

# Thermal Conductivity and Heat Capacity of ABS Resin Composites

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**ABSTRACT:** Thermal conductivity and heat capacity of composites of ABS resin with glass beads and/or titania were measured. For ABS–glass-beads composites, the thermal conductivity data are in good agreement with values calculated by the Maxwell and Bruggeman equations in a temperature range above a critical temperature, but much deviation was observed below this temperature. Similarly for the heat capacity, the measured data are in excellent agreement with the calculated values assuming additivity above the critical temperature, while the measured data are clearly less than the calculated values below this temperature. On the other hand, for the ABS–titania the measured data of heat capacity are higher than the additivity in the whole temperature range, though linearity was found among titania and the composites also in the whole temperature range. The thermal conductivity observed for this composite is in good agreement with the theoretical value calculated by the Maxwell and Bruggeman equations except in a low temperature range. By dynamic viscoelastic observation, it was found that a new dissipation occurs around 95°C in the composite of the glass beads. These facts suggest that interaction exists between the resin and the fillers, and this interaction causes the deviation from the Maxwell and Bruggeman equations in the thermal conductivity and deviation from the additivity in the heat capacity below the critical temperature. For the composite of titania no new dissipation was found, but a small dissipation originally observed for the resin was not seen. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1279–1286, 1997

**Key words:** ABS resin; titania; glass beads; composite; thermal conductivity; heat capacity; viscoelasticity; interaction; hot wire method

## INTRODUCTION

Along with advancement in plastics molding technology, such as computer-aided design, thermophysical property data of high precision and high accuracy are needed. For instance, plastics products of complicated shapes are used in electronics

equipment, and molds for these purpose are expensive, so computer simulation becomes a powerful tool for designing molds for such products. Computer simulation of the cooling process is also useful in strand production. For these simulations, thermophysical properties such as thermal conductivity, heat capacity, p-v-T property, melt viscosity, etc., are essential.

For this purpose, we have measured thermal conductivity and heat capacity for ABS resin (blend of acrylonitrile–styrene copolymer and

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polybutadiene) composites with glass beads and/or titania powder as fillers. The measurements were carried out in a temperature range from room temperature to a temperature above the glass transition. The hot-wire method<sup>1</sup> was applied to thermal conductivity measurement, and differential scanning calorimetry (DSC) was used for heat capacity measurement.<sup>2</sup>

The obtained data have been compared with the calculated data using theoretical relations, namely the Maxwell,<sup>3</sup> Eucken,<sup>4</sup> and Bruggeman<sup>5</sup> equations for thermal conductivity and additivity for heat capacity. Above a critical temperature, excellent agreement can be seen for the ABS-glass-beads composite. Below the critical temperature, however, much deviation was found for both properties. For the ABS-titania, observed heat capacity was higher than the theoretical value but linear relation was found among the composites and titania in the whole temperature range. Good agreement was found between the observed thermal conductivity and the theoretical values except in a low temperature range.

To elucidate the mechanism for these discrepancies, dynamic viscoelastic observation has been made for ABS resin and its composites. Dissipations are discussed in relation to the above critical temperature for the thermophysical properties. The interaction seems a cause for the deviation in thermophysical properties, and the deviation of heat capacity from the additivity can be a measure for the interaction, which has not yet been observed quantitatively. These results are described in this report.

