Thermally Conductive Polymer Composites for Electronic Packaging

X. LU, G. XU

Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario L8S 4L7, Canada

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ABSTRACT: Polyurethane composites filled with alumina or carbon fibers were prepared to study the thermal conductivities and dielectric properties of polymer composites under humid environments. The thermal conductivities of these polymer composites in relation to filler concentrations and filler sizes were investigated and it was found that the thermal conductivities can increase up to 50 times that of pure polyurethane. The results were analyzed using Agari's model to explain the intrinsic reasons to affect the thermal conductivities of composites. The dielectric loss of these polymer composites were also measured to estimate the influence of moisture under various humid environments. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2733–2738, 1997

Key words: polymer composites; thermal conductivity; dielectric loss; moisture resistance; electronic packaging

INTRODUCTION

There has been long-standing interest in flexible polymer materials for electronic packaging, which are both thermally conductive and electrically insulating under a humid environment.[1,2] For example, in thin-film flat-panel electron luminance device (TFEL), people are looking for such packaging materials which can be easily applied onto the panel as coatings, to conduct the heat generated during the light emission, as well as to act as an insulation layer against moisture attack.[3]

However, although being good insulators, polymers are, in general, poor thermal conductors, not to mention that their dielectric properties are easily affected by the presence of moisture. One solution to this problem is to make polymer composites with increased thermal conductivity. Although many articles have been published on the improvement of thermal conductivities of polymers by fillers[4–6] and several on the thermal conduction mechanism and models,[7–9] little has been done on polymer materials providing both thermal conductibility and resistance to moisture. It was, therefore, the purpose of this report to find a polymer composite system to meet the above challenges.

In this article, we present data on polyurethane (PUR) composites filled with alumina (Al_2O_3) or carbon fibers (CF) under various volume fractions and studied their thermal conductivities in relation to the filler sizes. Then, we fit the data to investigate the difference of thermal conductance between PUR/Al_2O_3 and PUR/CF systems. Finally, the dielectric relaxation measurements were conducted to estimate the effect of moisture on the electric properties of these polymer composites.

EXPERIMENTAL

Materials

For the polymer matrix, polyurethane (PUR) was chosen because, normally, it generates no small

Correspondence to: G. Xu.

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Table I Properties of Materials

Material	Dimension (μm)	Thermal Conductivity (W m^{-1} K^{-1})
Polyurethane (PUR)	(MW ≈ 10,000)	0.31
Carbon fiber (CF)	$\phi 8 \times 30$	209
	$\phi 8 \times 100$	209
Al_2O_3	20	33
	100	33

molecule byproduct during the polymerization. It was purchased from Normac Adhesive Products Inc. (BR-3S). Alumina (Al_2O_3) powders were from Alfa Co. Two series (20 and 100 micron average diameters) were selected. The carbon fibers were also from Alfa Co. They are PAN-type fibers of 8 microns in diameter and 6.4 mm in length on the average. To cut the fibers into short lengths, they were rolled in a ball-grinding miller for either 30 or 90 min. The resulting average lengths became 100 and 30 microns, respectively. The properties of these materials are summarized in Table I.

Specimen Preparation

After drying in 200°C for 4 h, alumina or carbon fibers were mixed into the polyurethane solution using chloroform as the solvent at 60°C. When most of solvent was evaporated, the mixture was cast onto a Teflon® plate to form a film. Finally, the specimens were dried in a vacuum oven at 40°C for 24 h to remove residual solvent and moisture. Dry samples were then stored in a desiccator.

Characterization

The thermal conductivities of the composites were determined by measuring the temperature drop across a flat sample.[10] According to the Fourier's law of heat conduction,

$$Q = \kappa A \Delta T / x \quad (1)$$

where Q is the heat flow rate; κ, the thermal conductivity; A, the sample cross-sectional area; x, the sample thickness; and ΔT, the temperature drop across the sample. The experimental arrangement is shown in Figure 1 with the sample being sandwiched between the two aluminum blocks. Q was held constant by fixing the electrical power input into the heater. Also, A was kept the same for all samples. Several standards with known thermal conductivities were used to establish a calibration curve for thermal conductivities. For the unknown test sample, the thermal conductivity is given by

$$\kappa_c / \kappa_p = x_c \Delta T_p / x_p \Delta T_c \quad (2)$$

where the subscript c refers to the unknown, and p, to the standards.

