The influence of siloxane modifiers on the thermal expansion coefficient of epoxy resins

J. I. Meijerink, S. Eguchi*, M. Ogata, T. Ishii, S. Amagi and S. Numata
Hitachi Research Laboratory, Hitachi Ltd, 1-1, Omika-cho 7-chome, Hitachi-shi, Ibaraki-ken, 319-12 Japan

and H. Sashima
Hitachi Chemical Co. Ltd, 1772-2, Kanakubo, Yuki-shi, 308 Japan
(Received 22 March 1993)

The thermal expansion behaviour of unmodified and siloxane-modified epoxy resins has been investigated to clarify the mechanism by which siloxane modifiers lower the thermal expansion coefficient of epoxy moulding compounds containing inorganic fillers. A mechanism that accounts for all the observed characteristics is proposed. The thermal expansion coefficient of epoxy resins is increased by siloxane modifiers with carboxyl end groups, and the degree of the increase is dependent on the molecular weight of the modifiers. This increase is considered to be due to two effects: an increase in the local free volume in the epoxy matrix caused by the development of thermal stresses, and the building of siloxane molecules into the network structure. For sufficiently low molecular weight siloxane modifiers the latter effect is dominant, whereas with increasing molecular weight the former effect dominates. The increased coefficient of epoxy resins due to siloxane modifiers is likely to result in thermal stress near the filler–polymer interface because of an increased difference in the thermal expansion coefficient between the materials. This is one factor causing siloxane-modified epoxy moulding compounds to have a lower thermal expansion coefficient than unmodified ones.

(Keywords: epoxy resins; siloxane modifier; linear thermal expansion)

INTRODUCTION

Epoxy moulding compounds are used in the electronics industry to encapsulate semiconductor devices in order to protect them from their surroundings and connect them to printed circuit boards[1]. Such epoxy moulding compounds are composed of many raw materials. Nowadays, *o*-cresolnovolac epoxy resins are widely used as the base material because they have good pot lives and formability, and they show excellent humidity and heat resistance. They are normally used in combination with phenolnovolac resin hardeners and Lewis bases that act as accelerators for the cure reaction. Other materials are added to the epoxy resin, such as flexibilizers, fillers, and coupling, release and colouring agents[1].

Today, package sizes are being reduced to achieve compact mounting on circuit boards. This requires low-thermal-stress encapsulation materials[1–4]. Internal stress is caused by shrinkage during resin curing and disparity of shrinkage between the device and the encapsulant during cooling to room temperature (r.t.) after manufacture. The latter reason is considered to be the principal cause of thermal stress build-up[2].

* To whom correspondence should be addressed

Several authors have drawn attention to siloxane-modified epoxy moulding compounds as encapsulation material. Both the elastic modulus (E) and the thermal expansion coefficient (α) can be decreased without lowering the glass transition temperature (T_g) of the material[5–7]. The mechanism by which siloxane modifiers lower α of epoxy moulding compounds is still obscure.

The present study examines this mechanism by investigating the influence of siloxane modifiers on α of epoxy resins.

EXPERIMENTAL

Materials

Polyglycidyl ether of *o*-cresol-formaldehyde novolac (ESCN 195-6) was chosen as the control epoxy resin, and was supplied by Sumitomo Chemical. Its average epoxy equivalent weight was 196 g mol^{-1} eq. Phenol-formaldehyde novolac (H 100), supplied by Meiwa Kasei, was the curing agent. Its average hydroxy equivalent weight was 106 g mol^{-1} eq. Triphenylphosphine was used as accelerator. Various poly(dimethyl siloxane) modifiers, with different molecular weights and with carboxyl functional end groups, were used to modify the epoxy

0032-3861/94/010179-08
© 1994 Butterworth–Heinemann Ltd.

Table 1 Carboxyl equivalent weights of the siloxane modifiers

Siloxane modifier	Carboxyl equivalent weight ($g\,mol^{-1}$ eq)
A	690
B	1400
C	2420
D	2910
E	5900
F	9070

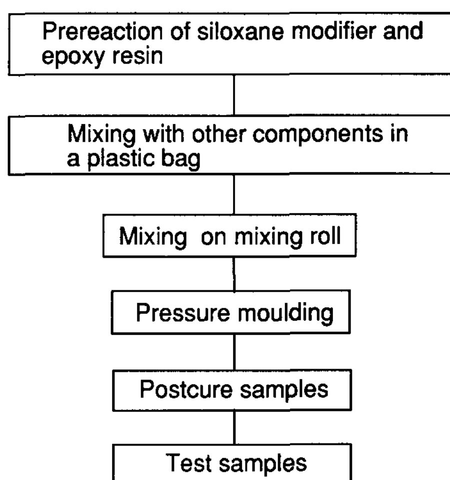

Figure 1 Production scheme for siloxane-modified epoxy resins

resin. These siloxane modifiers were supplied by Toray Dow Corning Silicone. *Table 1* lists their carboxyl equivalent weights; their molecular weights were twice these values.

