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Transient Characteristics of Thermal Conduction in Dispersed Composites[1]

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The effective thermal conductivity of dispersed composites with a hot-melt-adhesive matrix, measured using the steady-state method, is compared with the apparent thermal conductivity calculated from the average heat capacity and from the thermal diffusivity measured by the laser-flash method. The transient effect has been observed obviously at higher volume percentages for various dispersed particle sizes and ratios of the thermal conductivity values of dispersed and continuous phases. All of the experimental results are compared with those calculated by existing models and by the finite element method (FEM). An attempt has been made to show how the criterion for the homogeneity of dispersed composites under transient conditions is affected by the percentages of dispersed phase, dispersed particle size, and ratio of the thermal conductivity values of dispersed and continuous phases.

KEY WORDS: criterion of homogeneity; dispersed composites; finite element method (FEM); laser flash method; thermal conductivity; thermal diffusivity; steady-state comparison method.

1. INTRODUCTION

For heterogeneous materials, an effective thermal conductivity can be defined by the extended Fourier law, using the average value of the temperature gradient over a region that is large compared to the scale of the heterogeneity. Considerable progress has been made in relating the effective steady-state thermal conductivity of the composite to the conductivities of

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the individual components. However, under transient conditions there are no simple models to relate the heterogeneous thermal diffusivity to that of the individual components as in the steady-state case. In fact, as pointed out by Kerrisk [1, 2], the meaning of the thermal diffusivity as a characteristic property of a heterogeneous material is not clear since the thermal conduction equation in which the thermal diffusivity appears as a transient-state characteristic constant applies only to homogeneous materials. An effective thermal diffusivity for transient thermal problems should be defined under conditions for which the heterogeneous material can be considered as a homogeneous material. Experimentally, the criterion of homogeneity was studied in an early paper of Lee and Taylor [3], but an obvious difference between the results by the laser-flash method and the steady-state model was not observed under 30 vol% of dispersed particles. No further work on experimental comparisons between the unsteady- and the steady-state values, especially for high volume percentages, has been found in the literature.

The purpose of the present work is to investigate experimentally the criterion for the homogeneity of dispersed composites under transient conditions. The effective thermal conductivity measured using the steady-state method is compared with the apparent thermal conductivity which is calculated with the average heat capacity and the thermal diffusivity measured by the laser-flash method for a wide range of volume percentages of the dispersed phase. Furthermore, the experimental results are compared with those calculated using existing models and using a numerical model which is solved using the finite element method (FEM). The limitation of the concept of effective thermal diffusivity as a transient-state characteristic constant of a dispersed composite is discussed for various volume percentages of dispersed phase, dispersed particle size, and ratio of the thermal conductivity values of dispersed and continuous phases.

2. EXPERIMENTS

Experimentally, the transient characteristic of heat conduction in dispersed composites can be investigated by comparing the values of thermal conductivity from the steady- and unsteady-state methods.

2.1. Measuring Methods

In the present work, the widely used steady-state comparison method is employed as the steady-state method to measure the effective thermal conductivity, λ_e. For the unsteady-state method, the well-known laser-flash method is employed to measure the thermal diffusivity, a; then the apparent thermal conductivity, λ_a, can be obtained from

$$\lambda_a = (c\rho)_m a \tag{1}$$

For two-phase dispersed composites,

$$(c\rho)_m = c_d \rho_d V_d + c_c \rho_c (1 - V_d) \tag{2}$$

where c, ρ, and V are the heat capacity, density, and volume fraction, and the subscripts d and c denote the dispersed and continuous phases, respectively.

2.2. Specimens

Two kinds of two-phase dispersed composites were prepared for the measurements. First, aluminum spheres dispersed in hot-melt adhesive and, second, alumina spheres dispersed in hot-melt adhesive were prepared. The hot-melt adhesive is composed of ethylene vinyl acetate copolymer (49.751% by mass), tackifier resin (49.751% by mass), and antioxidant (0.498% by mass). The thermophysical properties of the dispersed and continuous phases are given in Table I.

