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Transverse Thermal Conductance of Thermosetting Composite Materials During Their Cure

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The transverse thermal conductance of thermosetting advanced composite materials during their cure was modeled analytically and then investigated experimentally. AS4/3501-6 graphite/epoxy was used for the experiments. A model for the effective transverse conductivity of a material with cylinders arranged in rectangular order, first derived by Lord Rayleigh, was modified to account for the possible effects of a fiber/resin contact resistance and for the transversely anisotropic behavior of the composites' thermal conductivity. A model was derived that accounts for the effect of resin heat generation on the measured thermal conductivity of an uncured thermosetting composite. These models were investigated experimentally using a guarded hot plate apparatus to measure the thermal conductivity of the graphite/epoxy laminates as a function of independent cure variables. Good agreement was found between the models and the experimental data.

Nomenclature

A_x = differential element facial area
a = radius of the average fiber
H_r = resin heat of reaction
h_c = thermal contact conductance
J_x^∞ = applied temperature gradient in the x direction
K = thermal conductivity
p = function of fiber volume fraction, Eqs. (6) and (8) for square and rectangular orders, respectively
q_{in} = heat flux input by guarded hot plate
q_x = heat flux per unit area
$\dot{q}$ = rate of resin heat generation per volume
r = radial distance from the center of a fiber
T = temperature
t_c = thickness of the interphase region
V_f = fiber volume fraction of the composite
v = ratio of fiber to matrix thermal conductivity
v' = function of material conductivities, Eq. (4)
α = resin degree of cure, percentage of cross linking
δ = side of matrix rectangle parallel to temperature gradient
ε = side of matrix rectangle perpendicular to temperature gradient
θ_p = in-plane angle of rotation defined in Fig. 1
ρ = density

Subscripts
C = cold surface
c = interphase region property
comp = composite property
eff = effective composite property
f = fiber property
g = glass transition property
H = hot surface
m = matrix (resin) property

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Introduction

THE calculation of the effective transverse conductivity for a composite containing two or more different materials has been studied by some of the most illustrious names in science. Landauer[1] presents the early chronological development of this field from its beginning in the early 1800s. In his review, Landauer finds that Avogadro (1806–1807) and Faraday (1837) first proposed models of a dielectric which consisted of a series of metallic globules separated from each other by insulating material. However, Landauer states that discussion of the effective conductivity (thermal conductivity, electrical conductivity, diffusivity, electrostatic permittivity, and magnetic permeability are all calculated analogously) is generally first referenced to the work of Lorentz (1868) in most modern textbooks. Hashin[2] also presents an excellent review on the analysis of composite materials. Hashin begins with the work of Maxwell[3] in 1873 and Lord Rayleigh[4] in 1892. Maxwell derived an equation for the effective conductivity of spherical inclusions embedded in a material of different conductivity. Rayleigh computed an equation for the effective conductivity of cylinders as well as spheres arranged in rectangular order. According to Rayleigh,[4] these equations are valid "when the dimensions of the obstacles are no longer very small in comparison with the distances between them." The Rayleigh model has been refined by Meredith and Tobias,[5] McPhedran and McKenzie,[6] and Bergman.[7,8]

More recently, Hasselman and Johnson[9] have modeled the interfacial thermal barrier resistance (between fiber and resin) for dilute volume fractions of dispersions. They found that an interfacial barrier resistance is important to the determination of the transverse thermal conductivity when fiber coatings or electrochemical treatments have been used or when imperfect contact occurs between the fiber and resin due to processing conditions. Mijovic and Wang[10] measured large changes in the transverse thermal conductivity of a unidirectional graphite/epoxy laminate during its cure using a thermal conductivity apparatus described by Mijovic and Mei.[11] Scott and Beck[12,13] have used a transient estimation method to estimate the thermal conductivity of a thermosetting composite during its cure. They found a significant difference between the estimated transverse thermal conductivity of laminates with different stacking sequences.

In this research, a model for the effective transverse conductivity of a material with cylinders arranged in rectangular order, first derived by Lord Rayleigh,[4] was modified to account for the effects of a fiber/resin contact resistance and for the transversely anisotropic behavior of the composites' thermal conductivity. Previously derived cure kinetics relations[14] were used to model the effect that cure reactions have on the measurement of the thermal conductivity of an uncured thermosetting composite laminate. The transverse thermal conductivity of a graphite/epoxy composite was then measured as a function of temperature, resin degree of cure, fiber volume fraction, and the ply lay-up angles within the laminate. The first three of these parameters change during cure in an autoclave, while the ply angles are determined during the design of the composite laminate. The experimental results were compared to the modified Rayleigh model for relatively high volume fractions of fibers arranged in a statistically averaged square order as well as various rectangular orders. The cure kinetics relations and subsequent model were used to calculate the composite conductivity as a function of the resin degree of cure.

Theory

Transverse Thermal Conductivity with an Interfacial Resistance

The interphase region surrounding each fiber may strongly influence the transverse thermal conductivity of a fiber-reinforced composite. Drzal et al.[15–17] have observed and defined an interphase region around the fiber/matrix interface that has different physical properties than that of the bulk fiber and matrix materials. This interphase region may be caused by a fiber coating, fiber electrochemical treatment, or when poor adhesion between the fiber and matrix occurs due to processing conditions. Farmer[14] has observed that electrochemically treated AS4 fibers impregnated in a 3501-6 resin system are surrounded by a concentric interphase region, approximately 50-nm thick, which has a different chemical composition than that of the bulk matrix.