In the preparation of epoxy moulding compounds, two different types of silica fillers were used: spherical fillers (SF), and angular fillers (AF). The average particle diameters of the SF and AF were 24.7 and 5.5 mm, respectively. Glycidoxypropyl trimethoxysilane (Shinetsu Chemical Co. Ltd) was used as the coupling agent, and ethyleneglycol ester of montanic acid (Hoechst Japan Ltd) was the release agent.

Prereaction

Figure 1 depicts the production scheme for the test pieces. In the first step, the siloxane modifier was prereacted in toluene with ESCN 195-6 at the maximum solubility. The purpose of the prereaction was to chemically bind the siloxane modifier to the epoxy resin. This prevents both outflow of the siloxane modifier during mixing of the components on the mixing roll, and migration of the siloxane modifier to the surface during curing. Moreover, prereaction has been shown to be necessary in controlling system morphology[8–15].

Prereaction was carried out at 104°C for 3–9 h, depending on the molecular weight of the siloxane modifier. The required times were determined based on gel permeation chromatography (g.p.c.) of the products. The amount of accelerator added was 1.2 parts per hundred parts resin by weight (phr) in each case and the molar ratio of carboxyl to epoxy groups was 0.05. After prereaction, the solution was poured into a box covered with Teflon foil. The solvent was evaporated in air overnight and then under high vacuum at 50°C for 2 h. Thermal gravimetric analysis (t.g.a.) measurements showed that these samples contained less than 0.6 wt% toluene.

Preparation of cured epoxy resins

The prereacted siloxanes with epoxy resins were mixed with H 100, accelerator and the remainder of ESCN 195-6 on a mixing roll. The mixed amounts were chosen so that the amount of epoxy functional groups was equal to the sum of carboxyl and hydroxyl functional groups on the modifier and hardener, respectively, and the amount of siloxane modifier was such that the total weight fraction was 10% of the total network. Mixing on the mixing roll was carried out for 10 min at a temperature of 65–80°C. After cooling these materials to r.t., they were pulverized with a hammer. The gel time of these materials was about 24 s.

The test pieces were made by pressure moulding at 180°C for 3 min at a pressure of 7 MPa. The mould used was a circular disc with a thickness of 2 mm and a diameter of 90 mm. The test pieces were cured at 200°C for 6 h. Differential scanning calorimetry (d.s.c.) and Fourier transform infra-red (*FT*i.r.) measurements demonstrated that the cure was complete for these conditions.

Preparation of epoxy moulding compounds

The resin materials composed of the prereacted siloxane, H 100, and the remainder of ESCN 195-6 were mixed with filler, coupling agent and release agent on the mixing roll. The composition of the filler was SF/AF = 70/30 (wt/wt). In all cases, the filler volume fraction was 64%, and the respective amounts of coupling and release agents were 3.0 phr and 1.0 phr, respectively, to 100 phr of ESCN 195-6. Mixing conditions on the mixing roll were the same as for the cured epoxy resins. After pulverizing and forming tablets at r.t., epoxy moulding compounds were transfer-moulded in a transfer machine and cured under the same conditions as cured epoxy resins.

Linear thermal expansion coefficient measurements

The value of α was determined by a DuPont Instruments 943 thermal mechanical analyser (t.m.a.). The samples were 6 mm × 6 mm × 2 mm. In the first heating run the samples were heated from r.t. to 220°C at a heating rate of $20°C\,min^{-1}$. After that, the samples were cooled in the cell to 140°C and then removed for rapid cooling to r.t. In the second heating run the samples were heated from r.t. to 250°C at a heating rate of $2°C\,min^{-1}$. α was measured between 65 and 115°C.

Dynamic measurements

The dynamic modulus and the epoxy and siloxane T_g values were determined on a Rheology Engineering dynamic mechanical thermal analyser (d.m.t.a.). The measurements were made from −160 to 250°C at a frequency of 10 Hz with a heating rate of $5°C\,min^{-1}$. The samples were 2 mm × 2 mm × 20 mm.