The specimens are prepared as follows. The hot-melt adhesive is heated in a stainless container to 150°C; a measured quantity of particles is added into the molten adhesive, which is then mixed to disperse the particles; and the uniformly mixed particle–hot-melt adhesive mixture is injected into a mold and degassed in a vacuum oven at 120 to 160°C and 1 Torr and then cooled to room temperature. The uniformity of the distribution of the dispersed particles has been observed in profiles of the composites by examination under a microscope. The specimens for the steady-state comparison method (with a diameter of 30 mm and a thickness of 15 mm) and for the laser-flash method (with a diameter of 10 mm and a thickness of 1.5 mm) are listed in Table II. The two kinds of specimens are made from the same particle-hot melt adhesive mixture.

Table I. Properties of Dispersed and Continuous Phases

	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	Heat capacity ($kJ \cdot kg^{-1} \cdot K^{-1}$)	Density ($kg \cdot m^{-3}$)
Hot-melt adhesive	0.176	1.58	963
Aluminium	240	0.905	2700
Alumina	36	0.779	3880

Table II. List of Specimens

	Dispersed particle (diameter; μm)[a]									
	Aluminum,								Alumina	
	6		35		75		100		35	
	S.C.	L.F.	S.C.	L.F.	S.C.	L.F.	S.C.	L.F.	S.C.	L.F.
Volume percentage (%)			0	0	0	0			0	0
			5	5	5	5			5	5
			10	10	10	10			10	10
			15	15						
	20	20	20	20	20	20	20	20	20	20
			30	30	30	30			30	30
			40	40					40	40
					45	45				
			50	50	50	50			50	50

[a] S.C., steady-state comparison method; L.F., laser-flash method.

2.3. Experimental Results

The thermal conductivities of the two kinds of composites measured by the steady comparison method and the laser flash method are shown by a representative selection of curves in Figs. 1 and 2. Figure 1 shows the variation of the thermal conductivity with volume percentage of three kinds of dispersed particles for the steady-state and laser-flash methods. Figure 2 shows the dependence of the thermal conductivity on the size of the dispersed particles for the two measurement techniques. By selected comparisons of the experimental results, the effects of volume percentage, particle size, and conductivity ratio on the conductivities of the composites are found, as discussed below.

In Fig. 1, it is easy to find that these three groups of results have a common feature, although they have different sizes of dispersed particles or have different thermal conductivity ratios. That is, for a small volume percentage, as in homogeneous materials, thermal conductivities measured using steady-state and laser-flash methods are in general agreement. With increasing volume percentage, the difference between the steady and the unsteady methods becomes more apparent, i.e., the materials begin to show their heterogeneity or transient-state features. The larger the volume percentage of dispersed particles, the more significant the difference is.

