

## Thermal Properties of Metal-Filled Epoxies

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### Synopsis

Thermal expansion coefficients and glass transition temperatures for metal-epoxy composites were determined experimentally. Results were in fair agreement with existing theories when certain fundamental assumptions were fulfilled. The effects of filler content and particle size as well as of adhesion between matrix and filler particles were investigated. The latter, in particular, was found to be of cardinal importance for the properties examined in the present work.

### INTRODUCTION

Metal-filled polymers, apart from highly improved mechanical properties, also exhibit better electrical and thermal conductivity, lower thermal expansivity, and, in general, improved behavior at elevated operating temperatures. One of the methods by which such composites can be produced is by dispersion of metal powders into thermoplastic solutions or into the liquid mixture of thermosetting resins and their curing agents.<sup>1</sup>

Epoxy resins are most widely used in modern technological applications and, in addition, are very suitable composite matrices. Their rheological behavior<sup>2</sup> as well as their dynamic properties<sup>3</sup> have been extensively investigated. Investigations on static and dynamic properties of particular metal-filled epoxies have been reported,<sup>4-6</sup> while a complete account on the dynamic properties of an epoxy resin filled with aluminum and iron particles of various sizes over a wide temperature range has been given by the authors.<sup>7</sup> Also, a great volume of results on dynamic properties of epoxy matrices filled with many inclusions of different shapes is given by Jenness and Kline.<sup>18</sup>

The thermal expansion properties of particulate composites have been treated by numerous authors, and an account of most of the existing theories along with a great number of experimental results for composites based on polymers are given by Holliday and Robinson.<sup>8</sup> Theoretical bounds for thermal expansion coefficients have been given by Levin,<sup>9</sup> Van Fo Fy,<sup>10</sup> and Schapery.<sup>11</sup>

The present work contains a study of thermal expansion properties as well as determination of the glass transition temperature for a number of aluminum-epoxy and iron-epoxy composites. With the first, the effect of imperfect adhesion and agglomeration of the filler particles was examined; while with the latter, different particle sizes were applied.

The effect of imperfect adhesion was examined by Brassel and Wischmann,<sup>12</sup>

while the effect of filler on the glass transition temperature of a polymeric matrix was studied by Landel and Smith,<sup>13</sup> Schwarzl,<sup>14</sup> Turner,<sup>15</sup> and others.

Static tests of the materials concerned were also carried out, in order to determine the effect of fillers on the  $E$ -modulus of the composites at ambient temperature.

### THEORETICAL CONSIDERATIONS

As is the case with the mechanical moduli, thermal expansion properties of composites can be determined from the respective properties of the constituent materials in three main ways: (a) by means of empirical or semiempirical formulae, valid in particular cases and for limited ranges of the parameters involved; the linear mixture equation (LME) is in most cases the obvious empirical approach, although, under certain conditions, it may be derived theoretically. (b) Based on a large number of assumptions, covering physical, geometric, topologic, etc. aspects, a thorough description of the composite system is effected, and the thermal stress/strain fields are determined under mechanical and/or thermal loading; energy balance is then considered in order to determine the thermal properties of the equivalent macroscopically homogeneous system. (c) By means of the variational principles of thermoelasticity, effective bounds for the thermal expansion coefficients are determined, in terms of known or readily derived parameters such as thermal expansion coefficients and mechanical moduli of the constituents and volume fraction of the filler material.

The following notation is employed: Indices  $m$  and  $f$  denote matrix and filler, respectively, no index denotes composite;  $\alpha$  is linear coefficient of thermal expansion;  $\gamma = 3\alpha$  is cubical coefficient of thermal expansion;  $K$ ,  $E$ ,  $G$  are bulk, Young's, and shear moduli, respectively;  $\nu$  is Poisson's ratio; and  $v$  is volume fraction of filler.

For spherical particles the following relations have been developed:<sup>8</sup>

*Kerner:*

$$\gamma = v\gamma_f + (1 - v)\gamma_m - v(1 - v)(\gamma_m - \gamma_f)q$$

where

$$q = \frac{(1/k_m) - (1/k_f)}{(v/k_f) + (1 - v)/k_f + (3/4)G_m}$$

and the factor containing  $q$  expresses the deviation from the LME (with polymeric matrices, it is usually  $\gamma_m > \gamma_f$ ).