The effect such an interphase region has on the effective conductivity was studied by Hasselman and Johnson,[9] using a method first derived by Maxwell.[3] Chiew and Glandt[18] also studied the effect a resistance at the interface of spherical particles has on the effective conductivity using the method of Maxwell.[3] The Chiew and Glandt model represents the data well only for low dispersion volume fractions. Benveniste[19] also studied this effect for spherical particles, concluding that the self consistent scheme (SCS) method was valid for high dispersion volume fractions. However, Farmer[14] has experimentally shown that the SCS method used by Benveniste (equivalent to the lower bound model of Hashin[20]) is not valid for the effective conductivity of composites with high fiber volume fractions. Models previously derived by seven other authors[4,9,21–24] were also compared by Farmer[14] to his experimental data, and it was found that of these, only the Rayleigh model performed well through high fiber volume fractions. Therefore, the method of Rayleigh (he assumed perfect contact between fiber and matrix) was modified to account for an interphase region on the transverse thermal conductivity of the composite.

Most of the mathematics for the derivation of Rayleigh's[4] model are unnecessary for the current purpose and are not presented. Only the equations which are necessary to describe the modifications are presented, along with a verbal outline of Rayleigh's method. The Rayleigh paper should be read for complete mathematical detail of his derivation for the transverse conductivity of fibers arranged in a square order. The interfacial contact conductance is modeled by changing the boundary condition at the fiber/matrix interface, and Fig. 1 shows the geometry of Rayleigh's model. The applied temperature gradient is in the x direction. Rayleigh took the center of the P cylinder as the origin of the polar coordinates and observed the symmetry of the problem about both the x and the y axes so that

$$T_f = A_2 r \cos\theta_p$$
$$T_m = \left[A_1 r + \left(\frac{B_1}{r}\right)\right]\cos\theta_p \tag{1}$$

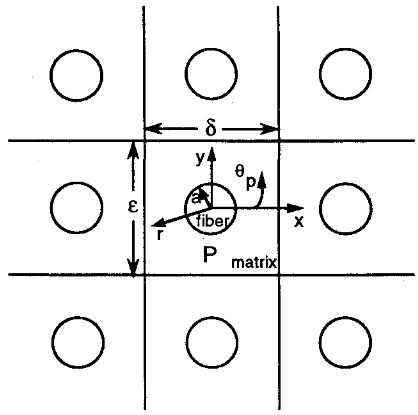

Fig. 1 Geometrical model for Rayleigh's method.

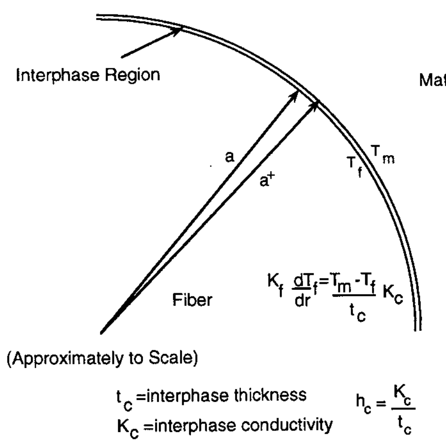

Fig. 2 Geometrical model of the interphase region.

where T_f and T_m are the temperature fields within the fiber and matrix, respectively, and A_1, A_2, and B_1 are unknown constants that will be determined. The other variables are defined in Fig. 1. A far-field temperature gradient (J_x^∞) is applied to the composite.

Rayleigh used two boundary conditions at the fiber/matrix interface: 1) radial heat flux as well as 2) temperature potential continuity. To model the interfacial contact conductance at the interface (which causes a temperature difference across the interphase region) the following boundary conditions can be used:

$$r = a \quad K_m\left(\frac{\partial T_m}{\partial r}\right) = K_f\left(\frac{\partial T_f}{\partial r}\right)$$
$$r = a \quad T_f - T_m = -\left(\frac{K_f}{h_c}\right)\frac{\partial T_f}{\partial r} \tag{2}$$

where h_c is the interfacial contact conductance [the interphase region conductivity (K_c) divided by its thickness (t_c)], while K_f and K_m are the fiber and matrix conductivities, respectively. Figure 2 shows the detail of this interphase region and how the second boundary condition of Eq. (2) is conceived by continuity of the radial heat flux at the fiber/interphase material region ($r = a$). This method of combining the interphase region thermal conductivity and thickness into one parameter (h_c) is generally necessary, because the interphase thickness is usually on the order of nanometers and is difficult to measure.

Applying the boundary conditions of Eq. (2) to the potential fields of Eq. (1), B_1 is solved in terms of A_1

$$B_1 = (a^2/v')A_1 \tag{3}$$

where ν' is defined as

$$\nu' = \frac{\left(\nu^{-1} + 1 + \frac{K_m}{ah_c}\right)}{\left(\nu^{-1} - 1 + \frac{K_m}{ah_c}\right)} \tag{4}$$

where $\nu = (K_f/K_m)$, and as h_c goes to infinity (i.e., interphase region resistance becomes negligible), ν' approaches the solution of Rayleigh.[4] Rayleigh applied Green's theorem to the contour of the region between the rectangle and the cylinder P. By doing so, the total flux across the contour caused by an infinite series of sources situated on the axes of the P cylinder in the x and y directions is calculated. Knowing the temperature gradient, the effective conductivity of the fiber elements in a square order is

$$\frac{K_{\text{eff}}}{K_m} \cong 1 - \frac{2p}{\nu' + p - \frac{3p^4}{\nu'\pi^4}S_4^2 - \frac{7p^8}{\nu'\pi^8}S_8^2 \ldots} \tag{5}$$

where the currently derived ν' is defined in Eq. (4). Where

$$p = (\pi a^2/\delta^2) = V_f \tag{6}$$

is the fiber volume fraction, the fibers are arranged in square order ($\varepsilon = \delta$) and Rayleigh calculated

$$S_4 = \frac{\pi^4}{60}(1.18034)^4$$
$$S_8 = \frac{\pi^8(1.18034)^8}{8400} \tag{7}$$

Figure 3 shows K_{eff}/K_m [Eq. (5)] plotted vs the V_f at various contact conductances for constant values of fiber radius and matrix conductivity. This figure shows that as the interphase region becomes less conductive (K_m/ah_c increases) the effective conductivity may actually decrease with an increasing V_f. Also, note that the nominal size of the fibers is now important for the determination of effective transverse thermal conductivity of the composite. For comparison, the Rayleigh solution is obtained when h_c goes to infinity. This is shown as $K_m/ah_c = 0.0001$ in Fig. 3.