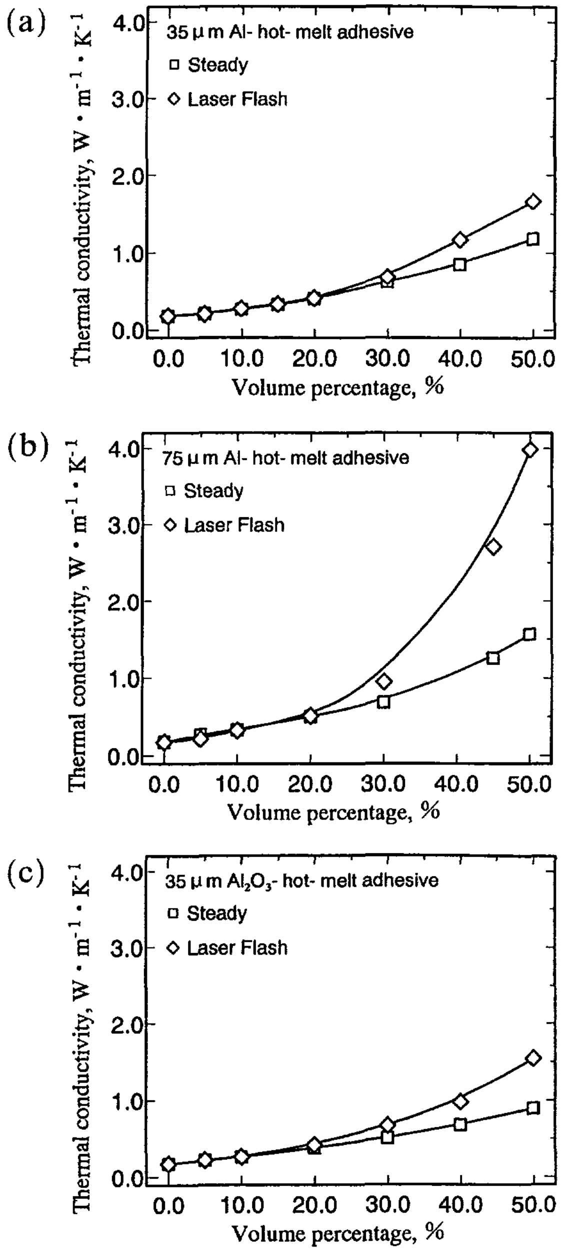

Fig. 1. Comparisons of thermal conductivities measured by the steady and laser-flash methods: (a) 35-μm Al; (b) 75-μm Al; (c) 35-μm Al_2O_3.

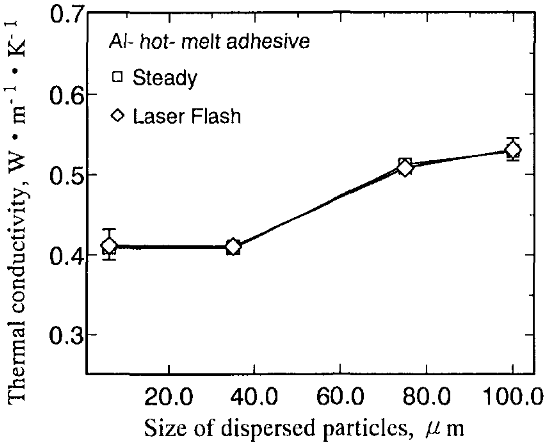

Fig. 2. Thermal conductivity of Al–hot-melt adhesive dispersed composites with different sizes of particles for a constant volume percentage (20%).

The effect of the particle size is demonstrated by comparing Figs. 1a and b. For the composites with 35-μm (median diameter with a standard deviation of 25 μm) dispersed particles, the differences in the measured thermal conductivities between the steady and the unsteady methods are still indistinguishable until the volume percentage reaches about 25%. For the case with 75-μm dispersed particles, however, the difference appears at about 15%. The large change in the size of the dispersed particles may shift the range in which the composite can be treated as a homogeneous material. In general, the larger the size of the dispersed particles, the more narrow the range of homogeneity is. Figure 2 shows the conductivity change with particle size for a fixed volume percentage of 20%. For each particle size, the results from the steady and unsteady methods are the same. But the conductivities of samples with large particles are obviously greater than those containing small particles. This phenomenon is also observed for volume percentages over 20% by comparing Figs. 1a and b.

Comparing Figs. 1a and c demonstrates the effect of the ratio of thermal conductivity of dispersed particles to that of the continuous phase. For aluminum–hot-melt composites (Fig. 1a), the thermal conductivity ratio is $\lambda_d/\lambda_c = 1364$, while for alumina–hot-melt composites, $\lambda_d/\lambda_c = 205$. Because the thermal conductivity of alumina is smaller than that of aluminum, all of the results in Fig. 1c are smaller than the corresponding ones in Fig. 1a. No obvious difference in the heterogeneity criteria for these two figures is observed. Compared with the other two parameters, the effect of the conductivity ratio is small.

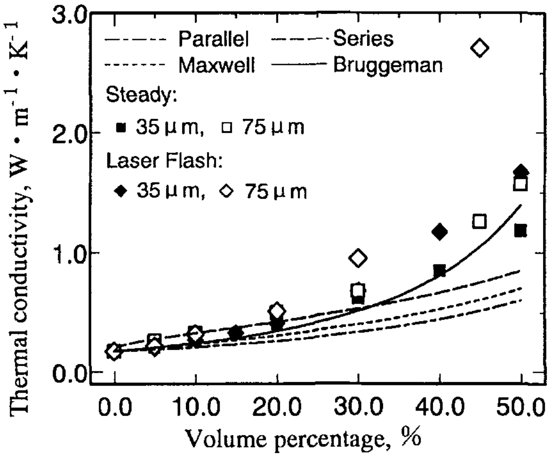

Fig. 3. Comparison of measured results with models (Al).