*Blackburn:*

$$\gamma = \gamma_f + \frac{3/2(1 - \nu_f)(1 - v)(\gamma_m - \gamma_f)}{\frac{1}{2}(1 + \nu_f) + (1 - v)(1 - 2\nu_f) + (1 - 2\nu_m)(E_f/E_m v)}$$

*Wang and Kwei:*

$$\gamma = \gamma_m - vq(\gamma_m - \gamma_f)$$

where

$$q = \frac{(3E_f/E_m)v}{(E_f/E_m)[2v(1 - 2\nu_m) + (1 + \nu_m)] + 2(1 - v)(1 - 2\nu_f)}$$

*Tummala and Friedberg:*

$$\gamma = \gamma_m - v(\gamma_m - \gamma_f)q$$

where

$$q = \frac{(1 + \nu_m)/2E_m}{(1 + \nu_m)/2E_m + (1 - 2\nu_f)/E_f}$$

Relations holding irrespective of filler shape are the following:

*Turner:*

$$\gamma = [(1 - v)\gamma_m K_m + v\gamma_f K_f] / [(1 - v)K_m + vK_f]$$

which for  $\nu_m = \nu_f$  becomes  $\gamma = [(1 - v)\gamma_m E_m + v\gamma_f E_f] / [(1 - v)E_m + vE_f]$ .

*Thomas:*

$$\gamma^a = (1 - v)\gamma_m^a + v\gamma_f^a \quad (-1 \leq a \leq 1)$$

which for small  $a$  becomes  $\ln \gamma = (1 - v) \ln \gamma_m + v \ln \gamma_f$ .

*Cribb:*

$$\gamma = q_1\gamma_m + q_2\gamma_f \quad \text{where } q_1 = \frac{K_m(K - K_f)}{K(K_m - K_f)}$$

and

$$q_2 = \frac{K_f(K_m - K)}{K(K_m - K_f)}$$

*Fahmy and Ragai:*<sup>12</sup>

$$\alpha = \alpha_m - \frac{3v(\alpha_m - \alpha_f)(1 - \nu_m)}{2(1 - 2\nu_f)(1 - v) \frac{E_m}{E_f} + 2v(1 - 2\nu_m) + (1 + \nu_m)}$$

*Schapery:*<sup>11</sup>

$$\hat{\alpha}^{(-)} \leq \hat{\alpha} \leq \hat{\alpha}^{(+)}$$

$$\text{lower bound: } \hat{\alpha}^{(-)} = \bar{\alpha} + \left( \frac{\bar{K}\alpha}{\bar{K}} - \bar{\alpha} \right) \frac{\left( \frac{1}{E_L} - \frac{1}{\hat{E}_m} \right)}{\left( \frac{1}{E_L} - \frac{1}{E_U} \right)} - \Delta\hat{\alpha}$$

$$\text{upper bound: } \hat{\alpha}^{(+)} = \bar{\alpha} + \left( \frac{\bar{K}\alpha}{\bar{K}} - \bar{\alpha} \right) \frac{\left( \frac{1}{E_L} - \frac{1}{\hat{E}_m} \right)}{\left( \frac{1}{E_L} - \frac{1}{E_U} \right)} + \Delta\hat{\alpha}$$

where

$$\Delta\hat{\alpha} = \frac{3 \left( \frac{1}{\hat{E}_m} - \frac{1}{E_U} \right)^{1/2} \left( \frac{1}{E_L} - \frac{1}{\hat{E}_m} \right)^{1/2}}{\left( \frac{1}{E_L} - \frac{1}{E_U} \right)} \left[ \left( \bar{K}\alpha^2 - \frac{\bar{K}\alpha^2}{\bar{K}} \right) \left( \frac{1}{E_L} - \frac{1}{E_U} \right) - \frac{1}{9} \left( \bar{\alpha} - \frac{\bar{K}\alpha^2}{\bar{K}} \right) \right]^{1/2} \cong 0$$

$$\bar{K} = (1 - \nu)K_m + \nu K_f, \quad \bar{G} = (1 - \nu)G_m + \nu G_f, \quad \bar{\alpha} = (1 - \nu)\alpha_m + \nu\alpha_f$$

$$\bar{K}\alpha = (1 - \nu)\alpha_m K_m + \nu\alpha_f K_f$$

$$\bar{K}\alpha^2 = (1 - \nu)\alpha_m^2 K_m + \nu\alpha_f^2 K_f$$

$$\frac{1}{E_L} = \frac{1 - \nu}{E_m} + \frac{\nu}{E_f}, \quad \frac{1}{E_U} = \frac{1}{3} \left( \frac{1}{\bar{G}} + \frac{1}{3\bar{K}} \right)$$

where  $E_U$  and  $E_L$  are upper and lower bounds for the uniaxial modulus, respectively,

$$\hat{E}_m = \frac{2}{\frac{1}{E_L} + \frac{1}{E_U}}$$

Levin.<sup>9</sup>

$$\hat{\alpha}^{(-)} < \frac{\alpha - \alpha_f}{\alpha_m - \alpha_f} < \hat{\alpha}^{(+)}$$

$$\hat{\alpha}^{(-)} = \frac{(1 - \nu)(3K_f + 4G_f)K_m}{rf3K_m K_f + 4G_f[(1 - \nu)K_m + \nu K_f]}$$

$$\hat{\alpha}^{(+)} = \frac{(1 - \nu)(3K_f + 4G_m)K_m}{3K_m K_f + 4G_m[(1 - \nu)K_m + \nu K_f]}$$