Electron microscopy

The morphology of cold-snap surfaces of cured specimens was determined by scanning electron microscopy (SEM). A Hitachi S-650 SEM apparatus was used at a magnification of 10 000 ×.

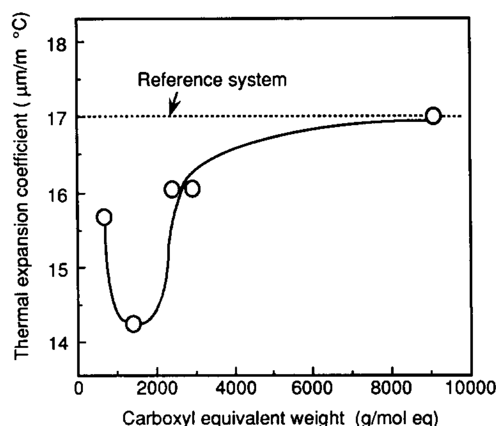

Figure 2 Linear thermal expansion coefficients of siloxane-modified epoxy moulding compounds as a function of the siloxane carboxyl equivalent weight

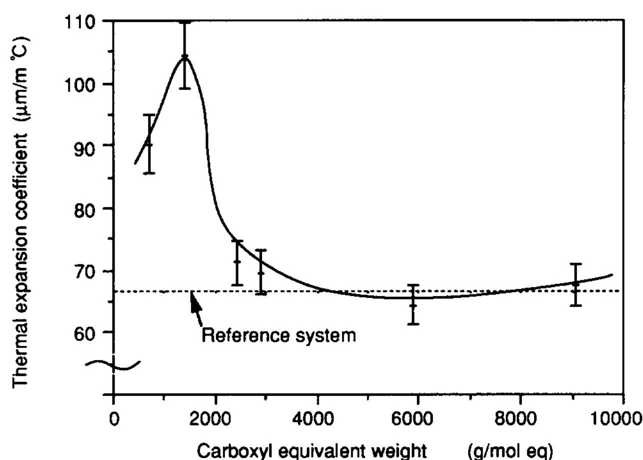

Figure 3 Linear thermal expansion coefficients of siloxane-modified epoxy resins as a function of the siloxane carboxyl equivalent weight

RESULTS AND DISCUSSION

Linear thermal expansion coefficient

The values of α for epoxy moulding compounds and resins are depicted in *Figures 2* and *3*, respectively, as a function of the siloxane carboxyl equivalent weight. It can be seen from *Figure 2* that α of the siloxane-modified epoxy moulding compound containing 64 vol% of filler is lower than α of the unmodified one, i.e. the reference system. A minimum occurs for the siloxane modifier with a carboxyl equivalent weight of $1400\,g\,mol^{-1}$ eq. On the other hand, the unfilled epoxy resins show the opposite thermal expansion behaviour, as seen in *Figure 3*. The maximum of α is observed for the same siloxane modifier (carboxyl equivalent weight $= 1400\,g\,mol^{-1}$ eq). Also, when the carboxyl equivalent weight is $690\,g\,mol^{-1}$ eq, α is increased significantly. For carboxyl equivalent weights above $2420\,g\,mol^{-1}$ eq, α is only slightly decreased and it tends to increase with increasing carboxyl equivalent weight of the modifier.

Since this thermal expansion behaviour of epoxy resins is one of the factors determining the behaviour of moulding compounds, the mechanism by which α is increased owing to siloxane modifiers should be clarified.

Morphology of epoxy resins

First, information about the morphology of the materials is derived by observing the colours of the cured modified epoxy resins. The material containing the lowest molecular weight siloxane modifier is transparent. When the carboxyl equivalent weight of the siloxane modifier is $1400\,g\,mol^{-1}$ eq, the material shows some whitening. The other siloxane-modified epoxy resins have a definite white colour. So the lowest molecular weight siloxane modifier might be completely miscible after cure with the epoxy resin. The other siloxane modifiers are probably partially miscible after cure with the epoxy resin. The degree of miscibility seems to decrease with increasing carboxyl equivalent weight.