3. DISCUSSION AND COMPARISON WITH CALCULATIONS

3.1. Comparison with Some Well-Used Models

Figures 3 and 4 show comparisons of the predictions of four well-used models with the experimental values obtained from measured data for aluminum-hot-melt adhesive and alumina-hot-melt adhesive composites, respectively. The models which are used are as follows.

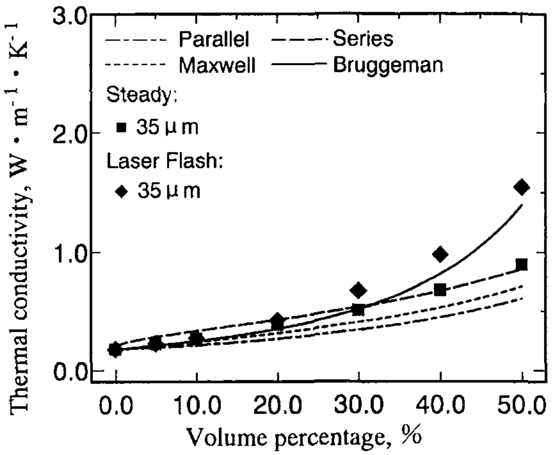

Fig. 4. Comparison of measured results with models (Al_2O_3).

Parallel model [4]—a simple Ohm's law model, assuming that the effective thermal conductivity may be determined by considering the equivalent electrical resistances in parallel tubes,

$$\frac{\lambda_e}{\lambda_c}=\frac{(V_d^{1/3}-V_d)\,\lambda_c+(1-V_d^{1/3}+V_d)\,\lambda_d}{V_d^{1/3}\lambda_c+(1-V_d^{1/3})\,\lambda_d} \tag{3}$$

where λ_d and λ_c are the thermal conductivities of the dispersed and continuous phases, respectively.

Series model [4]—a simple Ohm's law model, assuming that the effective thermal conductivity may be determined by considering the equivalent electrical resistances in series slabs,

$$\frac{\lambda_e}{\lambda_c}=\frac{(1-V_d^{2/3})\,\lambda_c+V_d^{2/3}\lambda_d}{(1-V_d^{2/3}+V_d)\,\lambda_c+(V_d^{2/3}-V_d)\,\lambda_d} \tag{4}$$

Maxwell model [5]—the effective thermal conductivity is established from the Fourier–Biot law under the assumption that there is no field interaction between the dispersed particles,

$$\frac{\lambda_e}{\lambda_c}=\frac{2+\lambda_d/\lambda_c-2V_d(1-\lambda_d/\lambda_c)}{2+\lambda_d/\lambda_c+V_d(1-\lambda_d/\lambda_c)} \tag{5}$$

Bruggeman model [6]—the effective thermal conductivity is derived using an effective medium approximation in which the interparticle interactions are considered

$$1-V_d=\frac{\lambda_e-\lambda_d}{\lambda_c-\lambda_d}\left(\frac{\lambda_c}{\lambda_e}\right)^{1/3} \tag{6}$$

In Fig. 3, for the specimens with 35-μm dispersed particles, the agreement of the experiment and the four models is quite good for volume percentages up to 20%, while at higher volume percentages, the experimental results approximately agree with the Bruggeman model and are larger than for the other models. For the specimens with 75-μm particles, at the higher volume percentage, the results from the laser-flash method are much larger than those from any of the four models. In Fig. 4, for quite a wide range of volume percentage, the agreement of the experimental results measured by the steady-state method and the models is quite good, while at higher volume percentages the results of the laser-flash method are a little larger than the values of the models.

