. Techniques

The photothermal setup that will be used in the present study is the so-called transverse geometry in which the sample surface 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, with heat being given to the region of the pump spot size with a dimension of about 10 μm. This disposition has proven to be very useful in order to "see" the single fiber bundles.

In the second geometry 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 in measuring the 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. The probe beam analyzed both the temperature gradient of the heated face and the temperature gradient of the opposite face. The diffusivity value is obtained from the ratio of the two temperatures.[9]

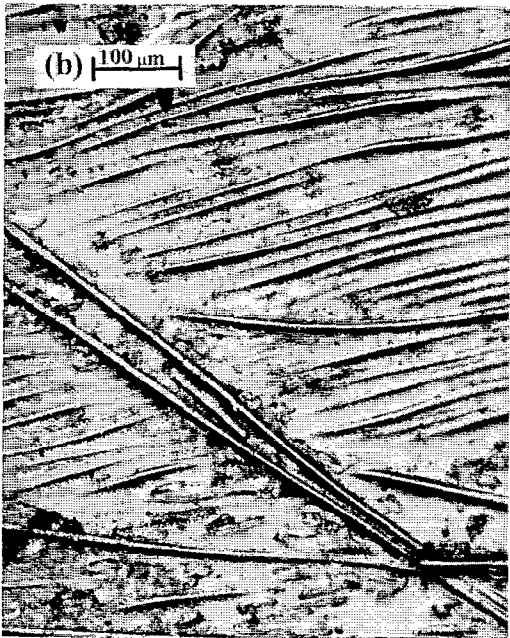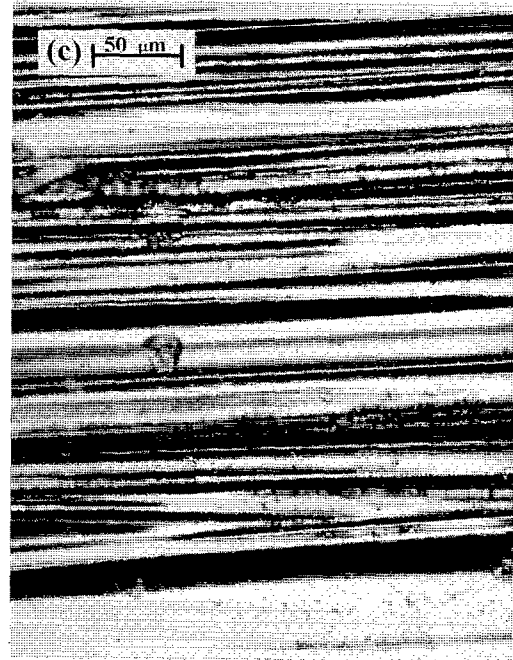The thermal diffusion length has been measured using the phase method.[10]

FIG. 1. SEM micrographs of the various composites: (a) the TPI-T800, (b) the PEKK-AS4LDF, (c) the PEEK-AS4.

B. Materials

The polymer-carbon fiber composites investigated in this work are preimpregnated plies ("prepregs") based on the thermoplastic poly(imide) from Mitsui-Toatsu (TPI), poly(ether-ether ketone) from ICI (PEEK), and poly(ether-ketone-keton) from Dupont (PEKK).

The carbon fibers used include: T800 from Toray, AS-4 continuous fibers from Hercules, and AS4-LDF^{TM} long discontinuous fibers from Hercules. Prepregs 200-μm-thick composite systems of TPI-T800, PEEK-AS4, and PEKK-AS4LDF^{TM} 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] To illustrate this feature scanning electron microscopy micrographs 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.

III. RESULTS

A. Thermal diffusion parallel to the sample surface

1. Spherical lens focusing

The setup 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
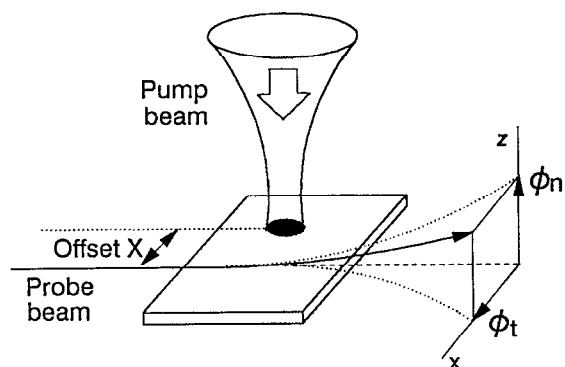
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FIG. 2. Typical disposition for the photothermal measurement with a spherical lens.