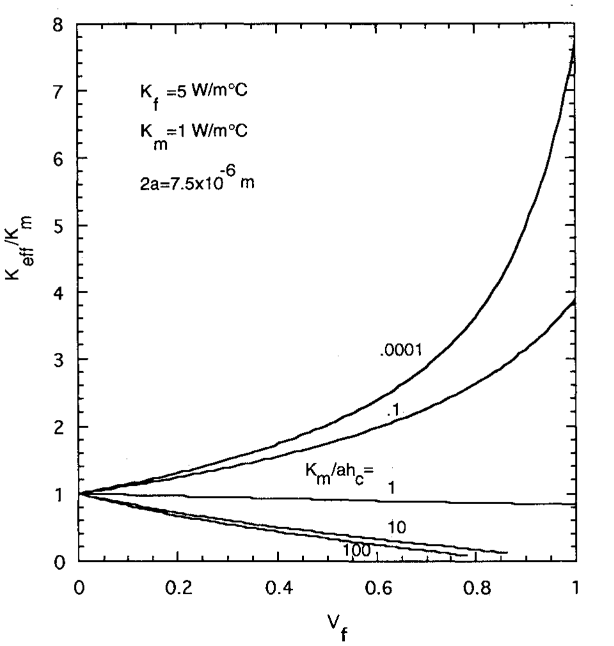

Fig. 3 Hypothetical transverse thermal conductivities for a composite with $\nu = 5$ for various values of K_m/ah_c.

Fibers Arranged in Rectangular Order

In his paper, Rayleigh stated that "the same mode of calculation may be applied without difficulty to any particular case of a rectangular arrangement."[4] Rayleigh found that the series expansion becomes unsymmetric with respect to the two directions when fibers are arranged in a rectangular order (now, $\delta \neq \varepsilon$). Therefore, a transverse anisotropy can be modeled. When the representative matrix rectangle has a moderate aspect ratio, the approximate effective conductivity may be calculated with

$$p = \frac{\pi a^2}{\delta^2} = \frac{\pi a^2}{\delta\varepsilon(\delta/\varepsilon)} = V_f\left(\frac{\varepsilon}{\delta}\right) \tag{8}$$

Eq. (5) can be used to calculate the conductivity in the x direction (parallel with δ), which is defined as being parallel to the direction of the applied temperature gradient. Therefore, Eqs. (5) and (8) can be used to predict a nearly linear relationship between the effective conductivity of a composite and the aspect ratio of the typical matrix rectangle surrounding a fiber. The rectangle aspect ratio used in Eq. (8) is defined as ε/δ, which can be measured statistically using photomicrographs taken by a scanning electron microscope.

Resin Heat Generation During Measurement of the Transverse Thermal Conductivity

The effect that resin heat generation has on the measured thermal conductivity of an uncured thermosetting composite is of interest for experiments conducted when the resin is not fully cured. The idea is to determine the thermal conductivity of a laminate with ongoing endothermic or exothermic reactions when the reaction rate is known from the cure kinetic equations measured for 3501-6 neat resin.[14]

The heat generation term is given by

$$\dot{q} = \rho_{\text{comp}}\frac{d\alpha}{dt}H_r \tag{9}$$

where H_r is for the composite, and $d\alpha/dt$ is the reaction rate of the resin. Figure 4 shows a differential element used for

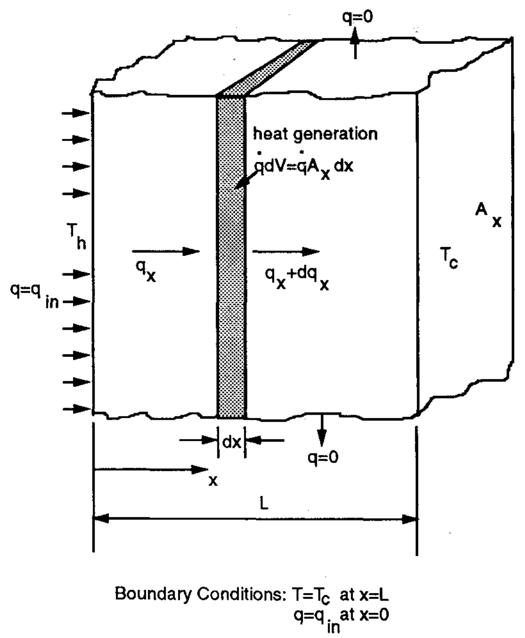

Fig. 4 Differential element and a control volume used for an energy balance. Boundary conditions for the thermal conductivity experiment are also shown.