More information about the morphology of the system is obtained from dynamic mechanical properties of epoxy resins, as shown in *Figures 4* and *5*. T_g data of the epoxy resins, obtained from the peak positions of $\tan\delta$ in the figures, are summarized in *Table 2*. The lowest molecular weight siloxane modifier decreases the epoxy T_g significantly, whereas the siloxane modifiers with a carboxyl equivalent weight of more than $1400\,g\,mol^{-1}$ eq have little influence on the epoxy T_g. It can be seen from *Figures 4* and *5* that the epoxy resins containing the latter siloxane modifiers show a clear siloxane T_g around $-120°C$. However, for the epoxy resin containing the siloxane modifier with carboxyl equivalent weight of $690\,g\,mol^{-1}$ eq, a siloxane T_g is not clearly observed. The lowest molecular weight siloxane modifier tends to be miscible while the other siloxane modifiers of higher molecular weight are not miscible after cure with the epoxy resin.

Finally, evidence for the observed phenomena is obtained by SEM. The morphologies of the cold-snap surfaces are illustrated in *Figure 6*. Small particles are observed in the epoxy resin modified with the lowest molecular weight siloxane. The particle diameter is about 0.2 mm. Also, small particles in the modified epoxy resins are observed for siloxane carboxyl equivalent weights of 1400 and $2420\,g\,mol^{-1}$ eq. The particle diameter seems unchanged. The other modified epoxy resins, containing higher molecular weight siloxane, contain only gaps. The diameter of the gaps increases with increasing carboxyl equivalent weight of the modifier.

These results show that the siloxane modifiers with carboxyl equivalent weights of 690 and $1400\,g\,mol^{-1}$ eq are partially miscible after cure with the epoxy resin. The degree of miscibility increases with decreasing carboxyl equivalent weight of the modifier. All the other siloxane modifiers are completely immiscible after cure with the epoxy resin. They show a clear multiphase nature of the modified networks, as described by Yorkgitis *et al.*[8].

With increasing carboxyl equivalent weight of the siloxane modifier, the weight fraction of functional groups

Table 2 T_g of siloxane-modified epoxy resins

Siloxane modifier	T_g (°C)
Reference	193
A	186
B	192
C	201
D	195
E	192
F	195

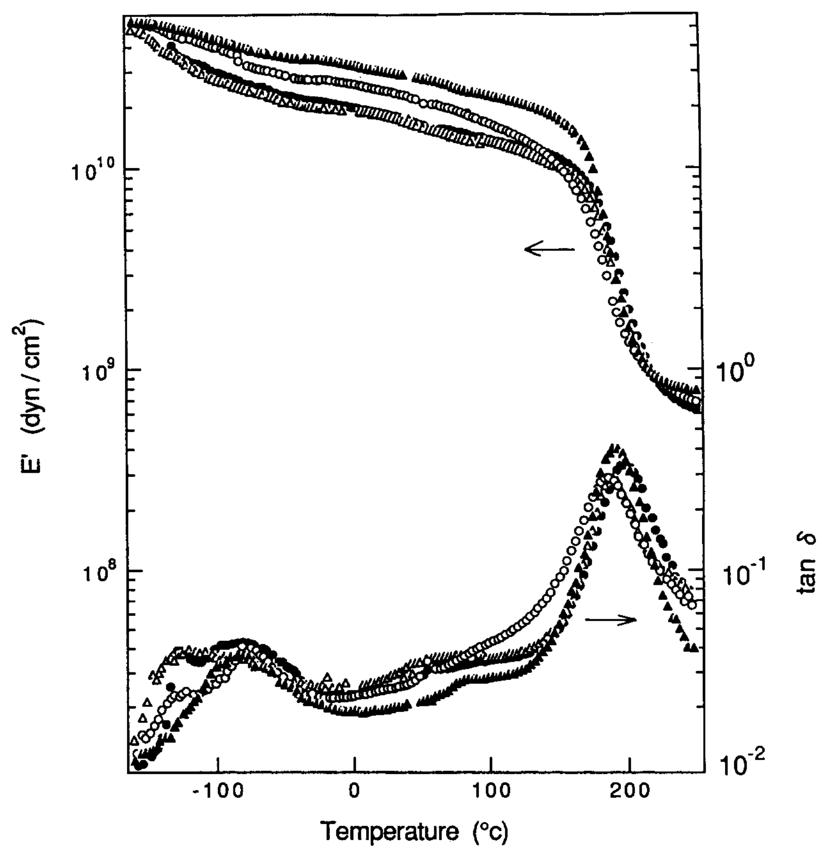

Figure 4 Dynamic mechanical properties of unmodified (▲) and siloxane-modified epoxy resins. Carboxyl equivalent weight of the siloxane modifier (g mol^{-1} eq): ○, 690; △, 1400; ●, 2420