The parallel, series, and Maxwell models assume that the dispersed particles are dilute. Consequently, for a high volume percentage of dispersed particles, the models may not be valid. The Bruggeman model is derived on the basis of an effective medium approximation, in which the interparticle interactions are considered, so it can be appropriate for a wide range of volume percentage of dispersed particles. For large particle sizes, or the results from the unsteady-state method at higher volume percentages, the Bruggeman model becomes quite inaccurate.

3.2. Comparison with Numerical Calculation

3.2.1. A Simplified Model of Dispersed Composites

Dispersed composites are considered to be described by a simple three-dimensional model as shown in Fig. 5. The spherical dispersed particles are arranged in a regular cubic array. A model composite is formed by stacking the unit cells in which the dispersed particles are located at the centers of the cubes. The thermal conductivities of the composites are determined by numerical analysis using the FEM under steady and unsteady conditions.

3.2.2. Transient Temperature Response

Figure 6 demonstrates the temperature responses at the center ($X=0$, $Y=0$) of the rear surface of a single cell, and for a composite of N cells heated by a pulse heat flux at the front surface. As N increases, the temperature response becomes slower. Ultimately, a single asymptote is approached for all N. This means that increasing the number of unit cells in the calculation has the effect of homogenizing the specimens.

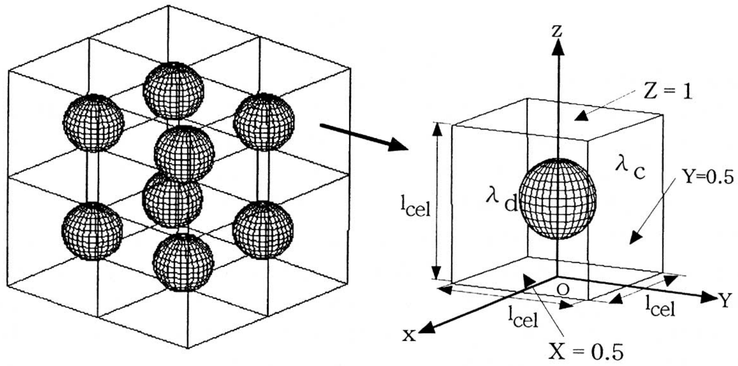

Fig. 5. Three-dimensional unit cell model of dispersed composites.

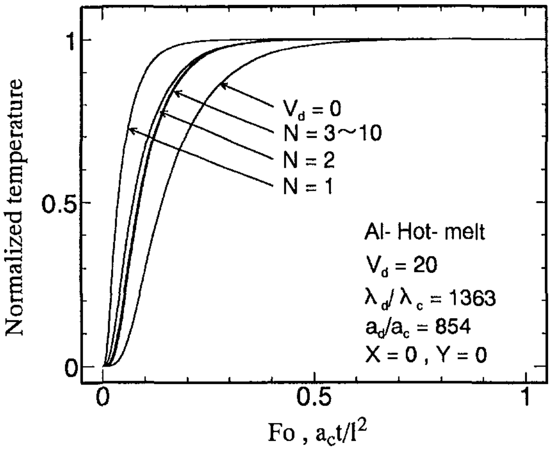

Fig. 6. Temperature responses of Al-hot-melt adhesive composites for various numbers of unit cells.

For the situation in which N is large enough that the composite can be treated as a homogeneous material, the transient thermal diffusion can be described by an effective property, the effective thermal diffusivity, which can be measured by the laser-flash method. The relationship between the effective thermal diffusivity, a_e, and the effective thermal conductivity, λ_e, is expressed in Eq. (1), with a_e and λ_e instead of a and λ_a, respectively.

The range of N for which the dispersed composites can be treated as homogeneous materials varies with the volume percentage of dispersed particles. This effect is considered for the situation where aluminum particles are dispersed in hot-melt adhesive (as shown in Fig. 7). Here the criterion of homogeneity is given as the calculated thermal conductivities approach a fixed value. The figure shows that, when $N > 3$ for 10% dispersed phase, and $N > 6$ for 40%, the composites may be treated as homogeneous materials.

3.2.3. Comparison of Steady and Unsteady Methods

The variation of the apparent thermal conductivity with the volume percentage of dispersed particles calculated under steady-state conditions is compared with the variation under unsteady conditions for aluminum–hot-melt adhesive composites. The calculations are performed with enough unit cells that the composites are treated as homogeneous materials. The differences in the results between the steady-state method and the laser-flash method for all volume percentages are in the range of calculation errors.