## EXPERIMENTAL

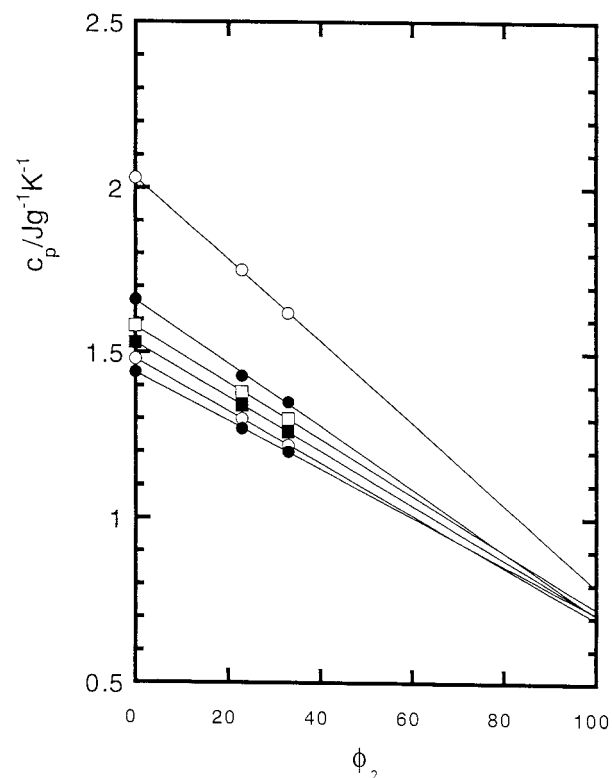
### Measuring Methods and Apparatuses

For thermal conductivity measurement a hot-wire method apparatus made by Shinku Riko Co. (Yokohama, TC 1000) was modified and used. The modifications, made to obtain linear temperature increase against logarithm of time for high precision and accuracy, are (1) inserting a stainless-steel net between the infrared lamp heat source and the sample assembly to maintain uniform heating; (2) painting the sample container and its supports with black body paint to increase uniformity of temperature in the sample; and (3) frequent changing of the thermocouple and heating wire. The measurements were taken in a nitrogen

atmosphere. With this apparatus the measurement in a temperature range below 80°C, except the room temperature, is difficult due to the instability of isothermal temperature control by the infrared lamp heating.

The precision and accuracy were estimated by using high-purity toluene (99.9% purity, purchased from Wako Pure Chemicals Co. Tokyo) as standard materials,<sup>6</sup> and the measurements were taken at room temperature. To avoid convection in toluene, the current to the heating wire was kept small. The accuracy is better than 3% and the precision is about 3%.<sup>7</sup>

For the resin and the composites, the sample was kept for more than 2 h at the desired temperature to achieve uniform temperature distribution within the sample. The temperature was changed step-wise, and the obtained data were compared with each other between those obtained at the heating mode and those at the cooling mode. The agreement was satisfactorily good, and the uniformity of the temperature was ascertained by this fact. This agreement also ensured the negligible



**Figure 1** Heat capacity versus mass fraction of glass beads at every 10°C from 60°C (bottom) to 120°C (top), except 110°C.

effect of sedimentation of the fillers in the composites above glass transition temperature ( $T_g$ ).

For heat capacity measurement, a differential scanning calorimeter (Perkin-Elmer DSC-7) was used by the usual method with synthetic sapphire as a standard material.<sup>2</sup> The run was made at the heating rate of 10°C/min under nitrogen gas flow. The temperature was calibrated by melting temperatures of pure *n*-octadecane and pure indium. The imprecision for the heat capacity measurements is less than 1%, except for titania. Flatness of a sample cell bottom and hence good thermal contact between the cell and its holder seem to ensure this high precision. For titania the imprecision is about 3% at room temperature and increases to about 6% at the highest temperature. The hardness of titania seems to be a cause for this low precision, due to the low thermal contact between the cell holder and the sample cell bottom roughened by hard titania powder.

The viscoelastic behavior was observed with an automatic apparatus of dynamic thermomechanometry, namely a Solids Analyzer RSA II Yanagitashi, (Rheometrics Co. Tokyo). The frequency,

the heating rate, and the load were 10.0 Hz, 2°C/min, and a tensile load, respectively.

### Materials

The ABS sample is Cevian V510 (Daicel Chemical Industries, Ltd., Osaka), which is a mixture of AS resin and 10 mass % of polybutadiene rubber. The density is 1.056 kg/dm<sup>3</sup> at 20°C.