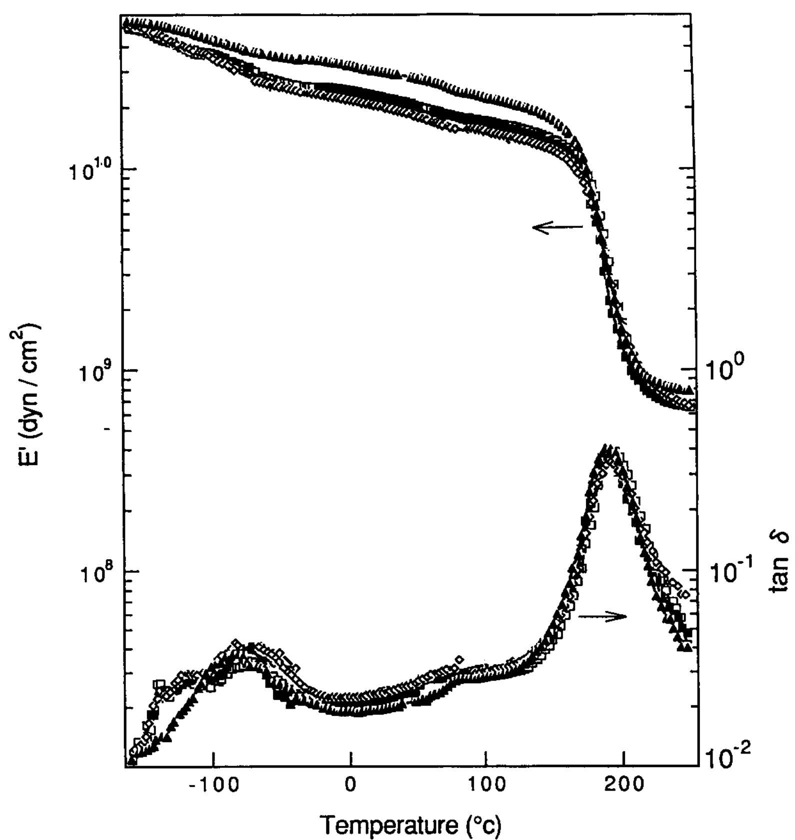

Figure 5 Dynamic mechanical properties of unmodified (▲) and siloxane-modified epoxy resins. Carboxyl equivalent weight of the siloxane modifier (g mol^{-1} eq): ◇, 2910; ■, 5900; □, 9070