The latter expressions are based on Hashin's<sup>16</sup> bounds for the bulk modulus of the composite and are subjected to the assumptions supporting these. Large differences between the mechanical moduli of the constituent materials (as with metals and plastics) pull upper and lower bounds far apart. Therefore, Levin's bounds are not applicable in the present case. On the contrary, Schapery's bounds, based also on a procedure minimizing their difference, conform in general with the experimental results obtained herein.

The above expressions generally refer to elastic composites, not taking into account the time-dependent behavior of a polymeric constituent. However, from the elastic solution, the viscoelastic one can be derived by means of the correspondence principle of linear viscoelasticity, provided that the constitutive equation of the material is given. Such an example for a Maxwell material is given by Levin.<sup>9</sup>

The question of the time dependence of the thermal expansion coefficient remains open. Regarding polymers, although such a behavior should be expected, according to Kowacz,<sup>17</sup> nothing of the sort was observed in the present cases. Composites should be time dependent, as their thermal expansion

coefficients are functions of time-dependent mechanical moduli. In the present work, some time dependence was observed with composite specimens at and around the glass transition temperature, however, it was practically negligible to the extent that the assumption of a time-independent thermal expansion coefficient was justified. This fact was also mentioned by Schapery.<sup>11</sup>

### EXPERIMENTAL

The matrix material was in all cases a cold-setting system based on a diglycidyl ether of bisphenol A resin (Epikote 828, Shell Co.) cured with 8% triethyl-enetetramine, which is slightly lower than stoichiometric. One particle size of aluminum powder with 0.2% Al<sub>2</sub>O<sub>3</sub> in the form of spheroidal grains with the following distribution was applied: +0.16 mm, traces; +0.125 mm; 0.5%; +0.04 mm, 10–12%; –0.04 mm, 80–90%.

On the other hand, three particle sizes of iron powder were used as follows:

Grain size, mm	Specific volume, cm <sup>3</sup> /100 g	Apparent density, g/cm <sup>3</sup>
0.15	38–41	2.6–2.4
0.30	40–44	2.5–2.3
0.40	38–41	2.6–2.4

The properties of the above materials are given in Table I.

The procedure of preparing the mixture of the liquid matrix phases and the metal powder and of rotating it in a closed mould, in order to obtain uniform distribution of filler particles, and the curing process, etc. are described in detail in reference 7.

The structural integrity of the specimens produced was checked by means of density measurements and by photomicrographs. In particular, with aluminum particles, where the small particle size may result in poor adhesion or particle agglomeration, "improved" specimens were also produced by means of more careful stirring and degassing, for comparison. The materials were tested on a du Pont 990 thermomechanical analyzer (TMA) in order to determine linear thermal expansion coefficients and glass transition temperatures.

Static properties of the materials were obtained by means of an Instron tester during creep experiments at room temperature.

TABLE I  
Properties of the Constituent Materials

	Aluminum	Iron	TETA-cured DGEBA resin
Young's modulus, N/m <sup>2</sup>	$7.0 \times 10^{10}$	$21 \times 10^{10}$	$0.353 \times 10^{10}$ <sup>a</sup>
Bulk modulus, N/m <sup>2</sup>	$7.3 \times 10^{10}$	$16.7 \times 10^{10}$	$0.421 \times 10^{10}$ <sup>a</sup>
Poisson's ratio	0.34	0.29	0.36 <sup>a</sup>
Density, g/cm <sup>3</sup>	2.70	7.80	1.19
Thermal expansion coefficient, °C <sup>-1</sup>			
$\alpha_1$	$22.4 \times 10^{-6}$	$15.0 \times 10^{-6}$	$65.26 \times 10^{-6}$
$\alpha_2$			$168.48 \times 10^{-6}$

<sup>a</sup> Properties determined during creep tests at 20°C and time  $t = 15$  sec.