The fillers are glass beads and titania (rutile) powder. The glass beads were produced by Toshiba Ballotini Co., Ltd. (Tokyo, EGB 731B), are made of E-glass, and consist of 2- to 30- $\mu$ m-diameter spheres. The thermal conductivity was reported to be 1.035 W/mK by the producer, and the density is 2.50 kg/dm<sup>3</sup>. The surface is covered with glycidic silane coupling reagent. Two types of titania powder are used. One is Tipaque R830 (93% purity), produced by Ishihara Sangyo Kaisha, Ltd. Osaka for plastics filler and composed of spheres of 250- to 400-nm diameter, whose surface is covered with alumina, silica, and zinc oxide. The thermal conductivity is reported to be 6.96 W/mK by the producer. Dispersing agent

**Table I Heat Capacity and  $T_g$  of ABS Resin, Glass Beads and Their Composites**

	Beads	Resin	Composite [100 : 30] <sup>a</sup>		Composite [100 : 50] <sup>a</sup>	
	$T_g$ (°C) <sup>b</sup>	102	106		105	
	Heat Capacity					
Temperature (°C)	Obs. (J/gK)	Obs. (J/gK)	(Obs.) J/gK	(Calc.) J/gK	(Obs.) J/gK	(Calc.) J/gK
60	0.80	1.45	1.27	1.29 (1.27) <sup>c</sup>	1.20	1.23 (1.20)
70	0.81	1.49	1.30	1.33 (1.30)	1.22	1.26 (1.22)
80	0.81	1.54	1.34	1.36 (1.34)	1.26	1.29 (1.26)
90	0.82	1.60	1.38	1.40 (1.38)	1.30	1.33 (1.29)
100	0.82	1.68	1.43	1.46 (1.45)	1.35	1.38 (1.35)
110	0.82	2.06	1.64	1.77 (1.74)	1.57	1.64 (1.61)
120	0.82	2.06	1.75	1.75 (1.73)	1.62	1.63 (1.59)

<sup>a</sup> Numbers in brackets are the composition ratios in mass.

<sup>b</sup>  $T_g$  is measured at the extrapolated onset temperature in the DSC curve.

<sup>c</sup> Numbers in parentheses are calculated assuming the heat capacity of the beads to be 0.71 J/gK.

*N,N'*-ethylene-bis (steramide) was mixed by 20 mass % with this titania, and the density became 2.40 kg/dm<sup>3</sup>. The other is pure titania powder (CR-EL) of similar diameter supplied by the same company, with a density of 4.12 kg/dm<sup>3</sup>.

The ABS-glass-beads composites were formed by mixing a certain content of the filler with the resin and by extrusion with a single-screw extruder to form pellets. For the ABS-titania composites with the dispersing agent, pellets were formed by twice extruding with a single-screw extruder; for the same composites without the dispersing agent, twice extruding with a double-screw extruder was made to maintain uniformity. These pellets were melted in the sample container for thermal conductivity measurements. For heat capacity measurements the pellets were hot-pressed into sheets to keep good thermal contact between the sample cell and the cell holder for high precision.