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 beams' axis (offset x) was zero.

Examples of the results obtained are shown in Fig. 3 which gives the amplitude (modulus) of the signal as a function of the position x in the sample for the (a) PEKK-AS4LDF, (b) TPI-T800 and (c) PEEK-AS4 samples and both phases for the (d) PEEK-AS4 sample. In all cases the specimens were moved parallel (the x direction) or perpendicular (the y direction) to the main axis of the carbon fibers. One can easily see that when the translation direction is parallel to the fiber bundles the signal is more stable, and when it is moved normal to the fiber bundles, large variations in the signal are seen which are reminescent of the dimensions of the bundles. In this case one obtains bundle dimensions which range between 30 μm for PEEK-AS4 and 150 μm for TPI-T800. Since the fiber dimensions are about 5 μm, this method is capable of revealing 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 PEEK-AS4LDF, the signal exhibits variations in both directions suggesting a smaller degree of fiber alignment than in the other two investigated cases.

2. Phase method

The phase method employed to measure the thermal diffusivity has been described in Ref. 10. In this method the probe beam is kept fixed in some region of the sample, and the pump beam 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 phase signal that fluctuates greatly is obtained when the pump beam is shifted perpendicular to the axis of the fibers. However, when the beam is shifted in the direction parallel to the fibers a more stable signal is obtained as shown in Figs. 4(a) and 4(b) for a TPI-T800 sample. In the case of the PEKK-AS4LDF sample, in which the fibers are less aligned, signals that fluctuate greatly are obtained in both directions [see Figs. 4(c) and 4(d)].
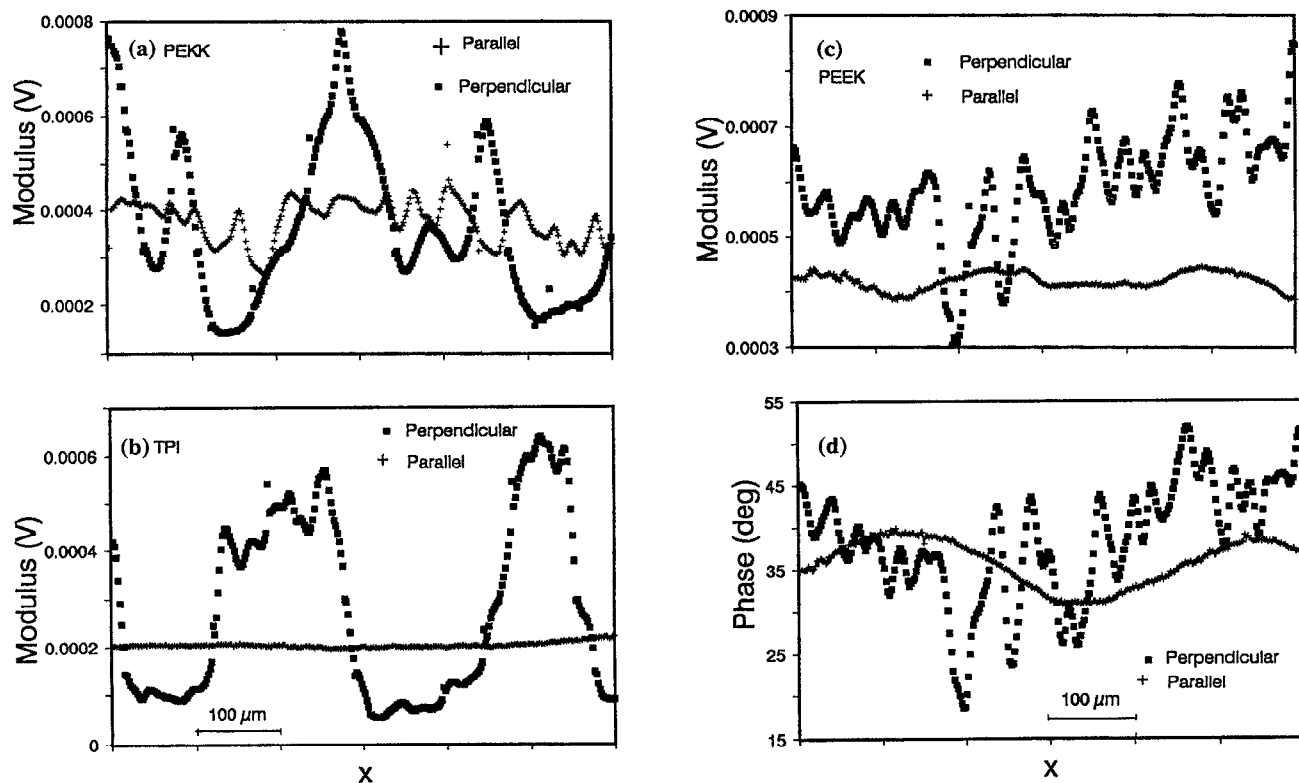

