ORIENTATION SPECIFIC THERMAL PROPERTIES OF POLYIMIDE FILM

Robert J. Samuels
School of Chemical Engineering
Georgia Institute of Technology
Atlanta, Georgia, 30332-0100 USA

Nancy E. Mathis
Mathis Instruments Ltd.
Fredericton, New Brunswick,
Canada, E3B 6C2, nancy@mathis.unb.ca

ABSTRACT

The present study examines the relationship between thermal conductivity and planarity in polyimide films. The samples tested were specially prepared to range in orientation from three dimensionally random to highly planar. The molecular structure and orientation of the polyimide film have been characterized by polarizing microcope techniques, while the thermal conductivity measurements were done using a new rapid nondestructive technique.

This correlation represents the first time thermal conductivity has been measured by modified hot wire techniques and related to the internal structure of polyimide. This work contributes to a deeper theoretical understanding of thermal conductivity and heat transfer mechanisms as they relate to orientation. Thermal conductivity evaluation could provide a new tool in the arsenal of structural characterization techniques.

This relationship between thermal conductivity and orientation is key for applications of directional heat dissipation in the passive layers of chip assemblies. Such a correlation has potential to speed the development cycles of new materials during formulation as well as assure properties during production.

INTRODUCTION

Polyimides are advanced materials which have good high temperature stability, excellent dimensional stability, and excellent mechanical, electrical, and chemical resistance properties. They can be molded (jet engine parts, glass fiber-reinforced blocks, printed wiring boards, etc.), produced as films (in electric motors, flat flexible cable and magnetic wire insulation for aircraft and missiles, etc,), or applied as coatings (semiconductor devices and electrical components). For these reasons polyimides are of particular interest to the aerospace, auto and electronic industries, as well as other industries that require high quality and performance.

The model single phase nematic polymer used in this study, PMDA-ODA polyimide [PI], is the oldest and most successful of the polyimides. It is a pyromellitimide made by reacting pyromellitic dianhydride (PMDA) with oxydianaline (ODA) [1]. It has become the standard material to which all new polyimides (and competing chemistries) are compared.

It is well known that morphological structure dictates properties in polymers [2,3,4]. Structure is also the factor that couples the fabrication process to the physical properties, and is the principal ingredient for predicting behavior. One property of particular interest to the packaging industry is thermal conductivity. The relationship between thermal conductivity and orientation is key for applications of directional heat dissipation in the passive layers of chip assemblies. Such a correlation has potential to speed the development cycles of new materials during formulation as well as assure properties during production [5]. The present study examines two questions; (a) can a nondestructive modified hot wire technique be used to obtain quatitative anisotropic thermal conductivity values; and (b) do the thermal conductivity values correlate with molecular planarity in polyimide films.

EXPERIMENTAL

Materials

A series of five Kapton films, designated PI-1 to PI-5, were supplied by duPont de Nemours and Company. This

series of films was designed to represent a wide range of sample planarity, from three-dimensionally random to very planar, with very little in-plane anisotropy.

Polarized Optical Microscopy

The principal birefringences and refractive indices of these films were characterized using a Carl Zeiss Universal R Pol microscope coupled with a Carl Zeiss quartz Ehringhaus compensator. In order to avoid any complications from interactions between the optical dispersion of the compensator and that of the polymer film, PMDA-ODA polyimide polymer retarders were used that have retardations high enough to insure that the value measured by the compensator is always within a small optical path difference, i.e., within the first order range (below 550 nm retardation). This eliminates any white light dispersion effects [6,7].

In order to characterize the amount of planar orientation in a material, the planarity index, Δ_p , is used. The planarity index is defined as:

$$\Delta p = \left[\frac{n_z + n_y}{2}\right] - n_x \qquad (1)$$

Where n_z and n_y are the refractive indices in the plane of the film, and n_x is the refractive index perpendicular to the plane of the film. The first term is the average of the in-plane refractive indices and Δ_p, the planarity index, is the birefringence between the randomized in-plane refractive index and the through-the-plane refractive index. The planarity index of an isotropic sample ($n_x = n_y = n_z$) takes on a value of zero, and increases with increasing planar orientation.