To determine the influence of moisture on the dielectric properties of the polymer composites, the polymer composite samples were treated under various humid environments. Several relative humidity (RH) values (38 and 75%) were obtained at room temperature by the saturated $NaI \cdot H_2O$ and NaCl solutions, respectively. The treatment was carried out in a closed water container where film samples were placed above the surface of the solution for about 48 h.

The electrical conductivity and dielectric properties of the polymer composites were measured on a Hewlett-Packard HP 4284A impedance analyzer, using a temperature scan from 77 to 293 K at an interval of 10 K. The use of a low-temperature scan is because at room temperature or higher, in addition to the absorbed moisture, intrinsic relaxations from a polymer chain itself will contribute much to the impedance data. Four frequencies (100 Hz and 1, 10, and 100 kHz) were used at each temperature. A liquid nitrogen cryostat was used to cool the sample mount on which the film sample was held between two electrodes made of platinum foil, and the data acquisition

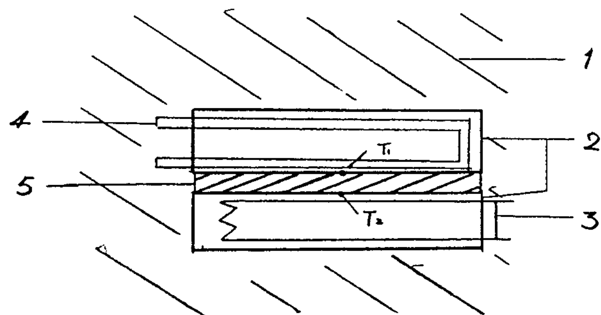

Figure 1 Schematic of apparatus used to measure thermal conductivity of materials: (1) insulating material; (2) aluminum blocks; (3) cartridge heater; (4) cooling water; (5) sample.

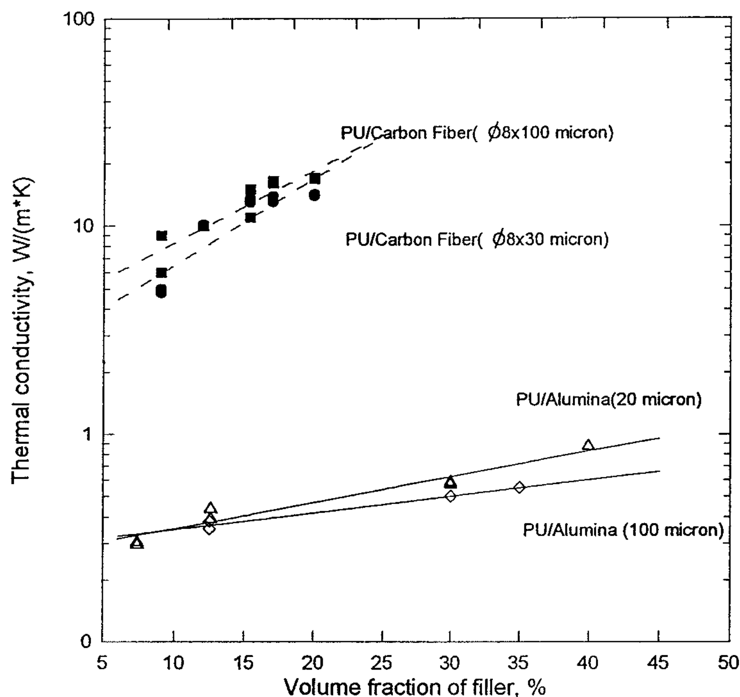

Figure 2 Thermal conductivities of polymer composites.

was performed during the warm-up ramp. A personal computer was interfaced with the impedance analyzer to facilitate data handling.

RESULTS AND DISCUSSION

Thermal Conductivities

The thermal conductivities of the polymer composites are shown in Figure 2, where the upper two curves are for the polyurethane mixed with carbon fibers (PUR/CF) and the lower two are for the polyurethane added with alumina (PUR/Al_2O_3). As one can see, the thermal conductivities in both polymer composites increase with the volume fraction of the fillers. In the PUR/Al_2O_3, at about 20% volume fraction, the thermal conductivity is five times that of pure PUR, while for the PUR/CF system, the increase is up to 50 times. In PUR/Al_2O_3 systems, the particle size has some effect on the thermal conductivities. The fact that the thermal conductivities with finer fillers are higher suggests that the smaller fillers are more effective to form heat conduction "bridges" to transfer heat through the sample. At a higher volume fraction, this effect becomes stronger. Moreover, it can be found that the logarithms of the thermal conductivity of PUR/Al_2O_3 is linearly proportional to the volume fraction of the fillers, which follows the model equation, derived from the theory of Agari,[6,11] that