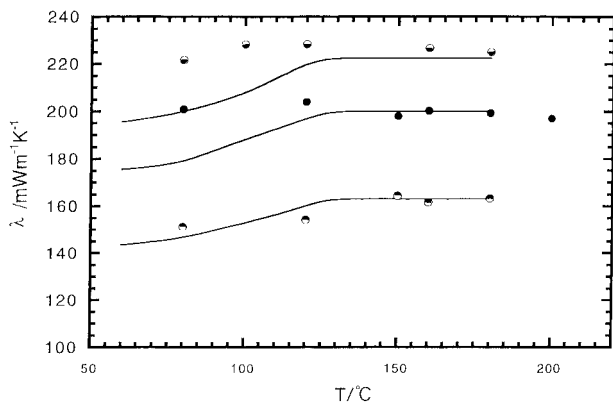
## RESULTS AND DISCUSSION

### ABS-Glass-beads Composite

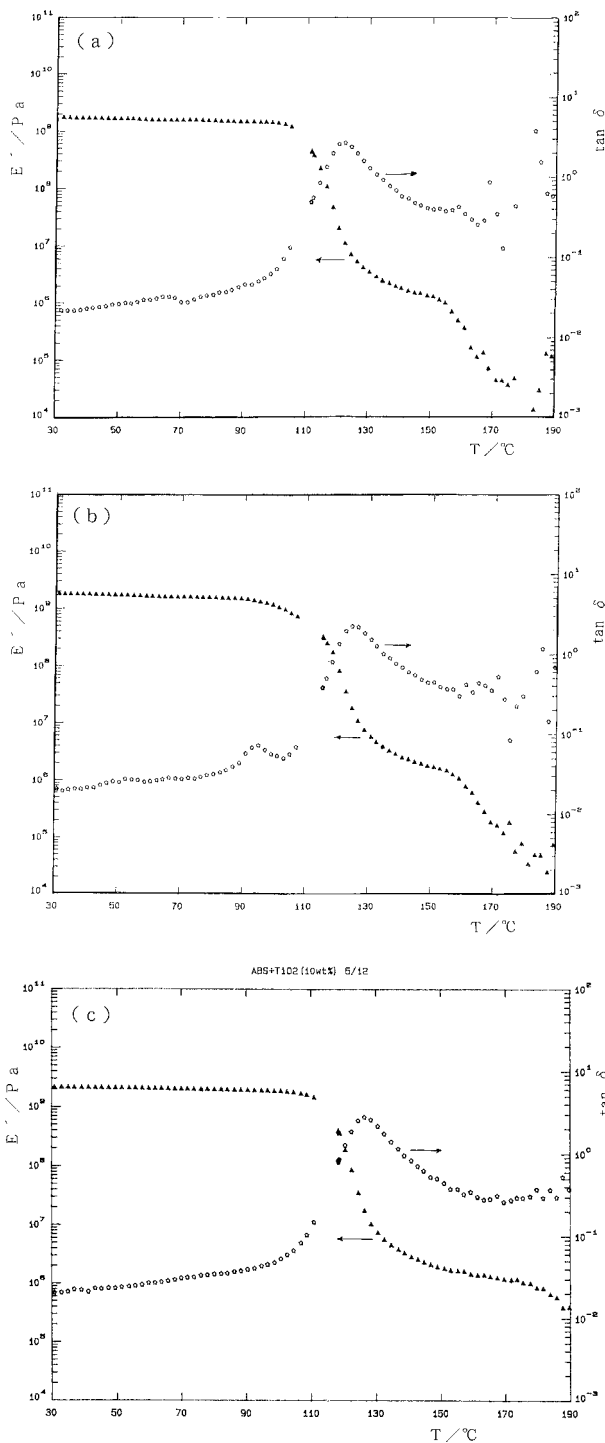
#### Heat Capacity

Dependence of the heat capacity on the composition was first examined, because additivity generally holds for a mixture, as follows:

$$c_{pc} = \phi_r c_{pr} + \phi_1 c_{p1} + \phi_2 c_{p2} \quad (1)$$



**Figure 2** Thermal conductivity versus temperature for composites of glass beads. From top to bottom: composite [100 : 50] (○), composite [100 : 30] (●), and resin per se (○). Lines are theoretical values from the Maxwell equation, except observed value for resin per se.



**Figure 3** Viscoelastic behavior for (a) resin, (b) composite of glass beads [100 : 30], and (c) composite of titania [100 : 10].

where  $c_p$  and  $\phi$  are, respectively, the specific heat capacity and the mass fraction; and the subscripts  $c$ ,  $r$ , 1, and 2 mean the composite, the matrix

resin, the first filler, and the second filler, respectively.

The results are shown in Figure 1, where the dependence of the specific heat capacity on the mass fraction is shown at every 10°C except one: the dependence at 110°C is not shown because reliable data were not obtained due to the relaxation. As clearly seen, the specific heat capacity is linearly dependent on the mass fraction. However, the extrapolated lines in a temperature range up to 100°C coincide on the ordinate of 100% glass beads. The value at this coincidence is 0.7 J/gK, and it deviates from the heat capacity of the glass beads as seen in Table I, where the measured heat capacity data are shown. In the other words, heat capacities of the composites calculated assuming this extrapolated heat capacity (see Table I) are in excellent agreement with the measured data. On the other hand, at 120°C, extrapolation of the linear dependence to 100% glass beads is equal to the measured heat capacity of the glass beads. Thus additivity of heat capacity simply holds at 120°C, but does not hold in a temperature range up to 100°C. One explanation derived from the plots in Figure 1 may be that the heat capacity of the glass beads decreases to 0.7 J/gK by the composite formation, but this is not plausible. On the contrary, it seems likely that something occurs not in the glass beads but in the resin, as described below.