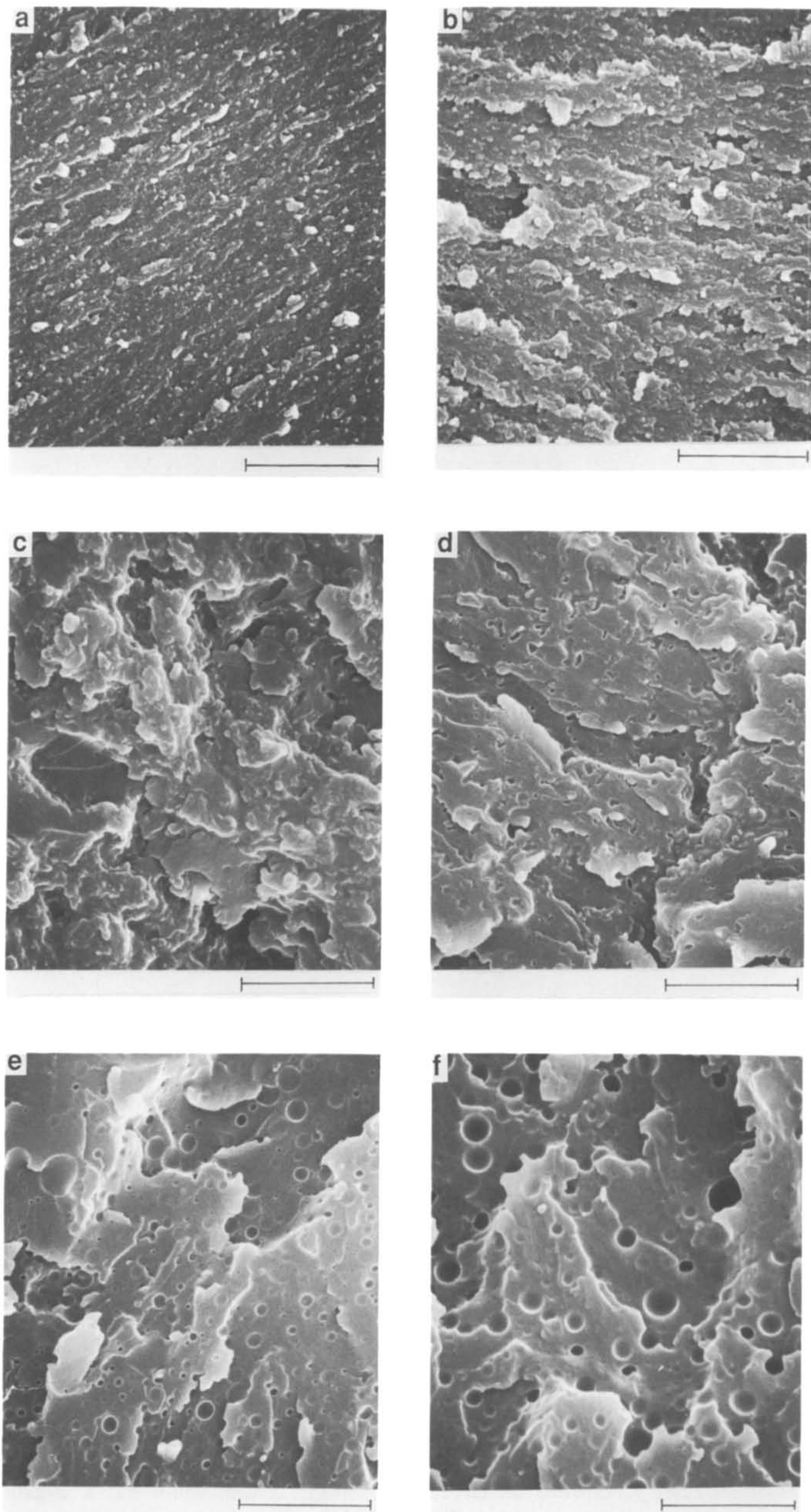

Figure 6 Scanning electron micrographs of fracture surfaces of epoxy resins modified with various siloxane modifiers. Carboxyl equivalent weight ($g\,mol^{-1}$ eq): (a) 690; (b) 1400; (c) 2420; (d) 2910; (e) 5900; (f) 9070. The scale bar represents 3 μm