Thermal Conductivity

The thermal conductivity of the films was measured using a TC Probe™, distributed by Perkin Elmer. This instrument is an interfacial device that contacts and detects heat flow from the same side of the sample. As thermal conductivity of a material increases, heat flow from the heating element increases and the temperature rise over time at the interface decreases. This inverse relationship between slope, m, of the temperature rise over time versus the thermal conductivity is the principle of operation that allows calibration to occur.

The instrument was calibrated with known standards and operated with parameters that included a test time of 0.25 seconds, with data evaluated from 0.05 seconds onward. The data acquisition rate was 400 Hz with cooling between tests of 15 seconds. The calibration plot relates instrument response in volts to the material thermal effusivity in $W\sqrt{s}/m^2 \cdot K$ (Figure 1). Thermal effusivity, $\sqrt{(k\rho c_p)}$, is defined as thermal conductivity, k, multiplied by density, ρ, and heat capacity, c_p.

After the instrument was calibrated, the measurements on the film were conducted using a blotter technique, as is prescribed by the manufacturer for samples less than 1 mm thick [8]. This method assures that only the film is tested,

$$Effusivity = E_{ff} = \sqrt{k\ r\ c_p} \quad \left(\frac{W\sqrt{s}}{m^2 \cdot K}\right)$$

$$Where:$$

$$k = thermal\ conductivity \quad (W/m \cdot K) \qquad (2)$$

$$r = density \quad (kg/m^3)$$

$$c_p = heat\ capacity \quad (J/kg \cdot K)$$

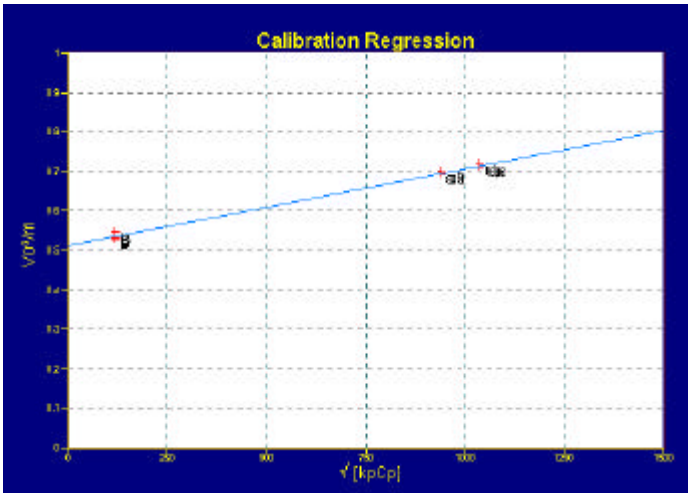

Figure 1: The TC Probe™ is calibrated with known reference standards to produce a linear calibration equation (r=0.996).

without influence of air on the opposite side of the sample. To test using this technique, the thin sample with cross sectional area over 5 mm x 50 mm is placed in contact with the sensor interface. At least two tests are run on each film sample: one with the blotter being a metal material and the second test with the blotter being an insulating foam. Refer to the experimental set-up provided as Figure 2.

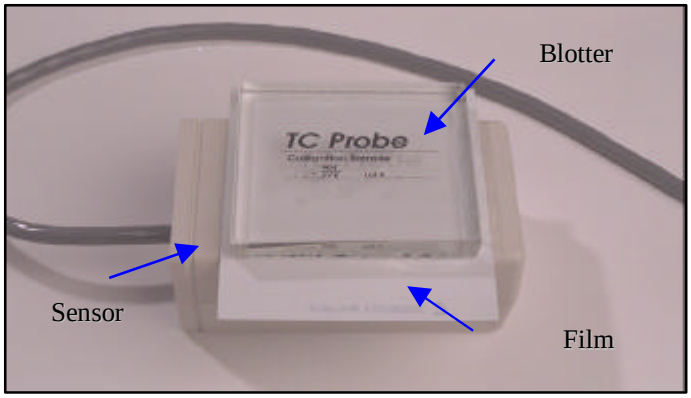

Figure 2: The thin film is placed between the sensor and the blotter so that the saturation point can be determined.

As the testing progresses in time, the heat wave passes through the film until $t^{1/2}$ equals $t_{deviation}$. During the time period of the heat wave being resident in the film, the temperature

detector is not aware of the blotting material so the slope of the data is the same for the two tests. After $t_{deviation}$, the heat wave penetrates far enough into the sample to reach the boundary between the film and the blotter. The data then deviates and the slope increases for the insulating foam and decreases for the conductive metal (see Figure 3).

