

NOTES

Interaction Between Fillers and Matrix in ABS Resin Composites Observed by Thermophysical Measurements

Composite materials of polymer matrix and inorganic fillers have drawn great interest for a few decades because of the improvement and adjustment of various properties, such as mechanical strength, thermal stability, and thermal expansion. Also, it has been pointed out that interaction between filler and matrix must have a certain role in their properties, such as glass transition,¹ but it has not yet been observed exactly by thermophysical measurements, such as heat-capacity measurements. However, theoretical equations have been derived for thermophysical properties of composites without the interaction in relation to those of the components. For instance, the Maxwell equation is well known as a relation of conductivities for two-phase composites of spherical fillers.² For heat capacity, a simple relation of additivity can be assumed for composites without interaction.

The authors measured the heat capacity and thermal conductivity of ABS resin composites containing glass beads and found deviation of the observed data from the above relations in a temperature range below the critical temperature. Here, the authors describe the results and discuss them using a dynamic viscoelastic observation, and the restriction of molecular motion by the interaction is postulated as the reason for the deviation.

Thermal conductivity was measured by a hot wire method³ from room temperature to a higher temperature above the glass transition. Accuracy of the measurement was examined using high-purity toluene as a standard⁴; the measurement was made with an accuracy better than 3% and with similar precision. The heat capacity was measured with a differential scanning calorimeter (Perkin-Elmer DSC 7) by the usual method⁵ in a similar temperature range with higher precision as seen below. Viscoelastic behavior was observed by dynamic thermomechanometry with a solid analyzer RSA-II (Rheometrics Co.); 10.0 Hz tensile stress was applied and the heating rate was 2°C/min. The specimens were made in our laboratory of ABS resin (Daicel Chemical Industries, Cevian V510) and spherical glass beads of 2–30 μm diameter with a silicone coupling agent on the surface (Toshiba Ballotini Co., EGB 731B).

The heat capacity and the glass transition temperature estimated at the extrapolated onset by heat-capacity measurements are listed in Table I, where the measured heat capacities are compared with the theoretical heat capacities calculated on the assumption of the additivity. Below a critical temperature about 100°C, much deviation is found between them, but agreement of the measured data with the calculated values is very good above the critical temperature. When the measured data are plotted against the mass fraction as in Figure 1, we can find clear linear dependence, and the extrapolated values to zero mass fraction of the resin are about 0.7 J/g K below the critical temperature, while that at 120°C is 0.82 J/g K, which is

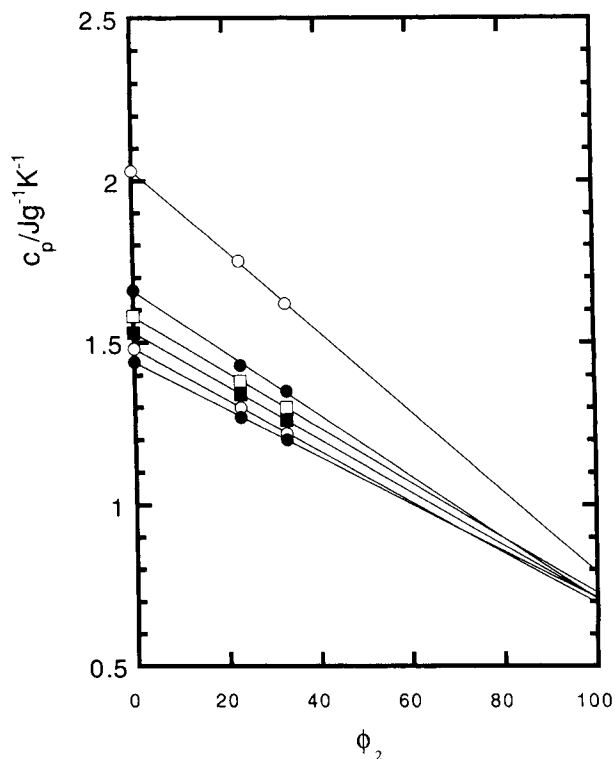


Figure 1 Dependence of heat capacity, c_p , on mass fraction percentage, ϕ_2 , of glass beads. Plots are from top to bottom 120, 100, 90, 80, 70, and 60°C, respectively. Data at 110°C are not plotted, because they are erroneous due to relaxation at the glass transition.