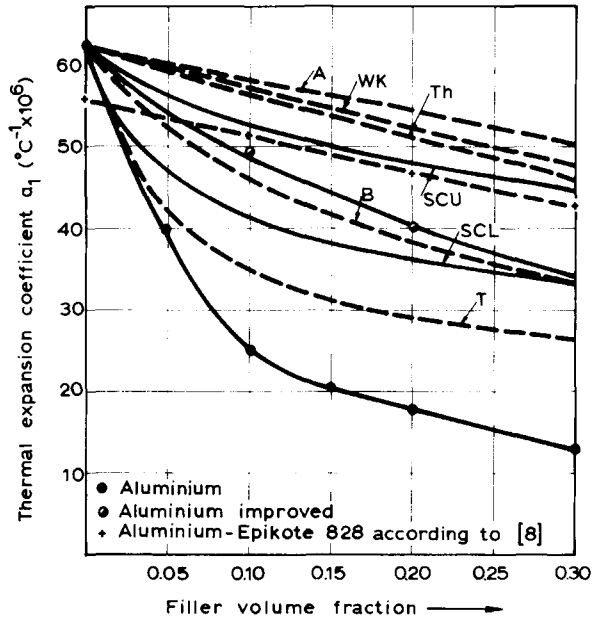


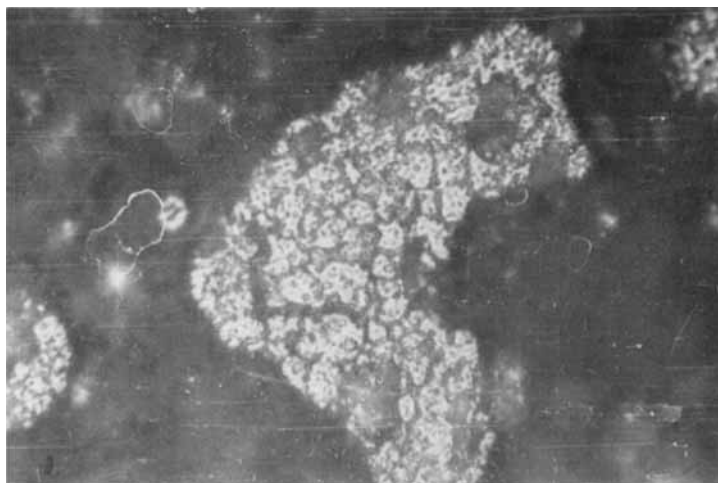
Fig. 1. Linear thermal expansion coefficient in the glassy region  $\alpha_1$  of aluminum-epoxy composites plotted against filler volume fraction and comparison with various theoretical predictions. A: Linear mixture equation, Kerner-Tummala; WK: Wang and Kwei; Th: Thomas; B: Blackburn; T: Turner; SCU-SCL: Schapery's upper and lower bounds.

## RESULTS AND DISCUSSION

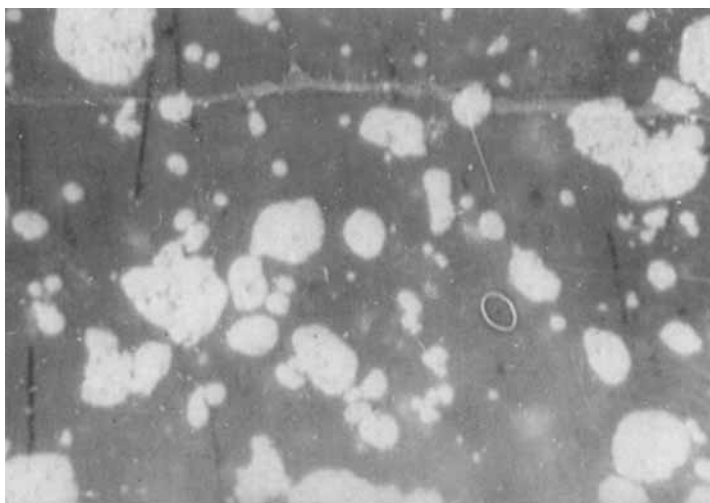
The linear thermal expansion coefficient of aluminum-epoxy composites in the glassy region (below glass transition) is given in Figure 1, plotted against the filler volume fraction. Respective values predicted by various theories are also plotted for comparison. Ordinary specimens fall well below all theoretical values, while improved ones, on the contrary, are within Schapery's bounds and are close to the experimental results obtained by others.<sup>8</sup> The different behavior should be explained by the formation of the microstructure, as it appears in Figure 2. With ordinary specimens, there is poor wetting of the particle surface by the matrix, due to the small particle size; and, in addition, the aluminum particles tend to agglomerate forming larger groups, held together during solidification by means of the stress fields created by the polymerization shrinkage. With improved specimens, no large groups develop, and individual particles are surrounded by the matrix with good adhesion conditions. In the first case, as the matrix expands faster than the inclusions, it tends to occupy existing voids and the overall thermal expansion coefficient is much lower than in the second case. Besides, the latter corresponds to the assumptions supporting the theories so far mentioned.