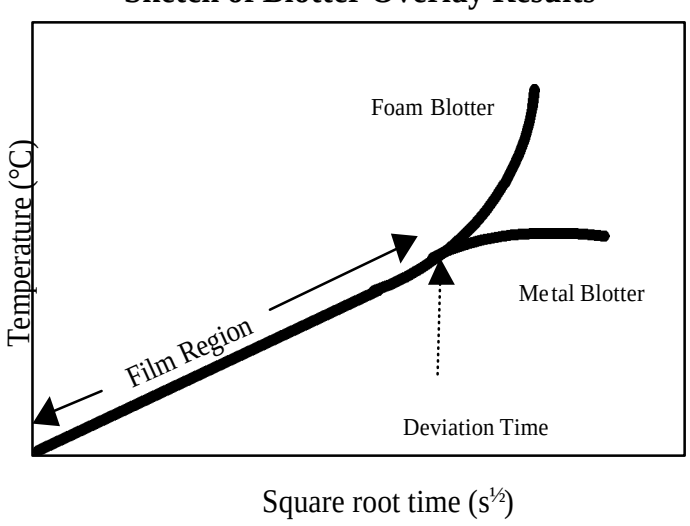

Figure 3: A sketch of blotter overlay results illustrates the effect of metal and foam blotters on the slope of the traces.

In practice, it is difficult to see the deviation point without overlaying the plots with two different blotters. The data must be evaluated by saving both tests and then using the retrieve function of the software to overlay the test plots. The deviation point can be seen clearly on the graph with the overlaid plot being zoomed for easier identification. The data in the initial region representing the film can then be regressed, either separately or as an averaged data set. If properly evaluated, the results of such regressions for two runs on the same sample, but different blotters, fall within ± 5%.

When 2 layers of polyimide film, labeled PI-1, were tested under these conditions, it can be seen from Figure 4, that there is no saturation occurring prior to 0.5 sqrt seconds. The mean effusivity ($\sqrt{k\rho c_p}$) for PI-1 with a two layer thickness of 0.246 mm (0.9836 mil) was 1091 $W\sqrt{s}/m^2 \cdot K$ ± 5.5%. The results for the remaining five samples tested are summarized in Table 1.

With transient methods such as this, density and heat capacity are required for the materials in order to calculate thermal conductivity from the instrument result of effusivity. Nominal values of ρ and c_p could not be used because they may have varied as an effect of orientation. If ρ and c_p are measured, the increase in time per material test may reduce the benefit of the rapid thermal conductivity measurement.

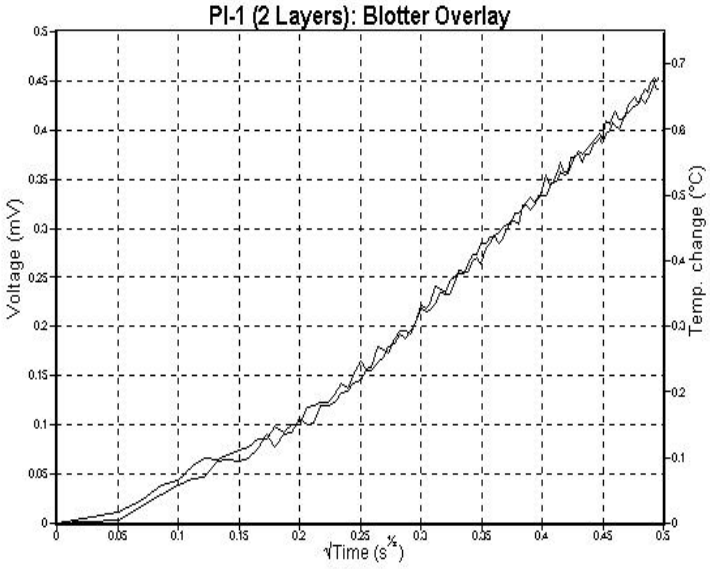

Figure 4: No deviation occurs between these two averaged blotter plots, indicating that the heat wave has not passed into the blotter material and that the results represent only the polyimide film.