FIG. 3. The photothermal signal obtained with the disposition of Fig. 2: the modulus of the signal as a function of the position x on the sample for PEKK-AS4LDF (a), TPI-T800 (b), and PEEK-AS4 (c); the phase of the signal as a function of position x for PEEK-AS4 (d).
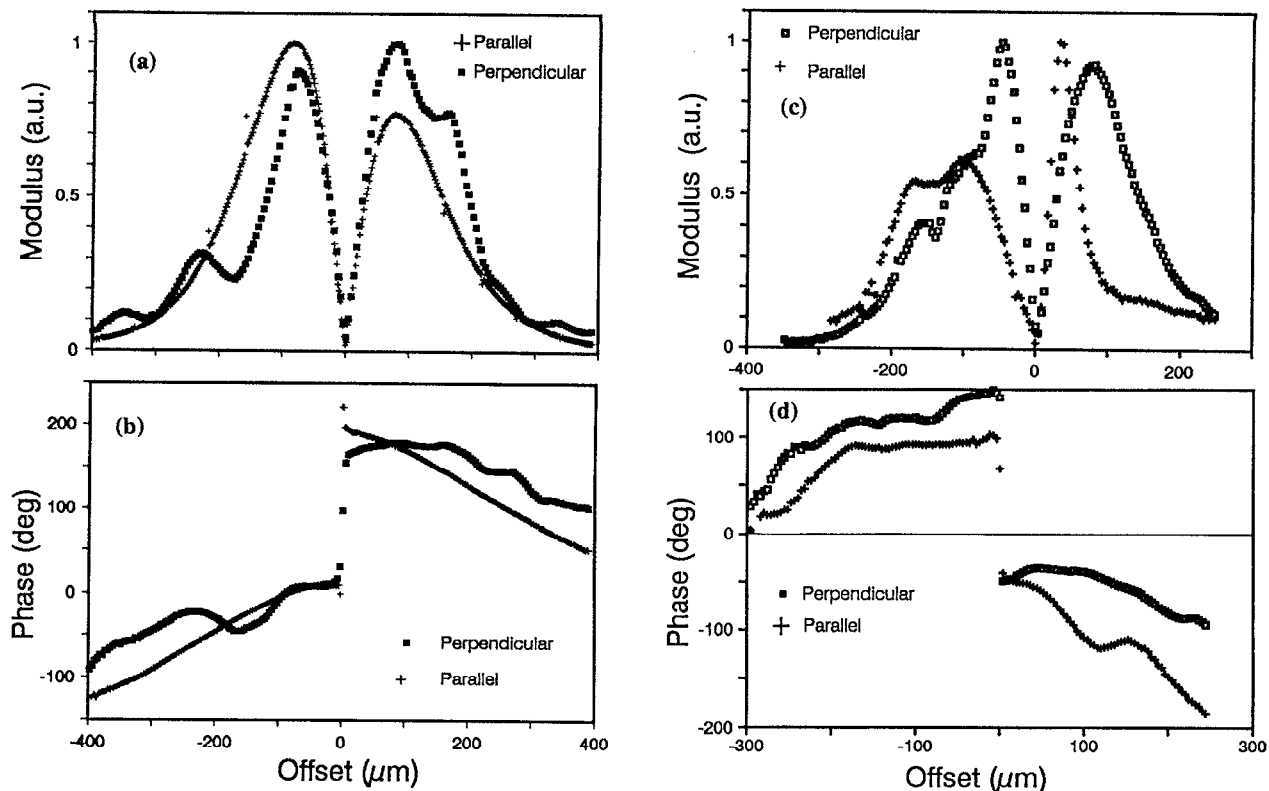
FIG. 4. Modulus [(a) and (c)] and phase [(b) and (d)] of the photodeflection signal as a function of offset between pump and probe beams in the disposition of Fig. 2 for a TPI-T800 [(a) and (b)] sample in both perpendicular (□) and parallel (+) directions, at a chopper frequency $f = 400$ Hz, and a PEKK-AS4LDF [(c) and (d)] sample in the perpendicular (□) and parallel (+) directions.