The same phenomenon, although much less pronounced, appears with thermal expansion properties above the glass transition temperature  $T_g$ , as presented in Figure 3.

With iron-epoxy specimens, coefficient  $\alpha_1$  (i.e., at temperatures lower than  $T_g$ ) is given in Figure 4 for all three particle sizes, along with theoretical predictions. Photomicrographs reveal that very little agglomeration occurs, except



(a)



(b)

Fig. 2. Surface photomicrographs of 20% aluminum-epoxy composites: (a) ordinary, (b) improved, indicating the difference between particle distributions. Magnification 250 $\times$ .

at high volume concentrations. Accordingly, experimental values are reasonably related to various theories; and, in particular, they all lie within Schapery's bounds, except higher than 20% specimens.

At high volume fractions, some agglomeration occurs, and the microphotograph of Figure 5 is of interest, where 0.3 mm iron particles under the action of shrinkage stresses are forming a perfectly spherical group. Coefficient  $\alpha_2$  (i.e., temperatures higher than  $T_g$ ) is shown in Figure 6.

The effect of iron particle size on both coefficients  $\alpha_1$  and  $\alpha_2$  for various filler volume fractions is presented in Figure 7. This effect appears to be increasing with filler volume fraction, in the fashion occurring with dynamic measurements,<sup>7</sup> and it is more pronounced with coefficient  $\alpha_2$ . Of course, it is expected that it

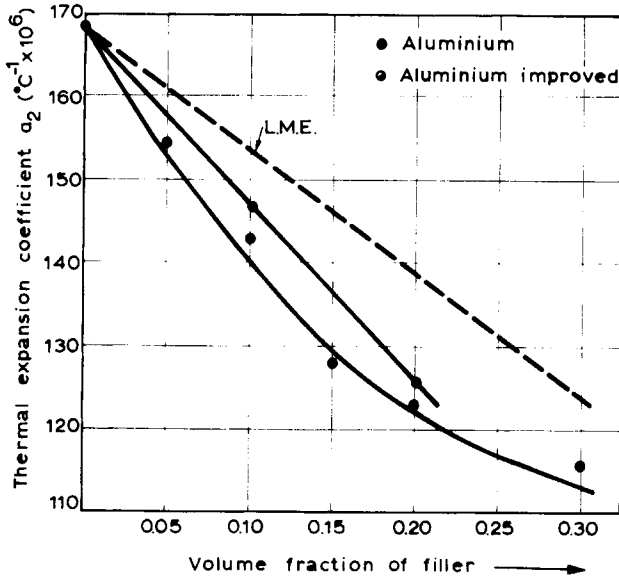


Fig. 3. Linear thermal expansion coefficient  $\alpha_2$  above glass transition temperature of aluminium-epoxy composites plotted against filler volume fractions.

is not the particle size itself which causes the effect, but the surface adhesion between matrix and filler particles, which is considerably affected by the particle size. As with dynamic measurements, at 0.3 mm particle size, the quality of adhesion acquires the highest value, corresponding to a maximum for each of the coefficients  $\alpha_1$  and  $\alpha_2$ .

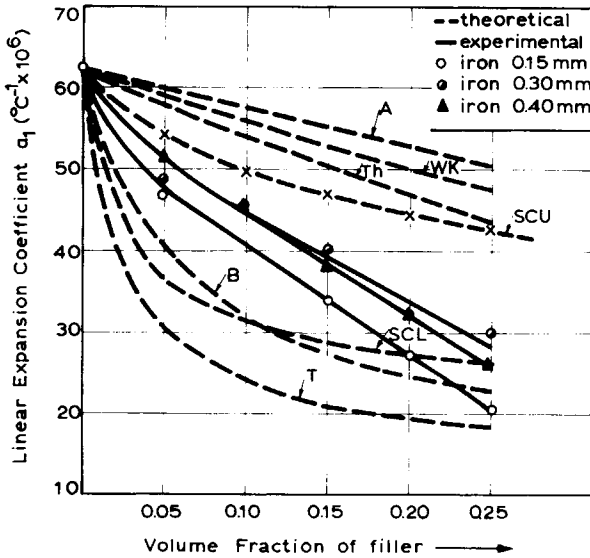


Fig. 4. Linear thermal expansion coefficient  $\alpha_1$  in the glassy region of iron-epoxy composites, with three different particle sizes plotted against filler volume fraction and comparison with various theoretical predictions. A: Linear mixture equation, Tummala; Th: Thomas for small "a;" B: Blackburn; T: Turner; WK: Wang and Kwei; SCU-SCL: upper and lower Schapery's bounds.