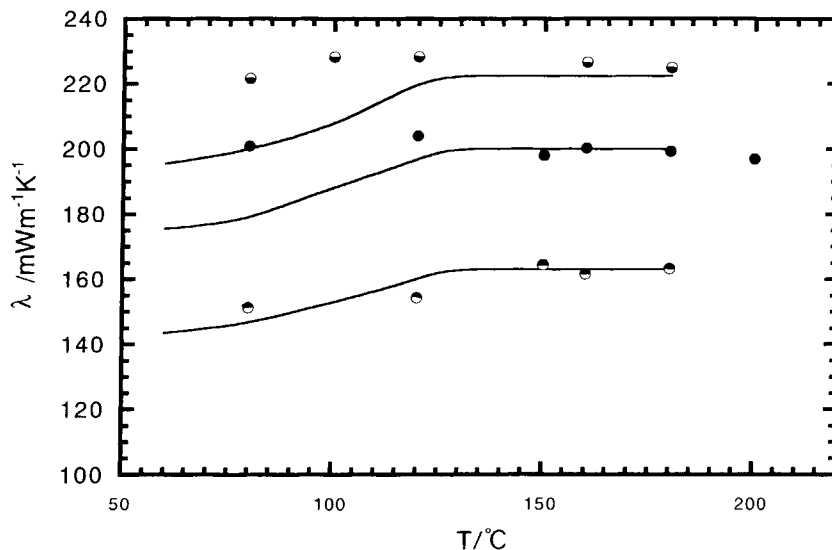


Figure 2 Dependence of thermal conductivity data, λ , of (○) the resin, (●) composite [100 : 30], and (◐) composite [100 : 50] on temperature, T . The calculated thermal conductivity is shown with the lines. The line for the resin per se is that by polynomial approximation.

in very good agreement with the measured data for the glass beads.

Calculated theoretical heat capacities using these values and the additivity are in excellent agreement with the

measured data, as seen in Table I. However, it is not likely that the heat capacity of the glass beads is decreased by composite formation below the critical temperature, but a plausible explanation is that the heat capacity of the

Table I Heat Capacity and Glass Transition Temperature of ABS Resin, Glass Beads, and Their Composites

	Beads Obsd (J/g K)	Resin Obsd (J/g K)	Composite [100 : 30] ^a		Composite [100 : 50] ^a	
			Obsd (J/g K)	Calcd (J/g K)	Obsd (J/g K)	Calcd (J/g K)
Heat capacity						
temp (°C)						
60	0.80	1.44	1.27	1.29 (1.27) ^b	1.20	1.23 (1.20)
70	0.81	1.48	1.30	1.33 (1.30)	1.22	1.26 (1.22)
80	0.81	1.53	1.34	1.36 (1.34)	1.26	1.29 (1.26)
90	0.82	1.58	1.38	1.40 (1.38)	1.30	1.33 (1.29)
100	0.82	1.66	1.43	1.46 (1.45)	1.35	1.38 (1.35)
110	0.82	2.05	1.64	1.77 (1.74)	1.57	1.64 (1.61)
120	0.82	2.03	1.75	1.75 (1.73)	1.62	1.63 (1.59)
Glass						
transition temp ^c (°C)	—	102	106		105	

^a The nos. in the brackets are the composition ratio in mass.

^b The nos. in the parentheses are calculated assuming the heat capacity of the beads to be 0.7 J/g K.

^c The glass transition temperature is measured at the extrapolated onset temperature in the DSC curve for heat-capacity measurement.