3. Cylindrical lens focusing

The setup in which the pump beam is focused on a line in the sample is shown in Fig. 5. In this case the probe beam is made to skim 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 dy-
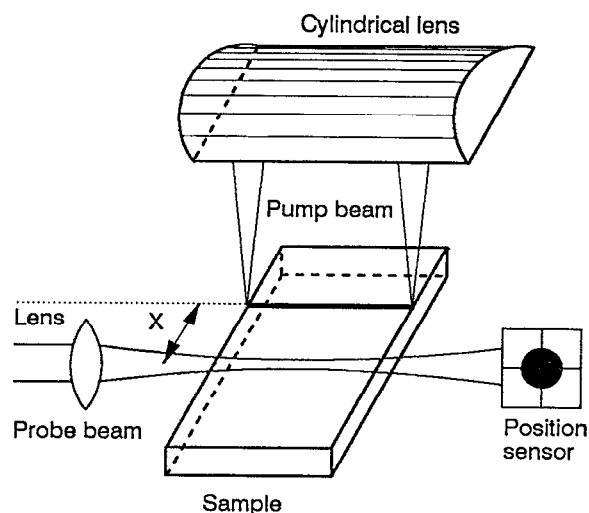
FIG. 5. Experimental disposition for the photothermal measurement by using a cylindrical lens.
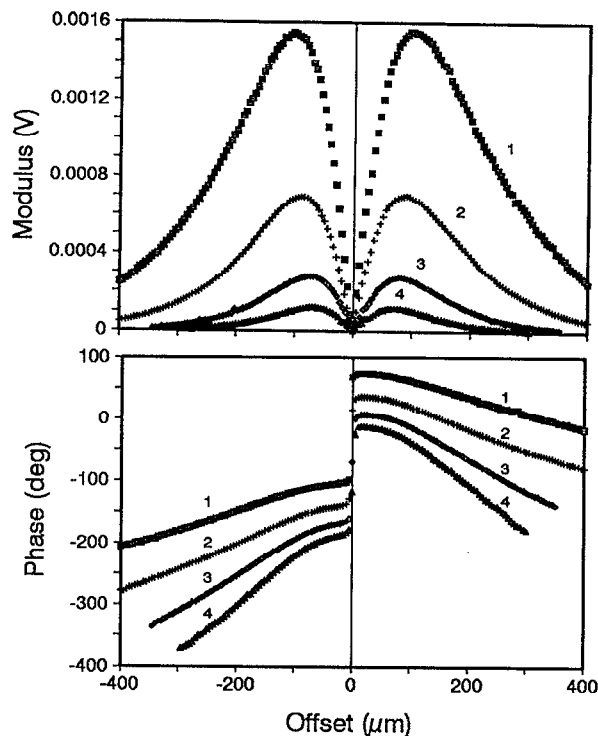
FIG. 6. Modulus and phase of the photothermal signal as a function of offset between pump and probe beams in the disposition of Fig. 5 in the direction parallel to the fiber bundles for different chopper frequencies for