Table 1: Effusivity values for Kapton samples

Sample	Sheet thickness (mm)	Number of layers tested	Sample thickness (mm)	Effusivity ($W\sqrt{s}/m^2 \cdot K$)
PI-1	0.123	2	0.246	1091 ± 5.5%
PI-2	0.077	4	0.308	1094± 3.0%
PI-3	0.0259	8	0.228	985.5± 5.2%
PI-4	0.025	3	0.0756	989.6± 6.2%
PI-5	0.022	12	0.259	989.2± 4.8%

This difficulty has been removed with the successful demonstration of a new data evaluation technique that produces thermal conductivity directly. The only additional physical property that is required is material thickness, overcoming the need for determination of density and heat capacity of the test material. The method uses the blotter technique to locate the time where the sample is penetrated. This time with the sample thickness can be used to find diffusivity based on the Einstein relationship (Equation 3). This relationship quantifies the distance travelled by 1% of a heat wave in a given time, through a material of known diffusivity. The constant, 4, is a nominal value related to the percentage of heat that saturates the sample. Through calibration, the coefficient for the TC Probe™ has been determined to be 2.00.

$$d = \sqrt{4at}$$

Where:

$$d = sample\ \ thickness\,(m) \tag{3}$$

$$a = diffusivity\ (m^2/s) = \frac{k}{r\ c_p}$$

$$t = time\,(s)$$

The diffusivity measurement can be conducted on thin or highly conductive material samples. Such materials must be stacked in order to evaluate effusivity. Otherwise, the heat transmits so rapidly that insufficient data is acquired to accurately determine the slope of the data for use in measurements.

The constant, 4, in the Einstein equation assumes that one percent transmission of heat can be detected. The TC Probe™ sensitivity to transmitted heat was unknown, but through experiments with materials of known diffusivity and thickness, the instrument constant was determined to be 2.00.

Using the calibration constant of 2.00 for this instrument's sensitivity [9], k can be calculated directly. First diffusivity is obtained by conducting at least two tests using the blotter technique and finding the deviation time. Then the slope of the data prior to the deviation time can be used to find effusivity under normal operating parameters.

$$From\ definition \mathrm{K}\ \ k = \sqrt{a}\cdot E_{ff}$$

or

$$k \equiv \sqrt{\frac{k}{r\ c_p}}\cdot\sqrt{k\ r\ c_p} \equiv \frac{\sqrt{k}}{\sqrt{r\ c_p}}\cdot\sqrt{k}\cdot\sqrt{r\ c_p} \tag{4}$$

$$Where: \sqrt{a} = \frac{d}{\sqrt{2.00\cdot t_{deviation}}}$$

$$Giving: k = \frac{0.707\cdot d\sqrt{k\ r\ c_p}}{\sqrt{t_{deviation}}}$$

The timing options utilized were established to ensure the test time was sufficient to achieve saturation for several layers of material as well as complete cooling between tests. Several blotter tests need to be conducted for each blotter material and the data saved. The saved files are then retrieved and overlaid on a single graph to verify that there are no deviations or anomalous spikes. The trials for each blotter are averaged to smooth instrument noise and facilitate the clear determination of the deviation time. The averaged data plot for the foam blotter is overlaid with that for the metal blotter to determine the deviation time from the zoom function of the software to examine the area of interest.

RESULTS

Figure 5 illustrates the results from testing one layer of PI-1. The foam and brass backing materials were each used to test the material for five repetitions. This deviation point was determined to be 0.3525 $s^{1/2}$. This yields a thermal conductivity result of 0.269 W/m·K. This process was repeated for four additional polyimide samples and the results are shown in Table 2.