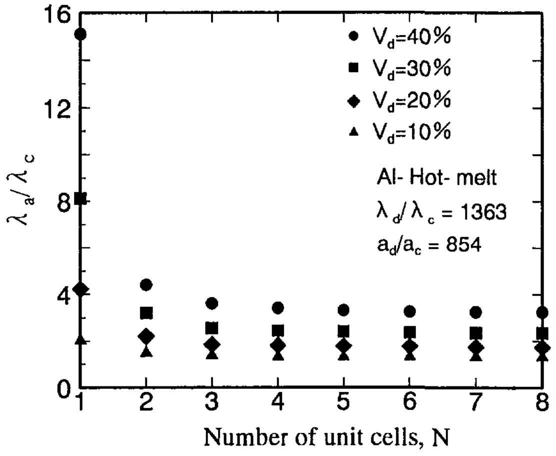

Fig. 7. Effect of the number of unit cells on thermal conductivity.

This means that the transient effect observed in experiments does not occur in calculations.

3.2.4. Comparison with Experimental Results

Figure 8 shows a comparison of the calculated results with the experimental values for 75-μm aluminum–hot-melt adhesive-dispersed composites. In the figure, the calculated results for a cell number N from 1 to 8 are shown. For small N the unsteady-state results are quite different from each other and from those for steady state, while for large N all the results approach the same value. When $N = 2$, the curve obtained from the calculation is similar to that obtained from the experiment. For other values of N, large differences between calculated and experimental values are observed. However, the real specimens (with a thickness of 1.5 mm, 75-μm dispersed particles) may contain at least 10 unit cells in the direction of the thickness. The obvious transient effect observed in experiments means that, for real composites, the macroscopic heterogeneity is important even when tens of unit cells are present in the direction of the thickness.

Comparing the FEM calculation values with the experimental values for steady state (Fig. 8) shows that, only for very low volume percentages ($<5\%$), the calculations agree with the experiments. This is maybe because the calculation model is too simple to model the real samples. Actually there are some significant differences in geometry between the model and the real samples, i.e., the dispersed particles of real samples are very different shapes and sizes, and in a random distribution. The effects of the

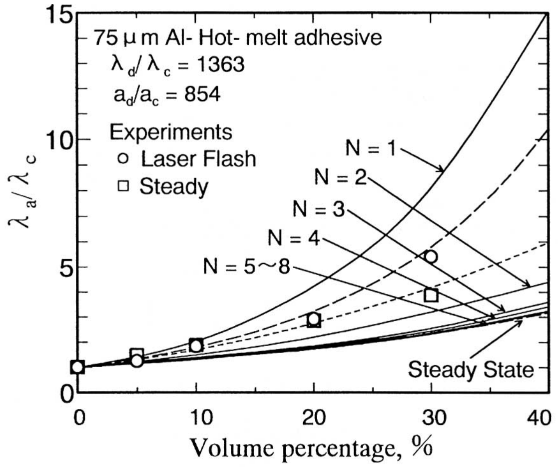

Fig. 8. Comparison of experimental and calculated results.

shape, size, and distribution of dispersed particles are not significant for very dilute dispersions. Comparatively, the Maxwell and the Bruggeman models are more reliable, if the FEM model cannot utilize a more realized geometry.

4. CONCLUSION

The criterion for the homogeneity of dispersed composites under transient conditions or the limitation of the concept of effective thermal diffusivity as a transient-state characteristic constant was investigated experimentally and theoretically. The differences between the steady and the unsteady methods, for both experiments and calculations, are discussed for various percentages of dispersed phase, dispersed particle size, and ratio of the thermal conductivity values of the dispersed and continuous phases. The obvious transient effect observed in the experiments at higher volume percentages is not predicted by the simplified calculation model with dispersed particles in a regular array. One reason is that the complexity of actual dispersions is not modeled. The thermal bridge caused by the percolation effect may be another reason, especially for high volume percentages of particulates.

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