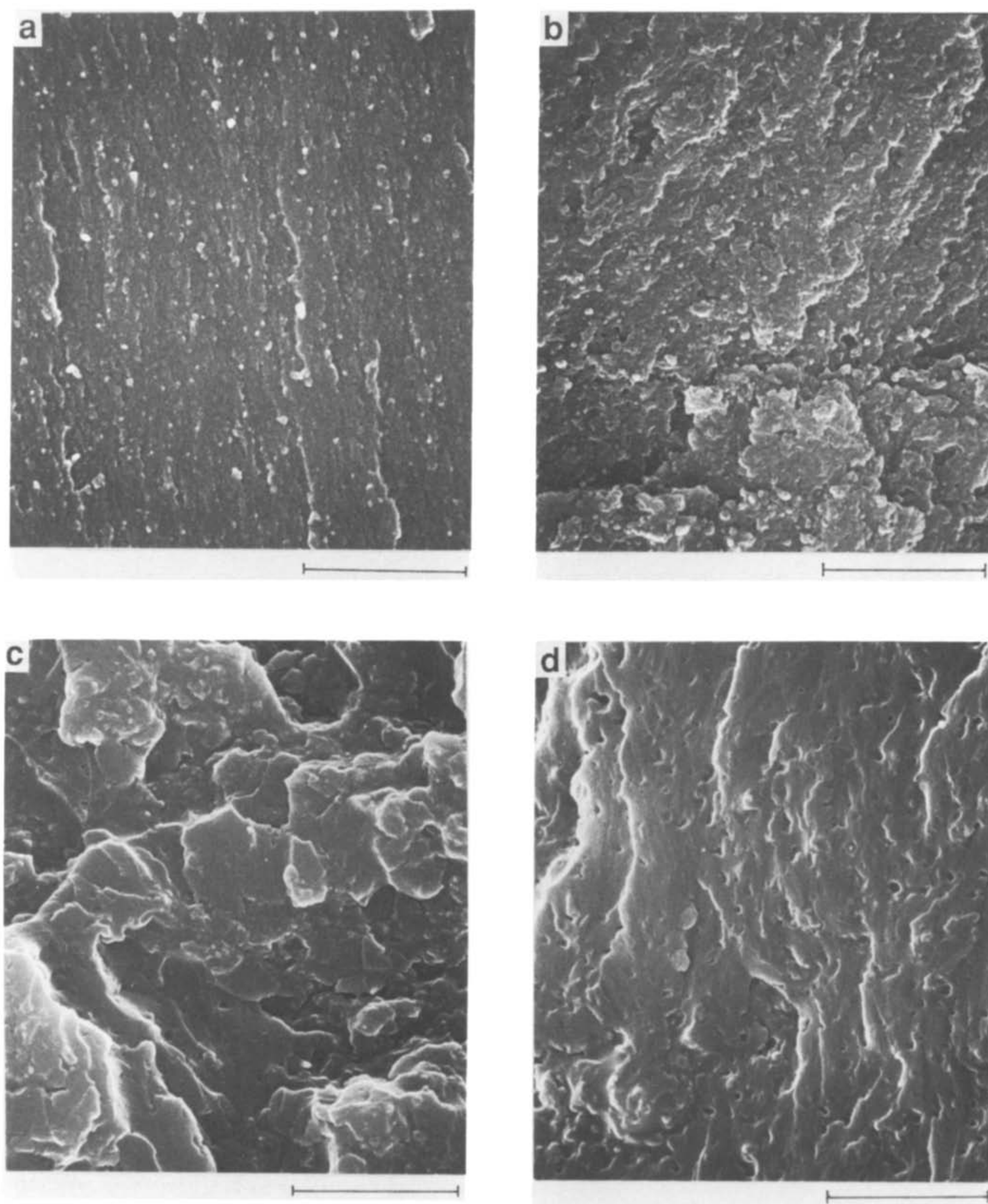

Figure 7 Scanning electron micrographs of fracture surfaces of epoxy resins modified with various siloxane modifiers after etching in tetrahydrofuran for 1 h. Carboxyl equivalent weight ($g\,mol^{-1}$ eq): (a) 690; (b) 1400; (c) 2420; (d) 2910. The scale bar represents 3 μm

decreases. So, it is expected that the adhesion strength at the interface between the siloxane particles and the epoxy matrix decreases with increasing carboxyl equivalent weight of the modifier. In order to illustrate this qualitatively, the cold-snap surfaces of the siloxane-modified epoxy resins were etched in boiling tetrahydrofuran for 1 h (*Figure 7*). Etching does not change the morphology of the modified epoxy resin containing siloxane with a carboxyl equivalent weight of $690\,g\,mol^{-1}$ eq. This indicates a miscible state of this siloxane in the epoxy matrix. The etched surface of the epoxy resin modified with siloxane with a carboxyl equivalent weight of $1400\,g\,mol^{-1}$ eq is very different from that of the unetched sample. Etching creates gaps and particles with less epoxy matrix material surrounding them. The number of particles seems to be increased. Comparing the etched and unetched surfaces of the epoxy resin with the siloxane modifier with a carboxyl equivalent weight of $2420\,g\,mol^{-1}$ eq shows that etching only increases the number of gaps. For the siloxane modifier with a carboxyl equivalent weight of $2910\,g\,mol^{-1}$ eq, the etched and unetched surfaces of the epoxy resins are the same: only gaps are observed. This indicates a strong adhesive strength at the interface between the siloxane particle and the epoxy matrix for the siloxane with the carboxyl equivalent weight of $1400\,g\,mol^{-1}$ eq. The adhesive strength seems to decrease with increasing carboxyl equivalent weight of the modifier. So the assumption is confirmed.

Dynamic modulus of epoxy resins

The dynamic modulus of the siloxane-modified epoxy resins is depicted in *Figure 8*. The dynamic moduli of the siloxane-modified epoxy resins are lower than that of the reference system, which has a dynamic modulus of 2.3 GPa. The siloxane-modified epoxy resins show a minimum for the siloxane carboxyl equivalent weight of $1400\,g\,mol^{-1}$ eq, and their values increase as a