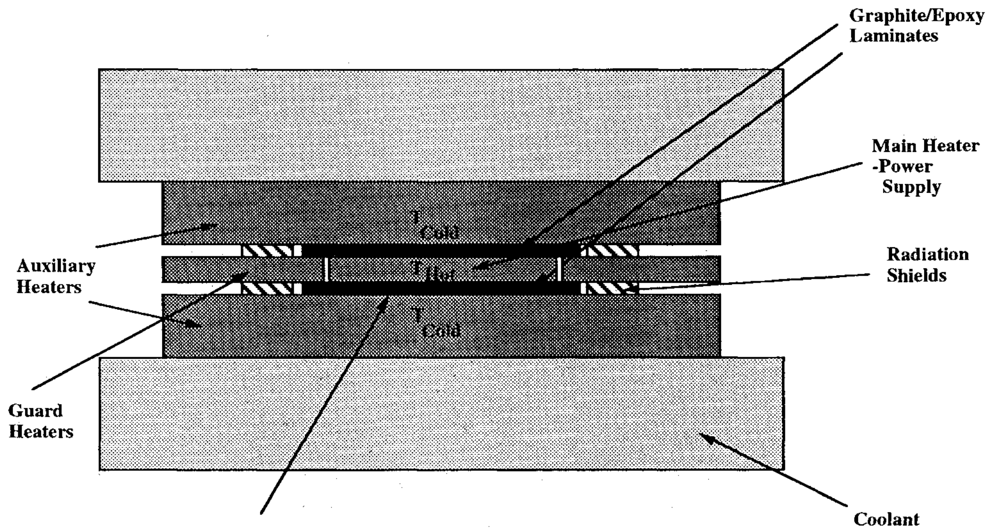

Fig. 5 Experimental setup enclosed in a vacuum for the thermal conductivity experiment using a guarded hot plate apparatus.

the problem where steady flow is assumed and a temperature gradient in only the x direction is applied by the guarded hot plate testing apparatus (described in the next section). Applying the "first law of thermodynamics" to the control volume (shaded region of Fig. 4) gives

$$q_x - (q_x + dq_x) + \dot{q}A_x\, dx = 0 \tag{10}$$

where A_x is a constant and q_x is in the x direction. Now, using Fourier's Law and eliminating q_x from Eq. (10) gives

$$\dot{q} = -\frac{d}{dx}\left(K_{\text{eff}}\frac{dT}{dx}\right) \tag{11}$$

where K_{eff} is the effective thermal conductivity of the material. Then, if K_{eff} is assumed to be constant and $\dot{q}$ does not vary within the volume element, integrating this equation twice and as shown in Fig. 4 applying the following two boundary conditions (in the experimental setup, the temperature is specified on one face of the laminate and the heat flux on the other)

$$\begin{aligned} T &= T_C && \text{at } x = L \\ q &= q_{\text{in}} && \\ &= -K_{\text{eff}}\frac{dT}{dx} && \text{at } x = 0 \end{aligned} \tag{12}$$

gives

$$T = -\frac{\dot{q}x^2}{2K_{\text{eff}}} - \frac{q_{\text{in}}x}{K_{\text{eff}}} + T_C + \frac{\dot{q}L^2}{2K_{\text{eff}}} + \frac{q_{\text{in}}L}{K_{\text{eff}}} \tag{13}$$

To solve Eq. (13) for the measured effective thermal conductivity, the temperature at $x = 0$ must be known, and is experimentally measured to be

$$T = T_H \qquad \text{at } x = 0 \tag{14}$$

and then substituting this into Eq. (13) and knowing that

$$\frac{(T_H - T_C)}{L} = \frac{dT}{dx} \tag{15}$$

gives

$$K_{\text{eff}} = \frac{dx}{dT}\left(q_{\text{in}} + \frac{\dot{q}L}{2}\right) \tag{16}$$

where K_{eff} is the measured effective thermal conductivity of a thermosetting composite. It has been assumed throughout this derivation that the thermal conductivity is not a function of temperature and that no heat loss occurs from the setup. In practice, both of these assumptions should be checked. It has also been assumed that $\dot{q}$ does not vary within the specimen being measured. This spatial invariance in resin reactions is accomplished by using low heating rates.[25] Equation (16) shows that if an exothermic reaction is occurring and the heat generation term is neglected, the measured thermal conductivity will be less than the actual for the material being measured. Of course, the opposite will occur for an ongoing endothermic reaction such as at the resin glass transition temperature T_g.

Manufacturing Procedure and Experimental Setup

Manufacturing Procedure

The advanced composite laminates were layed up by hand from a prepreg tape which had been stored below 0°F in a sealed container. A square jig was used to ensure that the plies were properly aligned during the lay-up. The lay-up was completed in a climate controlled room and the laminates were then cured in a Baron-Blakeslee autoclave. Special cure cycles and methods[14] were developed during this research to achieve composite laminates with unique properties. The plates were then cut using a water-cooled diamond grit cutting wheel. The laminates' final dimensions were 5.1 ± 0.25 mm thick, by 127 ± 2.5 mm wide and long. The thicknesses were measured exactly using a micrometer, while the length and width were measured using calipers.

Experimental Setup

A Dynatech TCFGM guarded hot plate was used to measure the thermal conductivity of the graphite/epoxy plates and is depicted in Fig. 5. The instrument is designed for measuring the thermal performance of materials of relatively low thermal conductivity.[26] The material tested must also be opaque and should ideally be homogeneous and isotropic. These last two material requirements are not met when testing an advanced composite, and therefore special precautions must be taken. These precautions will be described later.

The guarded hot plate is an absolute method of measuring the material thermal conductivity because no heat flux reference standards are required. The important components of the system include a guarded isothermal hot-surface plate (main heater) and two isothermal cold-surface plates. The main heater diameter is approximately 10.2 cm, and that of the concentric guard heater—which maintains the same temperature as the main heater—is 20.4 cm. These heaters are separated by a gap of 1.52 mm. Cooling plates are used at both ends of the stack as heat sinks to ensure that the stack does not overheat. The test specimens are placed between the isothermal surfaces, one on each side of the hot plate. The test method, therefore, averages the properties of two laminates which should have nearly identical properties. Therefore, each data point presented in this article is the average property of two nearly identical composite plates.