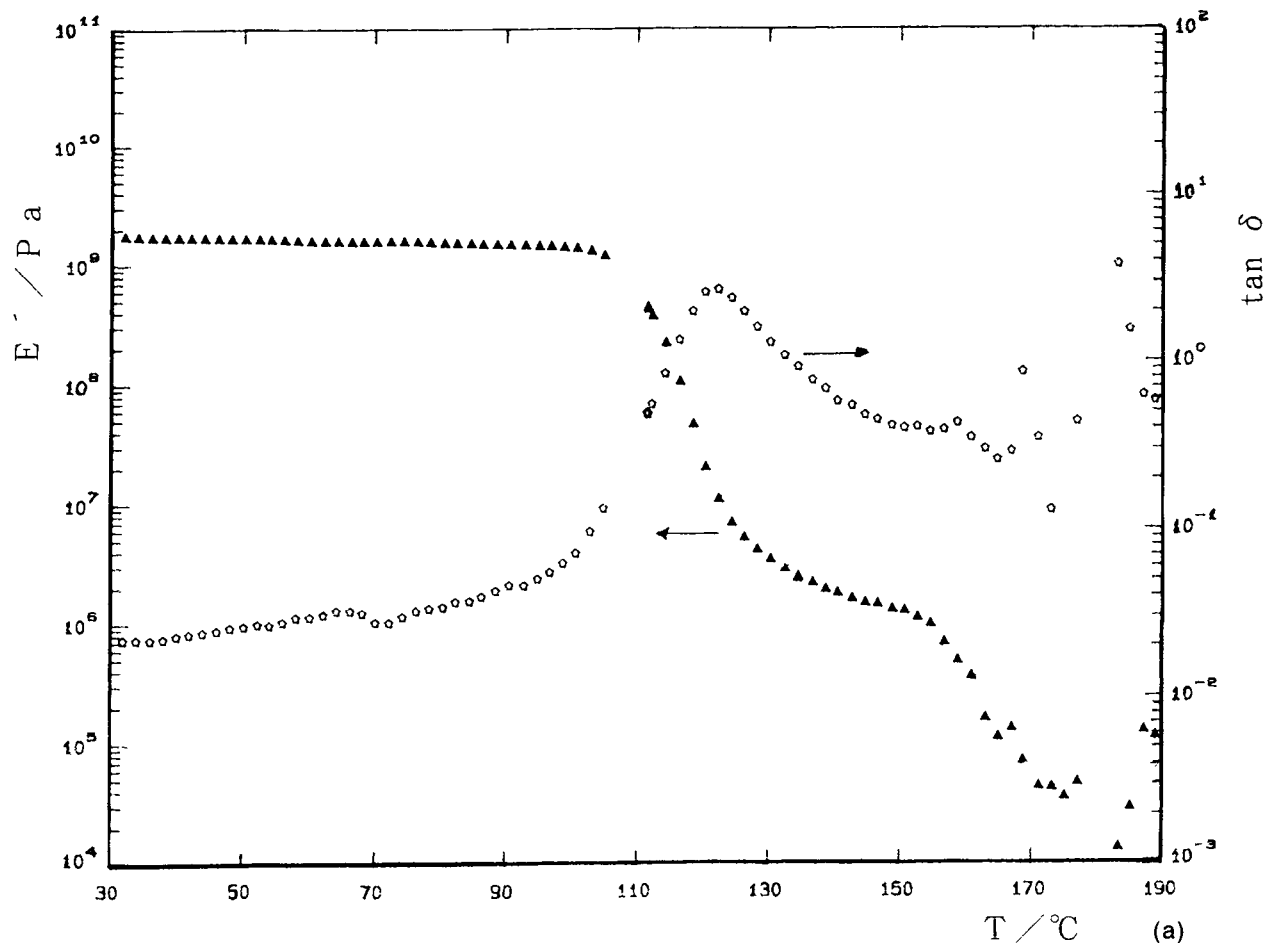


Figure 3 Dynamic viscoelastic observation of (a) the resin and (b) composite [100 : 30]. The storage modulus, E' and the loss tangent, $\tan \delta$, are plotted against the temperature, T .

resin surrounding the glass beads of a certain thickness is decreased by the interaction, and the decrease due to the interaction is in a clear linear relation with the mass fraction of the glass beads.

Similarly, results of thermal conductivity measurements are shown in Figure 2. Theoretical thermal conductivities were calculated using the Maxwell equation, measured thermal conductivity of the resin, and thermal conductivity of the glass beads (0.99 mW/m K), which datum was supplied by the producer, and they are also shown in Figure 2 as the above two curved lines. For applying the Maxwell equation, phase separation within the ABS resin is neglected and the ABS resin is assumed to be homogeneous, because the difference in thermal conductivity between them is small compared with the difference from the glass beads. Discrepancy between the measured data and the calculated data is found also below the critical temperature, while the agreement is good above this temperature. These results suggest the real existence of the interaction between the resin matrix and the glass beads below the critical temperature.

To confirm the interaction, the authors made a dynamic viscoelastic observation for the composites and the resin itself. Some of the results are reproduced in Figure 3. By comparing these two results, we can see that a new dissipation occurs by composite formation in a temperature range around the critical temperature (the dissipation peak at about 95°C), which is not observed for the resin per se. Except for this new dissipation, both curves for the composite and the resin are quite similar to each other. Therefore, this is also evidence for the interaction. For estimating the glass transition temperature, the temperatures at the peak of the loss tangent and at that of the loss modulus are observed, and they are, respectively, 124 and 111°C for the resin itself, 125 and 113°C for the composite [100 : 30], and 124 and 113°C for the composite [100 : 50].