a TPI-T800 sample for (1) $f = 169$ Hz, (2) $f = 400$ Hz, (3) $f = 900$ Hz, (4) $f = 1600$ Hz.
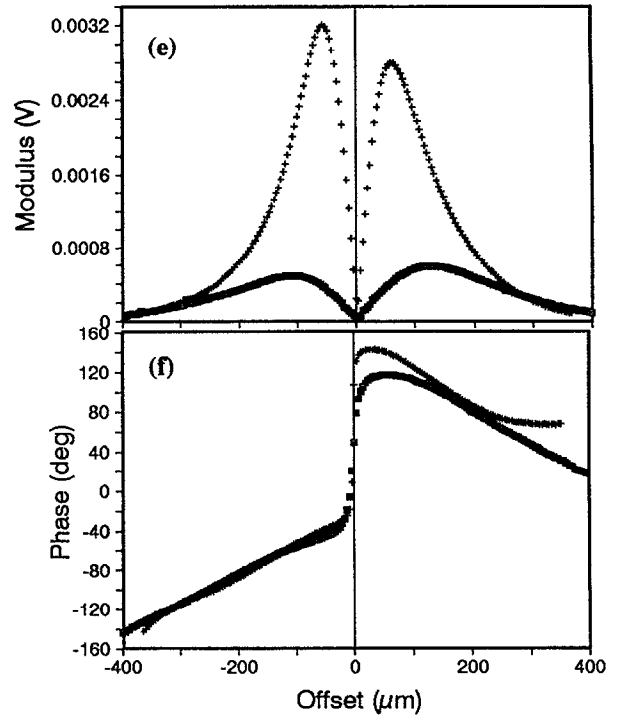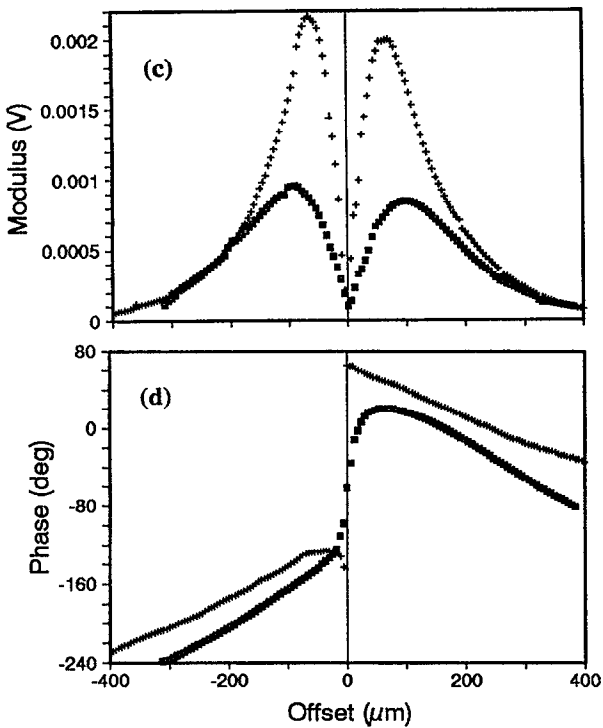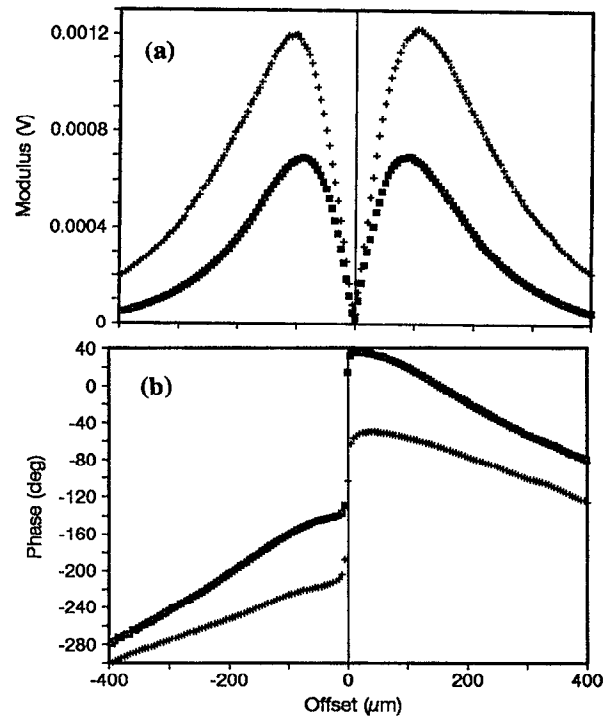
FIG. 7. Modulus [(a), (c), and (e)] and phase [(b), (d), and (f)] of the photothermal signal as a function of offset between pump and probe beams in the disposition of Fig. 5 at the fixed frequency $f = 400$ Hz for three samples in the parallel direction (□) and in the perpendicular direction (+): (a) and (b) the TPI-T800 sample; (c) and (d) the PEKK-AS4LDF; and (e) and (f) the PEEK-AS4 sample.