The power supplied to the main heater was measured as a voltage across the main heater and the current flow through the heater. This power, and therefore, the applied heat flux, was specified by the operator, and thus the heat flux was the known boundary condition at the isothermal hot surface. The isothermal cold surface temperature was also specified by the operator, therefore, the hot surface temperature was determined by the other two boundary conditions and was unknown until the system achieved equilibrium. The establishment of the above idealized conditions means that there are no radial components of heat flux (this was experimentally verified), and therefore the thermal conductivity of the plate in the direction normal to the isothermal plane was measured under steady-state conditions. In general, 5–10 h was necessary for the stack to achieve equilibrium. However, the rule used was that the stack was not in equilibrium until the measured temperatures changed less than 0.1°C in a half hour.

After all pieces of the stack were assembled, the top compression plate was lowered onto it and 20–30 lb of pressure was applied using a spring mechanism. The entire hot plate stack was placed under a bell jar and a vacuum was applied. A Varian SD 300 vacuum pump was used to first remove the moisture (15–20 min), and then the Varian Turbo-V200 vacuum pump was turned on and by the time steady-state conditions were established a vacuum on the order of 10^{-4} Torr had been achieved. The vacuum prevented convection away from the stack and across the gap between the main and the guard heaters. Preventing radiation of energy away from the stack was also important. The two critical areas where radiation must be prevented are 1) away from the main heater and 2) away from the composite plates. The guard heater prevented radiation from the main heater and silicone insulation was placed around the edges of the specimens. Finally, a grease (G-9030 silicone high vacuum grease—McGhan Nusil Corp.) was applied in a thin layer to both faces of all plate specimens. In a vacuum, this grease was necessary to promote thermal contact between the specimens and the aluminum plates, but was also a source of thermal resistance between the temperature measured by the thermocouples and the specimen. This contact resistance was measured and accounted for in the experiments.

Experimental Results

Transverse Thermal Conductivity as a Function of the Fiber Volume Fraction

The effective transverse thermal conductivity for plates of V_f = 0.0, 0.45, 0.57, and 0.64 was experimentally measured at temperatures of 95, 145, and 175°C. Figure 6 shows the modified Rayleigh model of Eq. (5) plotted with the experimental data at 145°C as well as the original Rayleigh model (h_c = infinite). In the figure, the bars represent an estimated 2% experimental error measured for the thermal conductivity experiments. A fiber diameter equal to 7.5 μm and K_m = 0.194 W/m°C were used in the model. A thermal contact conductance of $h_c = 4 \times 10^6$ W/m²°C was then used to best fit the experimental data. The Rayleigh model, with the inclusion of this small contact resistance between fiber and matrix, represents the data very well through relatively high-volume fractions. The Rayleigh model, when perfect contact between fiber and matrix is assumed (h_c = infinite), is shown to overpredict the conductivity at all fiber volume fractions.

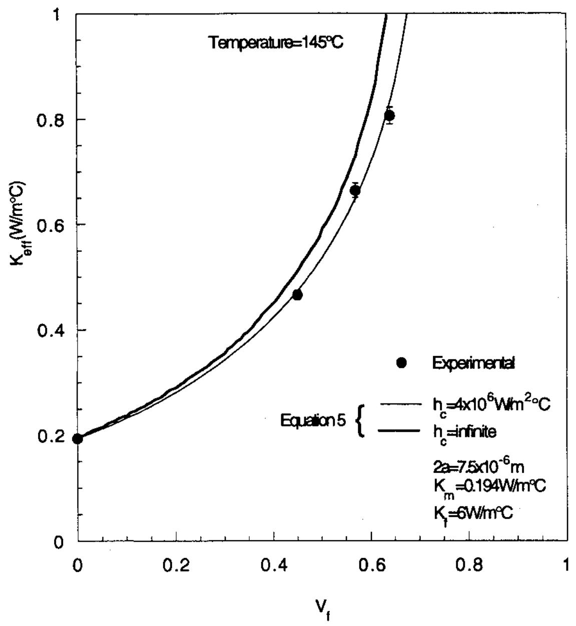

Fig. 6 Modified Rayleigh model with a small fiber/resin interfacial contact resistance plotted with the measured transverse thermal conductivity at 145°C.

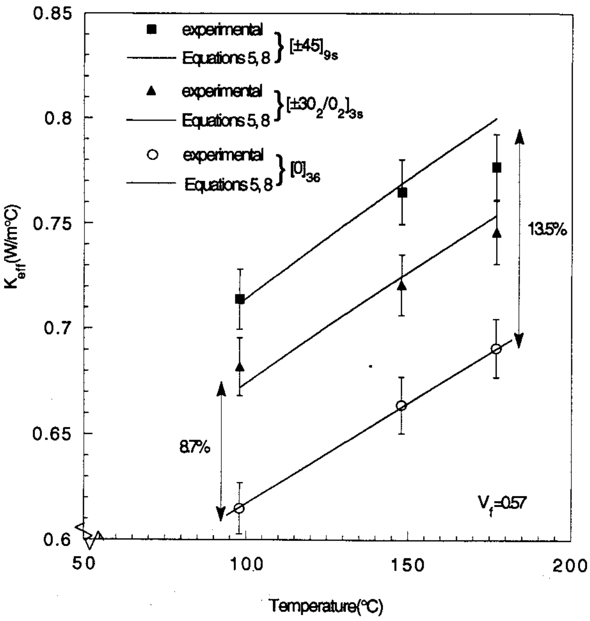

Fig. 7 Model based on typical resin element aspect ratio [Eqs. (5) and (8)] vs the experimental data.