From the above experimental results, we can conclude that interaction does exist between the ABS resin matrix and the glass bead filler and that this interaction causes the decrease in heat capacity and the increase in thermal conductivity below the critical temperature. One reasonable explanation for these facts is that molecular motion

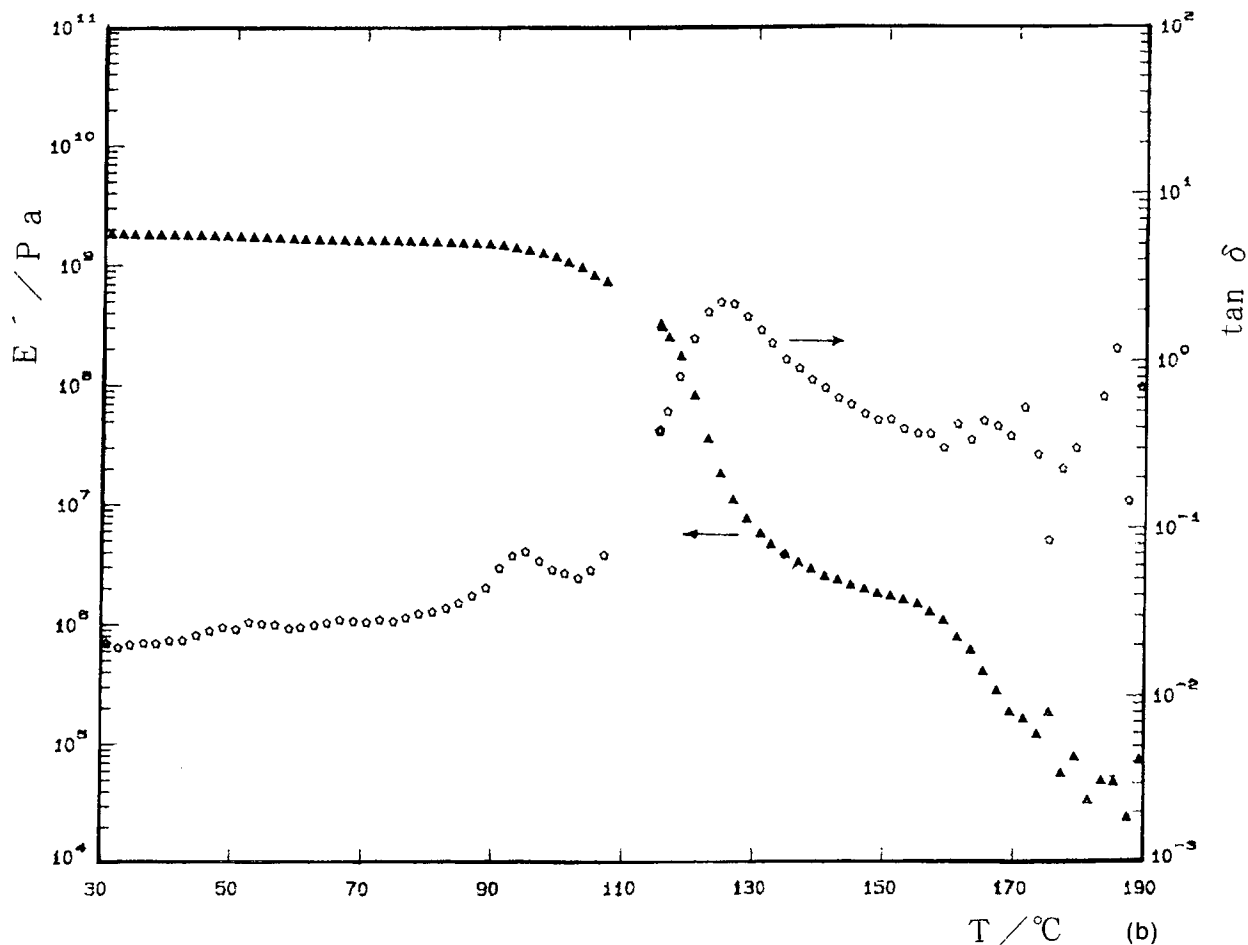


Figure 3 (Continued from the previous page)

of the resin molecule surrounding the beads is restricted, presumably by adhesion in the temperature range up to the critical temperature, above which the restriction and, hence, the interaction become diminished, as clearly observed by the additivity at 120°C for the heat capacity and also by the agreement of the thermal conductivity. It should also be noted that the extent of the interaction can be measured as the deviation of heat capacity from the additivity. It seems to be the product of the surface area of the filler and the strength of the interaction between the filler and the matrix. Therefore, heat-capacity measurements provide us with a quantitative method for evaluating the interaction.

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R. TSUKUDA

Polymer Laboratory Sakai Branch
Daicel Chemical Industries
Sakai, Osaka 590, Japan

S. SUMIMOTO

Research Center
Daicel Chemical Industries
Himeji, Hyogo 671-12, Japan

T. OZAWA*

Tsukuba Research Center
Daicel Chemical Industries
Tsukuba 305, Japan

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* To whom correspondence should be addressed.