$$\log \kappa = V_f C_2 \log \kappa_f + V_p \log(C_1 \kappa_p) \quad (3)$$

where κ is the thermal conductivity of the compos-

Table II C_1 and C_2 **of Agari's Model for the Polymer Composites**

System	Dimension (μm)	C_1	C_2	Thermal Conductivity at 10 vol % (W m^{-1} K^{-1})
PUR/Al_2O_3	20	0.1507	0.8818	0.125
PUR/Al_2O_3	100	0.1872	0.3812	0.122
PUR/CF	$\phi 8 \times 30$	26.83	6.134	0.410
PUR/CF	$\phi 8 \times 100$	67.11	6.882	0.800

ite, V is the volume fraction, p and f refer to the polymer and the filler, respectively; C_1 is related to the crystallinity and crystal size of the polymer matrix, and C_2 is related to the likelihood of forming connected filler pathways. Through data fitting, C_1 and C_2 for these systems are obtained and are shown in Table II.

For PUR/Al_2O_3 systems, the size of the Al_2O_3 powder affects C_2 more strongly than it does C_1. That is because the thinner the powders the easier it is for the fillers to diffuse into the polymer network. Thus, the formation of thermal conductive "bridges" in the composites will be more likely (increasing C_2).[12] But, in the meantime, smaller particles also tend to disturb the crystallization of the host polymer (reducing C_1). Therefore, the overall result is a slight increase in thermal conductivity. However, in the case of PUR/CF, both C_1 and C_2 for the system with longer fibers are higher. This is probably because the shorter fibers not only favor destroying the crystallization of the host polymer, thereby lowering C_1, but also have fewer advantages to form thermal conduction "bridges." On the other hand, long fibers, still very thin, are not limited from penetrating into the polymer network to form "bridges." Therefore, the overall result becomes the opposite to the PUR/Al_2O_3 system.

The higher thermal conductivities of PUR/CF, which are around 10 W m^{-1} K^{-1} for a 10% volume fraction, are about 10 times than that of PUR/Al_2O_3 and 50 times than that of pure polyurethane. They can be attributed to the graphite structure of carbon fibers, where electrons are delocalized. Although the carbon fibers can increase sharply the thermal conductivity of polymer composites, the electrical conductivity of PUR/CF was found to reach 10^{-8} S cm^{-1} at a volume fraction of 20% at room temperature, which makes their application as insulators inappropriate in certain cases.

Dielectric Properties Under Humid Environment

The dielectric losses of the polyurethane composite containing alumina (PUR/Al_2O_3), saturated with moisture at various relative humidities, are plotted against temperature in Figure 3. A peak (near 175 K) of dielectric relaxation is observed for the dry sample. It can also be found in the curves for samples treated with 40 and 75% RH. The difference in peak temperatures is within 10 K.

Usually, the dielectric loss in the temperature range of 150–250 K can be related to the presence of moisture in the polymers.[13,14] But in this case, a seemingly "intrinsic" relaxation exists, which

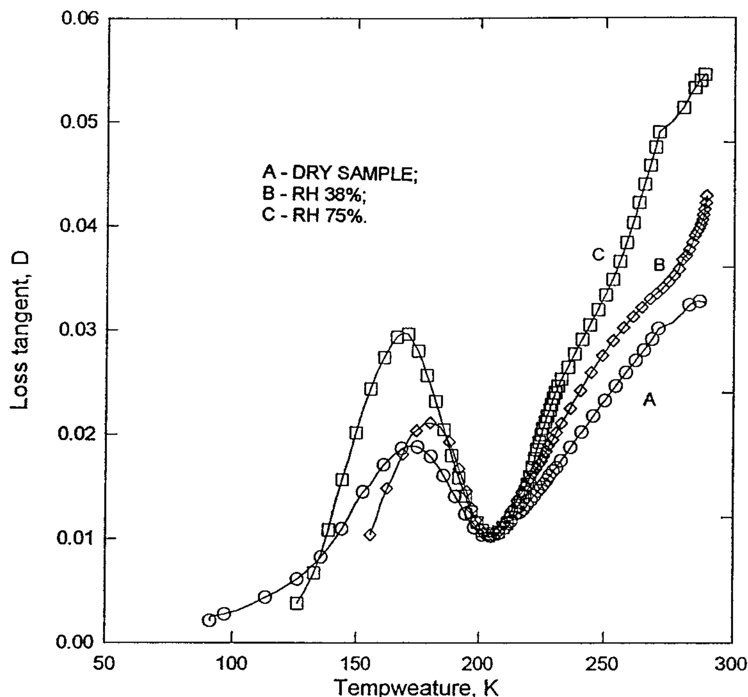

Figure 3 Dielectric relaxation spectra of sample PUR/Al_2O_3 after treatments in various RH at the frequency of 10 kHz.