There is presently no method of measuring the thermal conductivity of graphite fibers, so it is of considerable interest what value is extrapolated by the model. The present method, with the included interphase contact conductance, predicts a value of 6 W/m°C for the transverse thermal conductivity of the AS4 fibers (PAN-based fibers) at 145°C. The method also predicts values of 5.8 and 6.2 W/m°C at temperatures of 95 and 175°C, respectively.

Despite the physical reality of a fiber/matrix contact resistance due to a fiber coating, fiber electrochemical treatment, or poor adhesion, very little is known about its properties. The data presented by Farmer[14] offers evidence that an interphase region does exist around the surface of the AS4 fibers which have been electrochemically treated and were used for this research. It was found that the interphase region (50-nm thick) concentrically located around each fiber has a different chemical composition than the bulk matrix material. Equation (5) does predict a reasonable behavior (Fig. 3) for the effective conductivity as the interphase region becomes less conductive, but a value of $h_c = 4 \times 10^6$ W/m²°C was only chosen to best match the experimental data. Further experimental research remains to actually measure the h_c between the fiber and resin.

Transverse Thermal Conductivity as a Function of Ply Lay-Up Angle

Previous authors[27,28] have stated that the thermal conductivity of an advanced composite is a transversely isotropic property of the material. This suggests that the transverse thermal conductivity of a laminate should not vary with the ply lay-up angle. That is, a unidirectional laminate should have the same transverse conductivity as a multiangled laminate. However, Scott and Beck[12] have found that the transverse thermal conductivity of multiangled laminates is less than that of unidirectional laminates of the same volume fraction and at the same temperature.

Figure 7 shows the experimentally measured through-thickness transverse thermal conductivity of laminates with various ply lay-ups. It is seen that the transverse thermal conductivity of a $[\pm 30_2/0_2]_{3s}$ laminate is approximately 8.7% higher than a unidirectional laminate, and the $[\pm 45]_{9s}$ laminate has a measured conductivity of about 13.5% greater than the unidirectional case. At the same fiber volume fraction and temperature, the only possible explanation for this phenomenon is that the fibers of the multiangled laminates have settled closer together (in the measured through-thickness direction) during the cure than the fibers of a unidirectional laminate. In fact, Gutowski[29] has observed a similar phenomenon. He found that poor fiber alignment tended to decrease the V_f achievable at a given pressure during cure, which was perhaps due to more fiber-fiber touching in the transverse direction. This suggests that when fibers in a laminate are misaligned they tend to settle on (or at least closer) to each other more than in a "perfectly" aligned laminate.

Photomicrographs were taken using a scanning electron microscope (SEM) to test the hypotheses that the fibers of multiangle laminates are closer together in the measured (through-thickness) transverse direction than those of unidirectional laminates. Small samples from the $[0]_{36}$, $[\pm 30_2/0_2]_{3s}$, and $[\pm 45]_{9s}$ laminates were cut, polished, and photographed at 1000 magnification using the SEM. Six photomicrographs were analyzed from different areas of each laminate to obtain the representative matrix rectangle around a typical fiber. This was accomplished by measuring the resin distribution between fibers in both transverse directions on the photomicrographs. It was found that, in general, the average matrix element around a fiber was a rectangle, not a square as previously believed. It was found that the ratios of ε/δ for the laminates are

$$\begin{aligned} &[0]_{36} && \varepsilon/\delta = 1.02 \\ &[\pm 30_2/0_2]_{3s} && \varepsilon/\delta = 1.06 \qquad (17) \\ &[\pm 45]_{9s} && \varepsilon/\delta = 1.10 \end{aligned}$$

with all laminates having a $V_f = 0.57$. This proves that geometrically the fibers are, on average, closer together in the through-thickness direction of the plate (the direction of conductivity measurement) than perpendicular to it.

Equation (8) was used to calculate the ratio of fiber area to δ^2 utilizing the laminate V_f and the rectangle aspect ratios. Equation (5) was then used to calculate the effective conductivity of the three laminates with aspect ratios given in Eq. (17). A $K_f = 6.0$ W/m°C (extrapolated using the Rayleigh model), $K_m = 0.194$ W/m°C, $V_f = 0.57$, and no fiber/matrix contact resistance was assumed. The results of using Eqs. (5) and (8) are plotted with the experimental data in Fig. 7. It is seen that based on the typical resin element aspect ratio, the proposed model predicts the increase in conductivity for multiangled laminates as compared to a unidirectional laminate very well. This model is only valid for aspect ratios near 1.0 and has not been experimentally validated for aspect ratios greater than 1.10. Once again, it is emphasized that the transverse thermal conductivity varies with ply lay-up angle, because the average distance between fibers in the direction of measurement varies due to differences in fiber compaction during composite manufacture in an autoclave.

Transverse Thermal Conductivity as a Function of Resin Degree of Cure

To model the process of curing a thermosetting composite, its thermal conductivity must be known as the resin goes from an uncured state to being fully cured (degree of cure is equivalent to the percentage of resin chemical cross linking). A review of the literature showed that only Mijovic[10] had previously done this using a different thermosetting resin. His data show a large increase in composite conductivity as the resin cure progresses, and he predicts a 127% increase in composite thermal conductivity as the resin cures from approximately 10 to 90%. Mijovic attributes the increase in laminate conductivity to the chemical changes as the resin cure progresses.