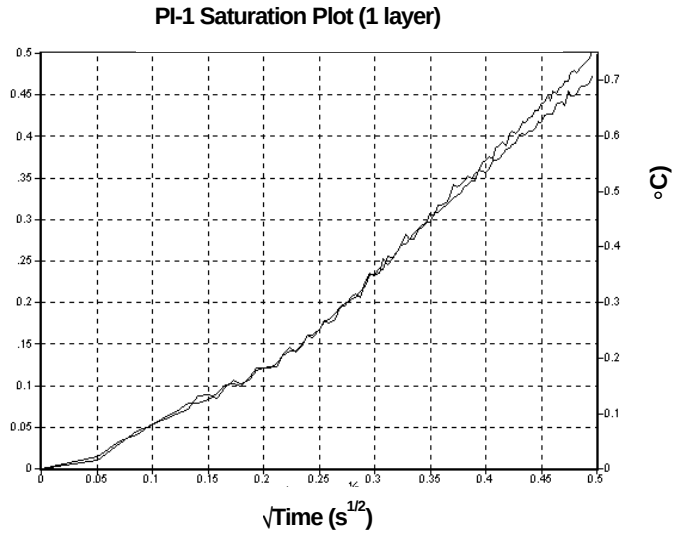

Figure 5: The separation of plots indicates the point where the heat wave has penetrated the PI-1 sample (0.3525 $s^{1/2}$).

Table 2: Thermal conductivity of oriented polyimide

Sample	Sample thickness (mm)	Effusivity ($W\sqrt{s}/m^2K$)	Deviation point ($s^{1/2}$)	k (W/m·K)
PI-1	0.123	1091	0.3525	0.269
PI-2	0.0770	1094	0.2236	0.266
PI-3	0.103	985.5	0.3460	0.208
PI-3	0.0775	985.5	0.2782	0.194
PI-4	0.126	990	0.3645	0.242
PI-5	0.173	989	0.4075	0.297
PI-5	0.130	989	0.3110	0.292
PI-5	0.0866	989	0.2240	0.271

Thermal conductivity was compared to previously obtained planarity index values that are listed in Table 3. The relationship between planarity and thermal conductivity is plotted as Figure 6.

Table 3: Planarity index of polyimide samples

Sample	Planarity index	k (W/m·K)
PI-1	0.0356	0.269
PI-2	0.0424	0.266
PI-3	0.1511	0.208
PI-3	0.1511	0.194
PI-4	0.1227	0.242
PI-5	0.0250	0.297
PI-5	0.0250	0.292
PI-5	0.0250	0.271

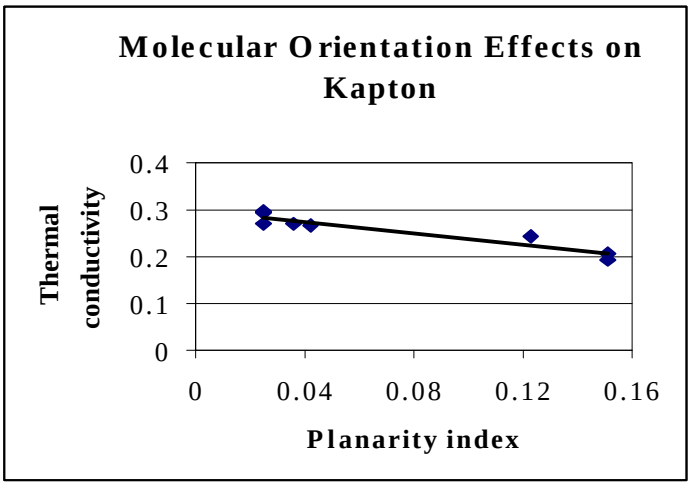

Figure 6: Thermal conductivity decreases with increasing planarity index.

DISCUSSION

Polymer molecules, as a consequence of their long chain construction, are inherently anisotropic. Thus any process which effects their alignment will result in materials which have different properties in their three principal directions. An example of such processes is spin coatings on silicon wafers. Here, a drop of polymer liquid is placed on a spinning wafer. The speed of rotation causes the liquid to spread symmetrically on the surface. This process creates an anisotropic system in which the molecules are symmetrically aligned within the surface but, depending on the speed of rotation, have greater or lesser alignment in the direction normal to the surface. That is, the system can range from isotropic to highly planar.

The PI films used in this study were fabricated to emulate spin coated materials. That is, they were processed to have essentially random molecular orientation in the plane of the film, with varying degrees of planar orientation with respect to the films thickness direction. By characterizing the films using the planarity index, any minor anisotropy in the plane of the film is effectively randomized by the planar averaging function in equation (1).