The  $T_g$  of the composites were also estimated by using the DSC curves for the heat capacity measurements, and they are listed in Table I.  $T_g$  is increased by a few degrees by the composite formation, and this change seems to be due to the interaction between the resin and the filler.<sup>8</sup>

### Thermal Conductivity

The thermal conductivity data are plotted in Figure 2. The theoretical thermal conductivity of the composites was calculated by using the measured thermal conductivity of the resin, the reported thermal conductivity of the glass beads, and the Eucken<sup>4</sup> and Bruggeman<sup>5</sup> equations. The Eucken equation is as follows:

$$\frac{\lambda_c}{\lambda_r} = \frac{1 + 2\psi_1 R_1 + 2\psi_2 R_2}{1 - \psi_1 R_1 - \psi_2 R_2} \quad (2)$$

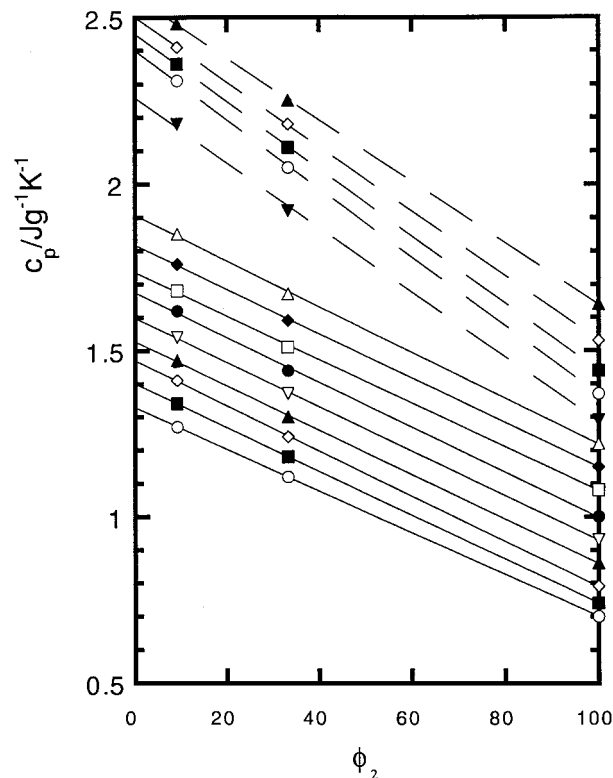
where  $\lambda$ ,  $\psi$ , and  $R$  are, respectively, thermal conductivity, the volume fraction, and a ratio given below:

$$R_i = (\lambda_r - \lambda_i) / (2\lambda_r + \lambda_i) \quad (3)$$

This equation becomes equal to the Maxwell equation<sup>3</sup> when either of the filler volume fractions becomes zero. The Bruggeman equation is the following:

$$1 - \psi = \frac{\lambda_1 - \lambda_c}{\lambda_1 - \lambda_r} \left[ \frac{\lambda_r}{\lambda_c} \right]^{1/3} \quad (4)$$

Similar to the heat capacity above, the data are in good agreement with the Maxwell equation in a temperature range above 100°C, but large deviation was observed in a lower temperature range (see Fig. 2). There is little difference between the values by the Maxwell and Bruggeman equations, and therefore the data is also in good agreement with the Bruggeman equation in the same temperature range. The reason for the small difference between the Maxwell and Bruggeman equations is that the volume fraction of the filler is low enough, for example, 11.3% for the composite (100 : 30 in mass) and 17.5% for the other compos-



**Figure 4** Heat capacity versus mass fraction of titania at every 10°C from 20°C (bottom) to 150°C (top).

ite (100 : 50) at 20°C. However, the values calculated by the equation of Cheng and Vachon<sup>9</sup> are significantly larger than those from the Maxwell and Bruggeman equations and also than the measured data.