In this work, the transverse thermal conductivity of AS4/3501-6 graphite/epoxy was measured at various stages of resin degree of cure. The degree of cure of each laminate was measured using a differential scanning calorimeter (DSC) and a method previously described[30] before its thermal conductivity was measured using the guarded hot plate. Figure 8 shows the experimentally measured apparent transverse thermal conductivity of a unidirectional laminate with a $V_f \approx 0.57$, and an initial resin degree of cure equal to $\alpha = 0.536$. The data show two offsets from a linear increase in conductivity with temperature. With increasing temperature the first offset is due to the endothermic phase transition known as the glass transition of the resin. It is seen that this reaction occurs in the region of 50–70°C, which compares favorably to the value of 60–70°C measured by a DSC[14] for a 50% cured graphite/epoxy sample. Farmer[14] also measured a reaction energy of 0.05 W/g using the DSC which compares favorably to the value of 0.06327 W/g necessary to cause the offset in Fig. 8 (each point represents a 1.5 hour test). The second offset is due to the exothermic cure reaction of the resin. That is, during the higher temperatures of this test, the resin is curing. At the initial temperature, 40°C, the laminate $\alpha = 0.536$, but when the last data point is taken, 177°C (test time is 1.5 h at 177°C which has been measured in the DSC to produce a $\alpha = 0.96$) the laminate $\alpha = 0.96$. By using Eqs. (16) and (9)

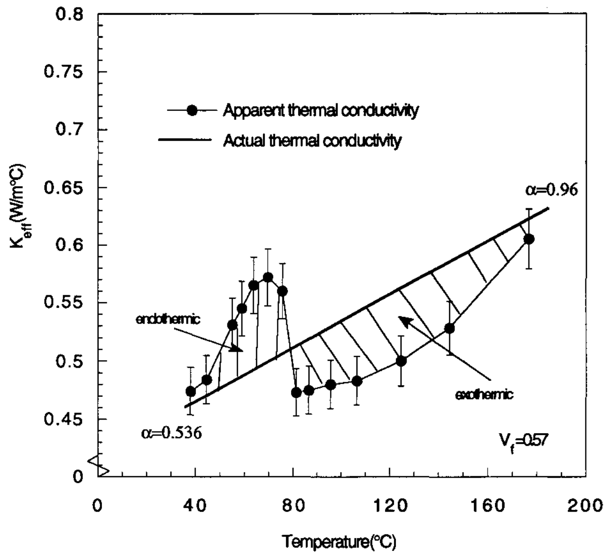

Fig. 8 Experimentally measured apparent conductivity as well as actual thermal conductivity calculated using Eqs. (9) and (16). The regions of the resin's reactions are also shown.

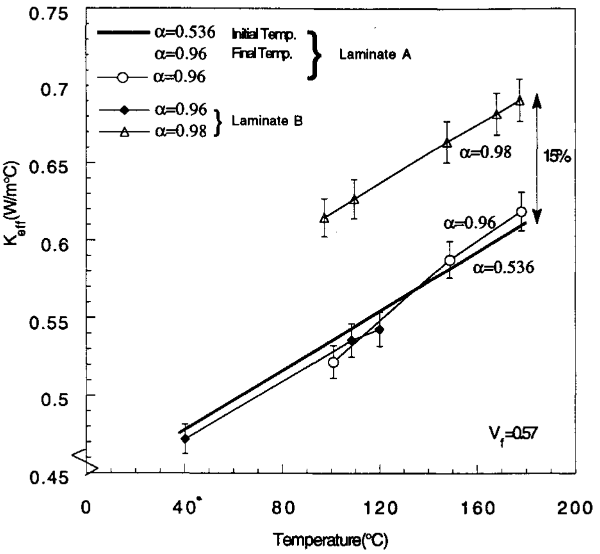

Fig. 9 Experimentally measured thermal conductivity as a function of the resin degree of cure.

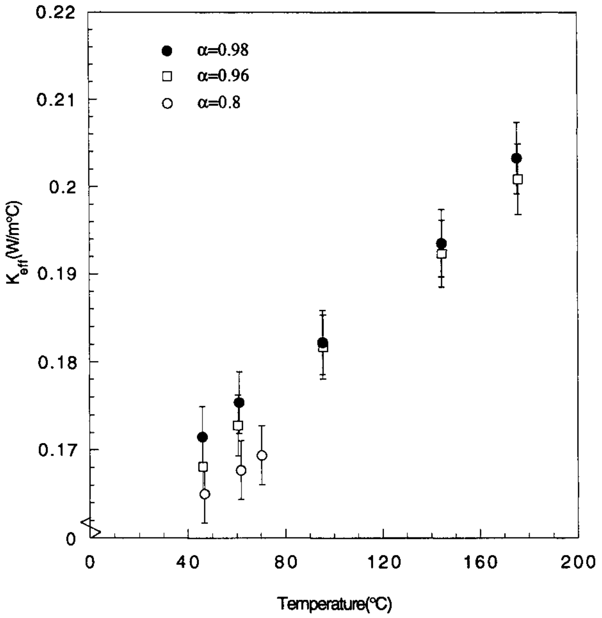

Fig. 10 Experimentally measured transverse thermal conductivity of 3501-6 neat resin cured to various degrees of cure.

to calculate the effect the heat generation has on the measured conductivity, it is found that the actual conductivity is a linear curve (within 10%) in this region as shown in Fig. 8. Accuracy greater than this cannot be expected due to the limitations of Eq. (9).[14]