The TC Probe^{TM} is a rapid nondestructive hot wire heat flow device. One goal of this study was to obtain the thermal conductivity of the planar PI films by utilizing the temperature - time curve produced by a modified procedure. This allows the effusivity to be obtained by combining the slope of the linear region (Figure 4) with the instrument calibration curve. The diffusivity could be obtained by using the blotter technique to determine the time where the sample is penetrated, measuring the sample thickness and combining this with the Einstein equation (Equation 3). Multiplication of the diffusivity by the effusivity then yields the desired thermal conductivity. This modified procedure makes the TC Probe^{TM} a unique tool for the rapid nondestructive determination of thermal conductivity of films.

The thermal conductivites obtained for the PI films are listed in Table 2. The TC Probe^{TM} is designed to measure the heat flow normal to the film surface being contacted. Thus the thermal conductivities listed in Table 2 represents heat flow in the samples x - direction (through the thickness). It is differences in orientation in the x - direction that the planarity index measures.

The thermal conductivity of the PI film is plotted against the planarity index in Figure 6. This correlation represents the first time thermal conductivity has been measured by modified hot wire techniques and related to the internal structure of polyimide. The thermal conductivity normal to the film surface is seen to be inversely proportional to the planarity index. This is reasonable since heat travels along the molecular chains faster than between chains.

Consider a three dimensionally random (isotropic) film. The planarity index for this film would equal zero. One could model this as having an equal number of chains aligned in all three directions. Since the highest thermal conductivity is along the chain axis, this would yield the same conductivity in all three directions. As the film becomes more planar, more of the molecules that were aligned perpendicular to the plane now align in the plane. This would lead to an increase in the thermal conductivity in the plane, and a decrease in the thermal conductivity normal to the plane. That is, the thermal conductivity normal to the film surface would be inversely proportional to the planarity index, as experimentally observed in Figure 6.

CONCLUSIONS

We can conclude from this study that (a) the TC Probe^{TM} nondestructive modified hot wire technique can be used to obtain quantitative anisotropic thermal conductivity values; and (b) the thermal conductivity values obtained correlate with the molecular planarity in polyimide films. The above correlation represents the first time thermal conductivity has been measured by modified hot wire techniques and related to the internal structure of polyimide. Thermal conductivity evaluation could provide a new tool in the arsenal of structural characterization techniques.

This work contributes to a deeper theoretical understanding of thermal conductivity and heat transfer mechanisms as they relate to orientation. Relationships such as the above between thermal conductivity and orientation is key

for applications of directional heat dissipation in the passive layers of chip assemblies. Such correlations have the potential to speed the development cycles of new materials during formulation as well as assure properties during production

REFERENCES

[1] P. E. Cassidy, Thermally Stable Polymers: Synthesis and Properties, Marcel Dekker, Inc., New York (1980).

[2] R. J. Samuels, "Structured Polymer Properties. The Identification, Interpretation, and Use of Polymer Structure," Wiley-Interscience, New York, 1974.

[3] R. J., Samuels, "Polymer Structure: The Key to Process-Property Control", special symposium issue of Polymer Engineering and Science entitled, "Polymer Process-Structure-Property Relationships", 25, 864 (1985).

[4] S. Hardaker and R.J. Samuels, "Quantitative Characterization of Anisotropic PMDA-ODA Film Properties", in "Polyimides: Trends in Materials and Applications", C. Feger, M.M. Khojasteh, and S.E. Molis, Eds., S.P.E. Pub., (1996) 267.

[5] Mathis, N.E., "New Instrument for Thermal Management Design", IMAPS International Symposium on Packaging Systems, San Diego, January 1999.

[6] C. Y. Cha, S. Moghazy and R. J. Samuels, "Optical Characterization of Three Dimensional Surface and Bulk Anisotropy in High Refractive Index Polymers",Polym. Eng. Sci., **32**, 1358 (1992).

[7] Cha, C. and R.J. Samuels, " Effect of Orientation on the Relative Dispersion of PMDA-ODA Polyimide and Polypropylene", J. Polymer Sci., Part B: Polymer Physics, 33, 259 (1995).

[8] Mathis, N.E., Browne, J., "Thermal Conductivity of Thin Film Carbon Fiber Die Attach", SPE RETEC, (1998).

[9] Mathis, N.E., "Eliminating Density and Heat Capacity Requirements in Transient Thermal Conductivity Measurements**",** SPE ANTEC, (1999).