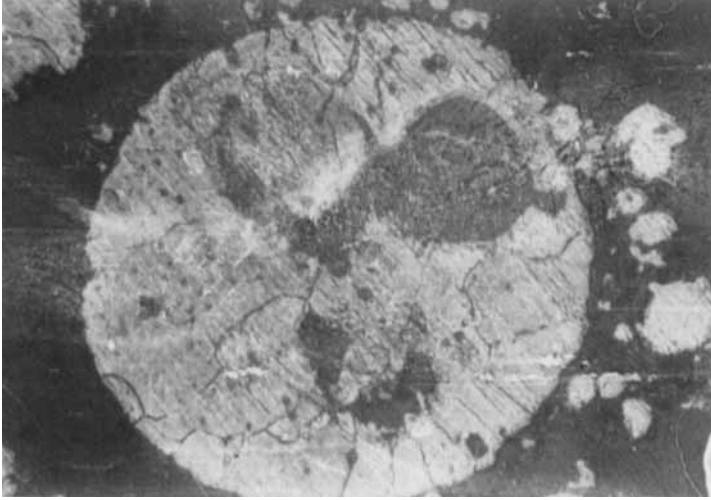


Fig. 5. Surface photomicrograph of a 20% 0.3 mm iron particle composite, indicating a spherical particle formation, due to the action of shrinkage stress fields. Magnification 250 $\times$ .

This similarity with dynamic behavior does not extend to static moduli. The latter were determined by means of creep experiments (at room temperature and time  $t = 15$  sec), and the results are presented in Figure 8. There is hardly any effect of the particle size, while the effect of the fillers generally conforms with existing theories.

A striking difference between aluminum and iron composites was observed as far as glass transition temperature  $T_g$  was concerned. Namely, with aluminum composites, according to Figure 9, introduction of filler causes  $T_g$  to drop from

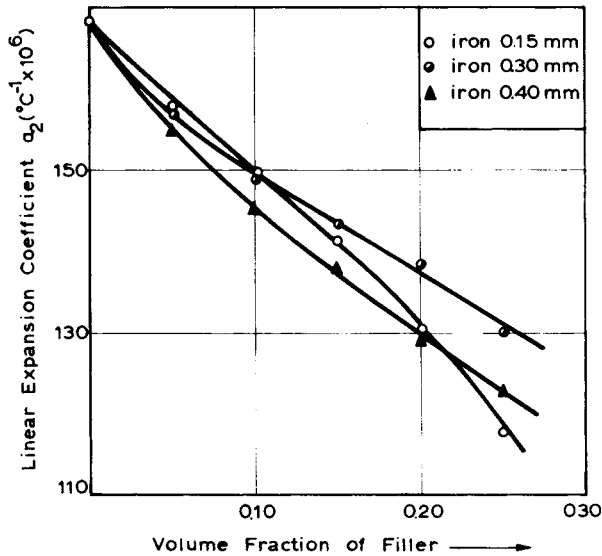


Fig. 6. Linear thermal expansion coefficient  $\alpha_2$  above glass transition temperature of iron-epoxy composites with three different particle sizes plotted against filler volume fraction.

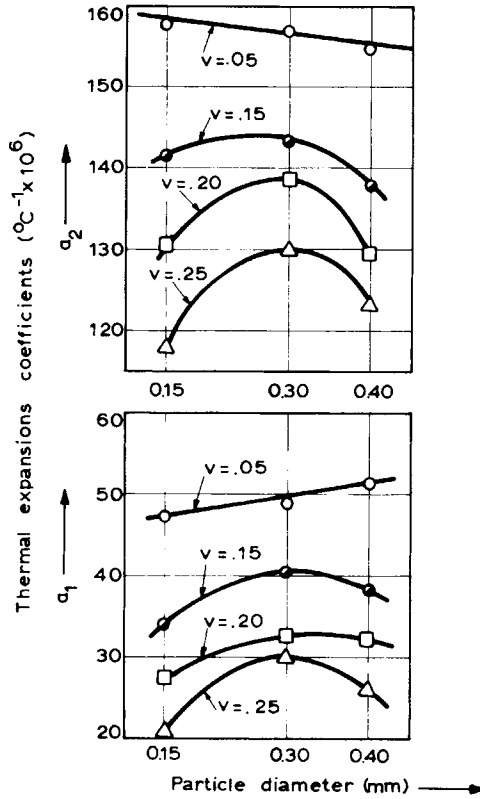


Fig. 7. Variation of thermal expansion coefficients with particle size for various filler volume fractions for iron-epoxy composites.

123°C to 110°C for ordinary specimens and to 84°C for improved ones. However,  $T_g$  appears thereafter to be independent of filler content in both cases. On the contrary, with iron composites,  $T_g$  is strongly dependent on filler content and on particle size as well, as shown in Figure 10.