namical problems arise. In this case[9] 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

$$T(x) = T(0)\exp(-x/l_t),\tag{1}$$

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

$$M(x)/M(0) = 2\exp(-x/l_t),\tag{2}$$

or

$$\ln[M(x)/M(0)] = \ln(2) - x\sqrt{\pi f/D},\tag{3}$$

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

$$\varphi = -x\sqrt{\pi f/D},\tag{4}$$

TABLE I. Experimental values of l_{eq} (μm) vs frequency for the three samples.

Sample	l_{eq} (μm)	Frequency (Hz)				
		169	256	400	900	1600
PEEK-AS4	‖	227	···	156	99	71
	⊥	347	275	211	132	90
PEEK-AS4LDF	‖	274	229	198	126	102
	⊥	354	···	203	126	99
TPI-T800	‖	230	···	143	98	75
	⊥	381	313	238	145	97

TABLE II. Thermal diffusivity values (cm²/s) for the three samples in the three (parallel, perpendicular, and along z) directions.

Sample	Thermal diffusivity (cm²/s)		
	‖	⊥	z
PEEK-AS4	0.25	0.71	0.0027
PEKK-AS4LDF	0.36	0.82	0.0047
TPI-T800	0.29	0.92	···

and perpendicular directions, respectively, for different frequencies.

B. 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 (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

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

Examples of the results obtained are shown in Figs. 6 and 7. In Fig. 6 the amplitude (modulus) and the phase of the signal for a TPI-T800 sample are shown as a function of offset for 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 all three samples for both parallel and perpendicular configurations.

First, the results indicate that the phase signal in the case of the line pumping has a smooth behavior 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 nonhomogeneous (see Fig. 4). Second, the slope of the phase signal is different depending on the direction chosen—either perpendicular or parallel to the fiber bundles. From these measurements a marked anisotropy results as shown in Table I. The thermal diffusion length l_{eq} derived from the slope of the phase curve (Ref. 10) is given in Table I for the different samples in the parallel
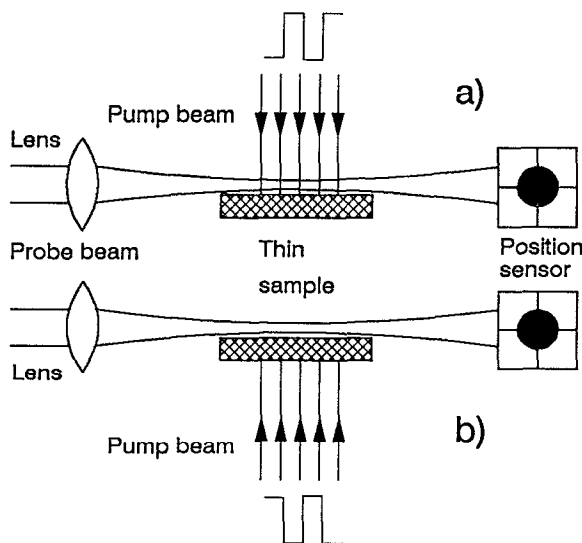
Geometry of the Experiment