This low-temperature deviation between the measured data and the values from the Maxwell and Bruggeman equations seems the same in nature as the deviation of the heat capacity from the additivity, because the deviations occur below the same critical temperature.

### Viscoelastic Behavior

It is likely that the deviations are related to molecular motion in the matrix resin. To confirm this, dynamic viscoelastic behavior was observed by dynamic thermomechanometry in a wide temperature range from -150°C to 180°C. Some of the results are reproduced in Figure 3. Comparing these two plots shows that a new energy dissipation occurs around 95°C, which corresponds to the above critical temperature, while the small dissipation originally observed in the resin per se around 60°C becomes smaller.

### Discussion

Generally, energy dissipation in viscoelastic behavior corresponds to commencement of molecular motion at the applied frequency. Therefore it can be concluded that some interaction occurs between the ABS resin molecule and the surface of the glass beads, presumably by adhesion, and that this interaction restricts motion in some part of the polymer molecules surrounding the glass beads in a certain thickness. The restriction

causes the decrease in the heat capacity of the resin and the decrease is proportional to the filler content; while the restriction increases the thermal conductivity like crosslinking, which restricts molecular motion and increases thermal conductivity.<sup>10</sup> Above the critical temperature, the restriction diminishes and the molecular motion commences. Hence, the additivity of the heat capacity and the Maxwell equation for the thermal conductivity hold.

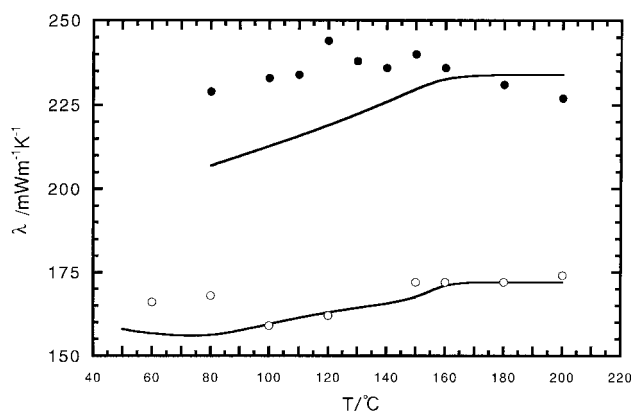
### ABS Resin-Titania Composites

#### Heat Capacity

For this composite similar plots were made but the results are quite different, as seen in Figure 4. Linearity was also found but among the composites and the titania filler, and the extrapolated lines to the resin do not agree with the heat capacities of the resin but cross at the higher values. Thus the tendencies are quite different from those of the resin-glass-beads composites.

#### Thermal Conductivity

Thermal conductivity of the composite containing 10 parts of the pure titania powder (2.57% volume fraction at 20°C) was measured and the results are shown in Figure 5, in which the estimated data are compared with the theoretical values (a line) by the Maxwell equation using thermal conductivity data of titania.<sup>11</sup> Good agreement is seen except in a low temperature range, but causes for this discrepancy in the low temperature range are not known. As to the theories of Bruggeman and



**Figure 5** Thermal conductivity versus temperature for composite of titania [100 : 10] (below) (○) and composite of three components (above) (●).

Cheng–Vachon, the situation is quite the same as for the composite of glass beads.

### Viscoelastic Behavior

Similarly to the above composites, viscoelastic observation was made for this composite but no new dissipation was found. Instead a small dissipation observed around 60°C for the resin disappeared [see Fig. 3(c)].

### Discussion

Because the titania powder is very fine, the surface area of this powder is much larger than that of the glass beads; therefore, interaction between the resin molecule and the powder surface is enhanced to a higher extent than that for the glass-beads composite. The tendency of the heat capacity observed can be explained by assuming that molecular motion of whole resin molecules is restricted due to the interaction of large surface areas with the powder and that the interaction increases heat capacity, presumably due to the change from rotational motion to vibrational motion, as is explainable by the disappearance of the

small viscoelastic dissipation. The increased heat capacity of the resin per se is tabulated in Table II as the extrapolated heat capacity data.