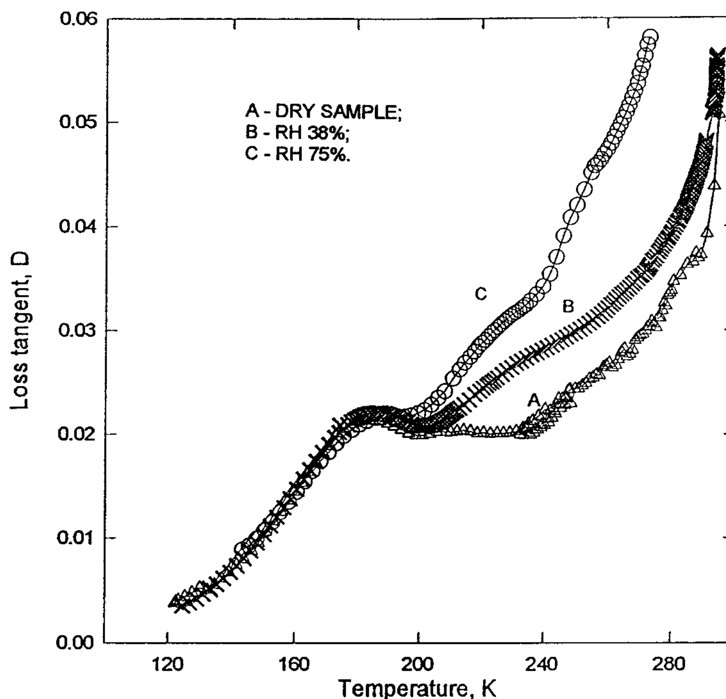

Figure 4 Dielectric relaxation spectra of sample PUR/CF after treatments in various RH at the frequency of 10 kHz.

might be due to the small chemical residuals trapped within the polymer network. When RH is increased from 0 to 40%, the loss tangent (*D*) for the peak close to 200 K increases by 20%. This "added" portion must be caused by the absorbed moisture. Furthermore, for the sample with 75% RH, a still larger increase in *D* is observed. These increases are, however, much smaller than those of other polymer systems (such as polyimide,[13] where they are up to 300–400%).

Figure 4 shows the dielectric loss as a function of temperature for the polyurethane composites containing carbon fibers (PUR/CF). The "intrinsic" peak can still be observed at 180 K, which is essentially not changed by the RH. When the temperature is increased to above 200 K, the loss tangent increases more dramatically with the RH. However, these increases above 200 K could also be associated with the moisture condensed on the sample mount. When the temperature is above 250 K, the loss tangents of both samples begin to increase sharply, which is caused by the relaxation of polymer chains, as well as by the moisture accumulated in the sample mount.

The difference in the dielectric loss spectra of two systems can be further traced. Alumina not only absorb moisture chemically, but also have the ability of physical adsorption. Physically adsorbed water molecules will also increase the dielectric loss of the composites and the effect becomes stronger when the humidity is higher. Thus, the systems with carbon fibers show a smaller effect of the moisture on the "intrinsic relaxation region" of the host polymer.

CONCLUSIONS

Ceramic powders, such as alumina, and carbon fibers can be used to improve the thermal conduction of pure polymers by mixing them into the polymer host. Because of their special structure, carbon fibers show a greater ability to increase the thermal conductivities of polymer composites which can reach 50 times that of pure PUR (11 W m^{-1} K^{-1} at 25% volume fraction). Also, their electric conductivity can be kept below 10^{-8} S cm^{-1}, which may be good enough for certain applications. The heat-conduction behavior of both PUR/Al_2O_3 and PUR/CF follows Agari's model. Through the data fitting, parameters describing the formation of heat-conduction "bridges" in the polymer composites, as well as the crystallization of polymer chains, have been obtained, which also have large effects on the thermal conductivity of polymer composites.

Compared with the PUR/Al_2O_3 system, the dielectric loss property of PUR/CF under various humid environments at low temperatures (70–250 K) shows little change, thus not being strongly affected by the moisture uptake of polymer composites. However, the physical adsorption of moisture in the polymer composites might be the cause of the increase of the dielectric loss of PUR/Al_2O_3 up to 50%, in comparison to the dry sample.

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