Figure 9 shows a second experimental test of the laminate previously discussed (laminate A), this time at $\alpha = 0.96$, as well as another laminate (laminate B) at $\alpha = 0.96$. The cure reaction rate has decreased enough at this stage of cure that effectively no exothermic reaction is occurring and the test is taken at a constant degree of cure, $\alpha = 0.96$. Note that before the resin reactions begin, the $\alpha = 0.536$ laminate has approximately the same conductivity as the $\alpha = 0.96$ laminate at 40°C. Note also that at 177°C the laminate with initial $\alpha = 0.536$ has cured to a measured $\alpha = 0.96$ (test time is 1.5 h at 177°C), and has approximately the same measured conductivity as the laminate with $\alpha = 0.96$. The comparison of these three experiments suggest that the thermal conductivity of the graphite/epoxy laminate does not vary with resin degree of cure in the region $0.536 \leq \alpha \leq 0.96$. However, Fig. 9 does show a large increase in the thermal conductivity with resin degree of cure in the region $0.96 \leq \alpha \leq 0.98$. The 98% degree

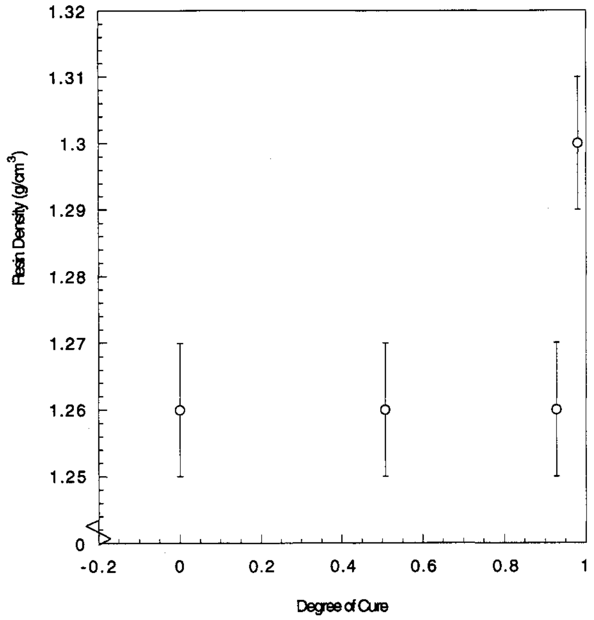

Fig. 11 Experimentally measured resin density at 21°C as a function of degree of cure.

of cure is achieved by curing the laminate at 177°C for 10 h. As previously stated, the chemical reaction has effectively ended when the resin reaches $\alpha = 0.98$.

Based on the previous discussion, an increase in thermal conductivity occurs in the region $0.96 \leq \alpha \leq 0.98$, but does not seem to increase in the region $0.536 \leq \alpha \leq 0.96$. This dramatic increase in laminate conductivity near the end of the resin cure could occur for two possible reasons: 1) an increase in the resin thermal conductivity or 2) an increase in resin density in the region $0.96 \leq \alpha \leq 0.98$.

Figure 10 shows the measured thermal conductivity of a 3501-6 neat resin slab cured to various degrees of cure. The $\alpha = 0.80$ sample was measured only below its glass transition temperature. It is seen that only a small increase in conductivity ($\approx$2%) occurs for $0.80 \leq \alpha \leq 0.96$, and another 2% for $0.96 \leq \alpha \leq 0.98$. The experimental error ranges for these three groups of data overlap, and therefore the data does not show a significant increase in resin conductivity in the range $0.80 \leq \alpha \leq 0.98$. Figure 11 shows that at room temperature the experimentally measured (using a specific gravity kit) resin density increases 3.1% from 1.26 g/cm^3 to 1.30 g/cm^3 upon reaching final cure at $\alpha = 0.98$. Therefore, it is probable that the increase in transverse thermal conductivity of a laminate is due to resin shrinkage upon final cure which increase the fiber volume fraction of the laminate, and therefore its transverse thermal conductivity. The increase is not due to a change in resin conductivity as the resin degree of cure increases.

Based on this research, the results of Mijovic[10] have to be questioned. He also studied a thermosetting resin, but nowhere in his paper does he mention how the ongoing exothermic reactions were accounted for when the conductivity of a partially cured laminate was measured. It is very possible that he was measuring an effect similar to the one shown in Fig. 8, and perhaps incorrectly concluded that the laminate conductivity increased with cure, when actually he was measuring an unaccounted-for resin exothermic reaction.

Conclusions

Rayleigh's model, which was originally valid for closely packed fibers in square order with perfect fiber/matrix adhesion, has been extended. The new model is capable of representing the effects an interphase region near the fiber surface, and an unequal resin distribution in the two transverse directions have on the effective transverse thermal conductivity of a fiber-reinforced composite. A model was derived that accounts for the effect of resin heat generation on the measured thermal conductivity of an uncured thermosetting composite.

These models were investigated experimentally using a guarded hot plate apparatus to measure the thermal conductivity of the graphite/epoxy as a function of temperature, resin degree of cure, fiber volume fraction, and the ply lay-up angles within the laminate. It was found that the Rayleigh model for square packed fibers, with the inclusion of a small contact resistance between fiber and matrix, represents the experimental data very well through relatively high volume fractions. It was also shown that this fiber/matrix contact resistance may have a dramatic effect on the transverse thermal conductivity, but further research remains to experimentally measure this contact resistance.

Good agreement between the model and experimental data was found for transversely anisotropic laminates with average rectangular matrix elements of aspect ratios up to 1.10. Using the method which accounts for resin heat generation, it was determined that the thermal conductivity of the composite does not change with resin degree of cure in the region $0.536 \leq \alpha \leq 0.96$. However, upon final cure ($0.96 \leq \alpha \leq 0.98$), a dramatic resin shrinkage causes the unidirectional composite thermal conductivity to increase 15%.

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