FIG. 8. The setup for the two measurements needed to determine the front (a) and back (b) temperature of the sample to measure thermal diffusivity perpendicular to its surface.
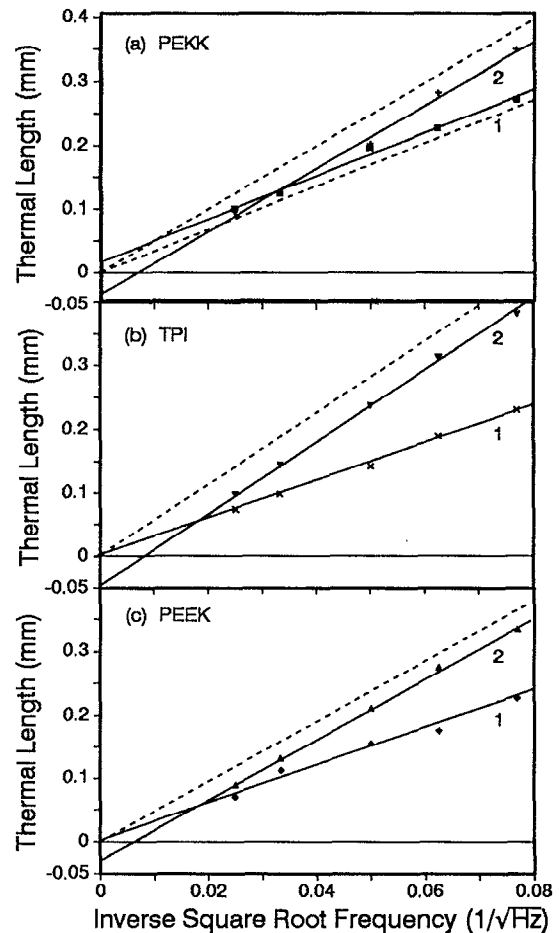

FIG. 9. Plots of the thermal diffusion length l_{eq} obtained by the slopes of the phase curves vs the inverse square root of frequency for (a) the PEKK-AS4LDF samples, (b) the TPI-T800PEEK-AS4, and (c) the PEEK-AS4 samples. Curves 1 refer to measurements performed in the parallel direction, curves 2 refer to measurements performed in the perpendicular direction.

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than the sample thickness), gives the ratio of the signal when heating from the back to the signal and when heating from the front[9]

$$\ln[M(L)/M(0)] = \ln(2) - L\sqrt{\pi f/D} \ , \qquad (5)$$

and

$$\varphi = -L\sqrt{\pi f/D} \ , \qquad (6)$$

where L is the sample thickness. From these expressions the thermal diffusivity can be obtained, as shown in Table II (the third column). The values of l_{eq} given in Table I are shown in Fig. 9 as a function of the inverse square root of the frequency of the three samples for the parallel (curves 1) and the perpendicular (curves 2) directions, respectively, in relation to the fibers.

To obtain the correct value of thermal diffusivity D, the technique described in Ref. 10 has been used. In this case

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

where l_t is the diffusion length and

$$K = \frac{l_{eq}(f_1) - l_{eq}(f_2)}{\sqrt{1/f_1} - \sqrt{1/f_2}} \qquad (8)$$

has been derived from Fig. 9.

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

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

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 on the state of the surface. In Ref. 10 it has been shown that for an homogeneous sample with a flat surface it has positive values. From the results presented in Fig. 9 one can see that when heat propagates in the direction perpendicular to the fiber's direction (curve 2) the value of C is always negative and high (about 50 μm); on the contrary for heat propagating parallel to the fiber's direction the C value is practically equal to zero. At the moment we have no reasonable explanation for this behavior.

From Eqs. (7)–(9) the thermal diffusivity can be obtained as shown in Table II, where the results for the thermal diffusivity are given in three directions. Sample TPI-T800 was too thin to apply the reported method to and it was not possible to determine the diffusivity perpendicular to the sample surface.

IV. DISCUSSION

The results obtained appear in contrast to 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 direction perpendicular to than in the direction parallel 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 6×10^{-3} cm^2/s). Furthermore, the thermal conductivity of the composites is expected to be larger along the fiber axis than perpendicular to it in analogy with the electrical conductivity measurements.[1] The thermal conductivity behavior can be qualitatively evaluated by measuring the width of the maximum amplitude of the photothermal signals (Fig. 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. Therefore, one has the unexpected result that $K_\perp < K_\parallel$ and $D_\perp > D_\parallel$. 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.[12] However, as shown in a previous work,[1] the polymeric matrices investigated in this work are amorphous. Unless heat treatment at about $T \geq 150$ °C is applied no crystallinity development should be expected. Therefore we need a different explanation that requires a detailed study of heat propagation in a composite structure that also takes into account the surface state of the specimens. Such a theoretical study is underway and will be presented elsewhere. We may conclude that the photodeflection method has proven very suitable for measuring anisotropies in composite materials, and may help in better understanding how heat is conducted in these structures.

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