Knowing that the difference between ordinary and improved aluminum specimens on the one hand and aluminum and iron specimens on the other is

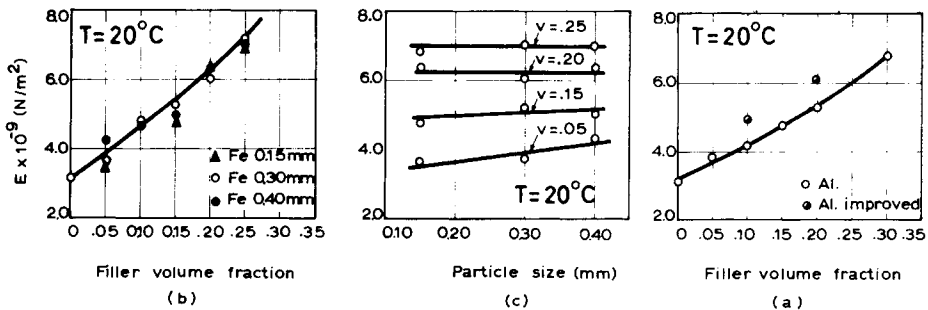


Fig. 8. Static  $E$  modulus of metal-epoxy composites: (a) effect of aluminum particle concentration for ordinary and "improved" specimens; (b) effect of iron particle concentration for three different particle sizes; (c) effect of iron particle size for various filler concentrations.

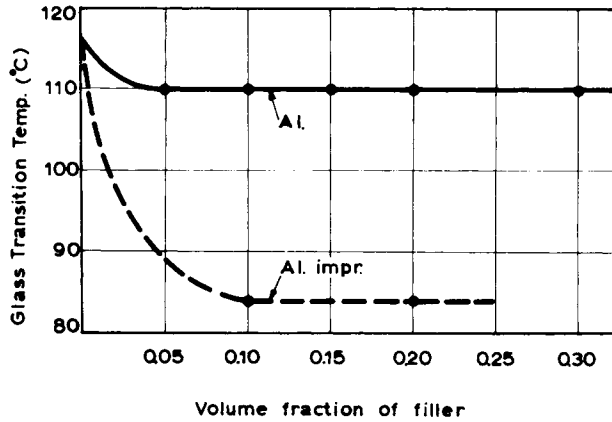


Fig. 9. Effect of filler volume content on glass transition temperature of aluminium–epoxy composites.

mainly the difference in the quality of adhesion between matrix and filler, one may conclude that the latter is a factor of decisive importance for the glass transition temperature of the composites.

Existing experimental results have so far neither confirmed nor rejected the possibility of  $T_g$  to be affected by the introduction of the filler,<sup>14</sup> as both phenomena have been observed on various occasions. This can probably be explained by means of the quality of adhesion, which is a factor not easy to determine.

The effect of particle size on  $T_g$ , presented in Figure 11, is, as already mentioned, indirectly acting through adhesion quality, which is optimized for 0.3 mm average diameter particles. Indeed, for this particle size, the drop of  $T_g$  acquires its maximum value.

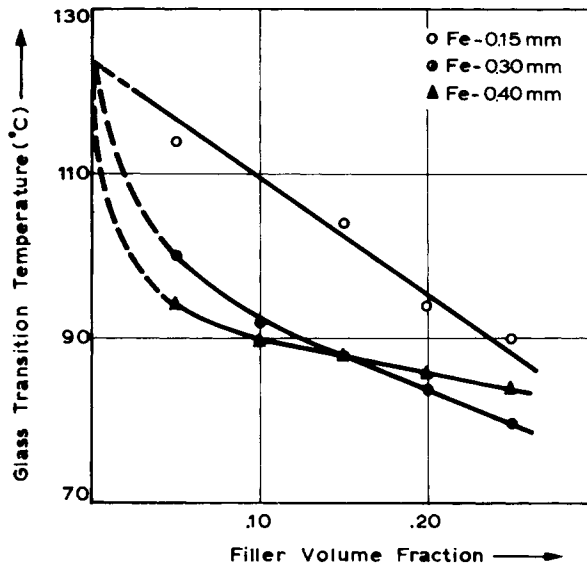


Fig. 10. Effect of filler volume content on glass transition temperature of iron–epoxy composites for various particle sizes.

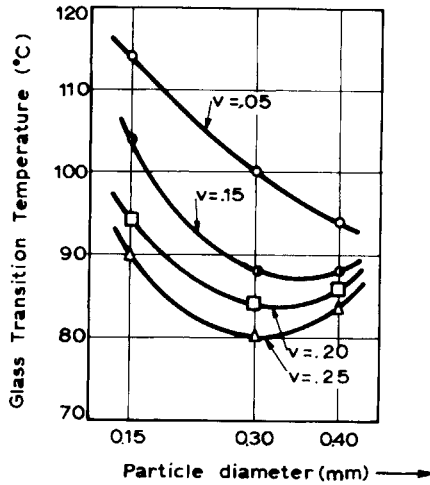


Fig. 11. Effect of iron size on glass transition temperature for various filler volume fractions.