This interaction, however, has little effect on the thermal conductivity, especially in the temperature range above 100°C. For the deviation below 80°C no plausible reason has been found, but steep temperature dependence of thermal conductivity of titania in this temperature range<sup>11</sup> and hence inaccuracy in the theoretical calculation may be one reason for the deviation.

### ABS–Titania Composites with Dispersing Agent

For the ABS–titania composites with the dispersing agent, everything is somewhat complicated. In the DSC curves a large endothermic peak was seen in a temperature range from 133°C to 141°C, presumably due to fusion of the agent with small peaks about 62°C and 100°C which may be transitions of the agent. The large peak becomes diffuse by the composite formation, which suggests to us a possibility that the agent dissolves into the resin on melting. For the heat capacity, no definite tendency was found as observed for the above two

**Table II Heat Capacity and  $T_g$  of ABS Resin, Titania, and Their Composites**

	Titania	Resin	Composite [100 : 10] <sup>a</sup>	Composite [100 : 50] <sup>a</sup>	
	$T_g$ (°C) <sup>b</sup>		102	106	106
	Heat Capacity				
Temperature (°C)	Obs. (J/gK)	Obs. (J/gK)	Extrap. <sup>c</sup> (J/gK)	Obs. (J/gK)	Obs. (J/gK)
20	0.70	1.28	1.33	1.27	1.12
30	0.74	1.32	1.40	1.34	1.18
40	0.79	1.36	1.47	1.41	1.24
50	0.86	1.40	1.53	1.47	1.30
60	0.93	1.45	1.60	1.54	1.37
70	1.00	1.49	1.67	1.62	1.44
80	1.08	1.54	1.74	1.68	1.51
90	1.15	1.60	1.82	1.76	1.59
100	1.22	1.68	1.91	1.85	1.67
110	1.29	2.06	2.26	2.18	1.92
120	1.37	2.06	2.40	2.31	2.05
130	1.44	2.12	2.45	2.36	2.11
140	1.53	2.16	2.50	2.41	2.18
150	1.64	2.21	2.56	2.48	2.25

<sup>a</sup> Numbers in brackets are the composition ratios in mass.

<sup>b</sup>  $T_g$  is measured at the extrapolated onset temperature in the DSC curve.

<sup>c</sup> Heat capacity obtained by extrapolating the linear dependence among those of the composites and titania.

composites. Some large deviations were found from smooth temperature dependence of the thermal conductivity, presumably due to the transitions and the fusion of the agent. The heats of transition and fusion cause false data for the thermal conductivity, because the hot-wire method is based on transient heat flow without any heat absorption and/or evolution in the sample.

### ABS Resin–Glass Beads–Titania Composite

Thermal conductivity was measured for the composite of three components: the resin, the glass beads, and the Tipaque titania powder with the dispersing agent. The content of each filler is 30 parts per 100 parts of resin, and the volume fraction of glass beads and titania are, respectively, 10.5% and 4.9%. In Figure 5, the results are compared with theoretical calculation by the Eucken equation. Agreement is fairly good in a high temperature range. Deviation in a temperature range from 100°C to 140°C may be caused by the influence of the dispersing agent, as mentioned above. Heat capacity was not measured, but definite relation may not be found because of the same reason as the composites containing the dispersing agent.

### CONCLUSION

The facts obtained in this research are essential for thermophysical properties measurement of the polymer–filler composites, and they are as follows:

1. The discrepancy found in the heat capacity between the additivity and the measured data is a newly found fact, and it can be used as a measure for the strength of the

interaction between the resin and the filler. Previously, only the change in the  $T_g$  is the evidence for the interaction, but new evidence is presented here.

2. The deviation of the measured thermal conductivity from the theoretical calculation, such as the Maxwell, Eucken, and Bruggeman equations, is more evidence for the interaction. These theories, however, are still useful only in a limited range.
3. The viscoelastic observation is a very useful tool for thermophysical properties measurement of polymer–filler composites, and it provides us with complementary information which can be used to explain anomalous data of thermophysical properties.

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