## CONCLUSIONS

The effect of metal powders introduced into an epoxy matrix on thermal expansion properties and glass transition temperature of the respective composites was investigated. One size of aluminum particles and three different sizes of iron particles were applied. Aluminum composites, generally exhibiting low adhesion between matrix and filler, as well as agglomeration of the filler particles, were manufactured as ordinary and improved ones, i.e., with better adhesion quality. Measurements of the parameters concerned were carried out by means of a du Pont 990 thermomechanical analyzer. Results obtained were in fair agreement with existing theories, except with ordinary aluminum composites, where poor adhesion and agglomeration of particles did not conform with basic assumptions of the theories concerned. Also, certain theories using effective bounds for the mechanical moduli of composites were not applicable in the present case, since large differences between the respective moduli of matrix and filler materials are pulling those bounds far apart, and no accuracy can be obtained.

It was proved that quality of adhesion is a very important factor for the parameters concerned. However, its influence was mainly pronounced on the coefficient  $\alpha_1$  of the composite, i.e., below the glass transition temperature, while  $\alpha_2$  was much less affected.

Particle size was found to affect indirectly thermal expansion through adhesion quality. The latter appears to be optimized for 0.3 mm particle size, as photomicrographs and also dynamic measurements have shown, and both coefficients  $\alpha_1$  and  $\alpha_2$  acquire their maximum values for this size. This is more pronounced at high filler volume concentrations.

Judging from the present results, the glass transition temperature of the composites is strongly dependent on the content of filler; however, adhesion quality is also of cardinal importance. Generally, introduction of filler results in decreased  $T_g$  for the composites; however, this decrease, with aluminum composites, i.e., poor adhesion, is independent of the filler content, while with

iron composites,  $T_g$  strongly depends on the latter. Again, with 0.3 mm iron particles, i.e., at the optimum of adhesion,  $T_g$  acquires its minimum value.

The present work was partly supported by the NATO Scientific Affairs Division, Contract No. 558, and by the Empeirikos Foundation of Greece. The authors express their gratitude to both agencies. Thanks are also due to the National Research Institute, Athens, for the donation of the Du Pont 990 Thermal Analyzer, which rendered the present work possible.

### References

1. J. Delmonte, *Metal-Filled Plastics*, Rheinhold, New York, 1961.
2. P. S. Theocaris, *J. Appl. Polym. Sci.*, **8**, 399 (1964).
3. T. Hirai and D. E. Kline, *J. Appl. Polym. Sci.*, **17**, 31 (1973).
4. G. E. Nevill, Jr., J. M. Loyd, Jr., and H. R. Fuehrer, *J. Comp. Mater.*, **3**, 174 (1969).
5. R. Sierakowski, G. Hemp, and A. Hokstad, *J. Comp. Mater.*, **5**, 417 (1971).
6. M. G. Sharma, M. Critchfield, and W. F. St. Lawrence, *The Shock and Vib. Bull.*, Nav. Res. Lab., Washington, D.C., 1967, p. 95.
7. S. A. Paipetis, G. Papanicolaou, and P. S. Theocaris, *Fib. Sci. Technol.*, **8**, 221 (1975).
8. L. Holliday and J. Robinson, *J. Mater. Sci.*, **8**, 301 (1973).
9. V. M. Levin, *Mekhanika Tverdogo Tela*, **2**, 88 (1967).
10. G. A. Van Fo Fy, *Soviet Phys., Doklady*, **11**, 176 (1966).
11. R. A. Schapery, *J. Comp. Mater.*, **2**(3), 380 (1968).
12. G. W. Brassel and K. B. Wischmann, *J. Mater. Sci.*, **9**, 307 (1974).
13. R. F. Landel and T. L. Smith, *Amer. Rocket Soc. J.*, 599 (1961).
14. F. R. Schwarzl, *On the Mechanical Properties of Unfilled and Filled Polymers*, Central Lab. T.N.O., Delft, The Netherlands (1961).
15. S. Turner, *Appl. Mater. Res.*, 10 (1965).
16. Z. Hashin, *J. Appl. Mech.*, **29**, 1 (1962).
17. A. Kowacz, *J. Polym. Sci.*, **30**, 131 (1958).
18. J. R. Jenness, Jr., and D. E. Kline, *J. Appl. Polym. Sci.*, **17**, 3391 (1973).

Received January 16, 1976

Revised March 2, 1976