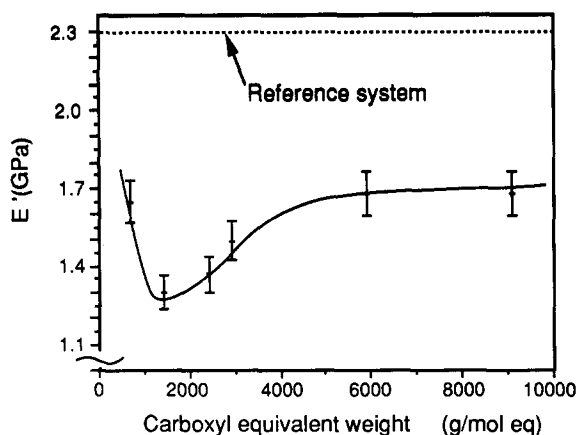

Figure 8 Dynamic modulus of the siloxane-modified epoxy resins

function of carboxyl equivalent weight. Important factors determining the dynamic modulus are the fraction of dissolved modifier in the matrix, the volume fraction of phase-separated modifier, and adhesion at the interface[8]. The lowest molecular weight siloxane modifier shows the highest degree of miscibility with the epoxy matrix after cure. It is known[8], that the dissolved modifier does not decrease the modulus as much as a phase-separated modifier. This explains the relatively high modulus of this material compared to the other modified materials. With increasing siloxane molecular weight, the volume fraction of phase-separated modifier probably increases due to the lower degree of miscibility, which results in a sharp decrease in modulus. However, the increase in modulus for the higher molecular weight siloxane modifiers cannot be explained by the factors mentioned so far; another factor must be at work.

Proposed mechanism for thermal expansion behaviour

Epoxy resins. The lowest molecular weight siloxane modifier shows the highest degree of miscibility with the epoxy resin after cure. Building siloxane molecules into the network structure results in an increased intrinsic thermal expansion of the network chains. This is seen as the dominant mechanism for increasing the linear thermal expansion coefficient (α) of the epoxy resin with this modifier.

The siloxane modifier with a carboxyl equivalent weight of 1400 g mol^{-1} eq increases the linear α of the epoxy resin most drastically. In this case, the intrinsic thermal expansion of the network chains is increased by partial miscibility between the modifier and the epoxy resin. Moreover, there is another factor that explains the extraordinarily high value of α for this material. It is known[16–19] that the addition of a modifier to the epoxy matrix, with a higher thermal expansion than the matrix, leads to the occurrence of radial tensile stresses that build up in the particle–matrix interface, accompanied by tangential compressive stresses in the surrounding matrix after cooling from the cure temperature to r.t. These stresses might increase the local free volume in the epoxy matrix[20,21] and thus increase the linear α[1]. This increase in local free volume might also explain the relatively low dynamic modulus for this material. As shown previously, the adhesion at the interface should be quite strong for this material, which is a prerequisite for stress build-up. When the adhesion at the interface is insufficient to support the stresses, gaps are formed and the linear α is unchanged[18].

The siloxane modifiers of higher molecular weight are completely immiscible after cure with the epoxy resin, as shown. Thus the increase of the linear α can only be caused by thermal stresses developing in the epoxy matrix; however, the effects are small. This might be due to low adhesion strengths at the particle–matrix interface. The tendency for the linear α to decrease with increasing carboxyl equivalent weight of the siloxane modifier can be explained by decreasing adhesion strengths at the particle–matrix interface, resulting in lower stresses, causing less increase in the local free volume with increasing carboxyl equivalent weight. This can also explain the increase of the dynamic modulus with increasing carboxyl equivalent weight.

Epoxy moulding compounds. Siloxane modifiers, which increase the value of α of the neat resins compared to the unmodified resin, tend to decrease α of the moulding compounds. The epoxy moulding compound modified with the silicon modifier of 1400 g mol^{-1} eq carboxyl equivalent weight seems to be very interesting because it has the lowest value of α.

The addition of silica fillers, with lower values of α than the resin matrix, has the opposite effect on stress compared to the case of silicon modifiers in the epoxy resins; that is, radial compressive stresses occur at the interface of the resin and the filler, and tangential tensile stresses occur in the surrounding matrix from the cure temperature to r.t.[18]. These stresses should reduce the local free volume in the resin matrix and thus decrease the value of α of the material. This effect is likely to become large in the epoxy resins with a high value of α, since a large difference in the value of α between the filler and the resin increases these stresses.

Thus, the siloxane modifiers are considered to cause an opposite effect on α in the moulding compounds as compared to the epoxy resins. However, other factors exist that determine the thermal expansion coefficient of moulding compounds, such as elastic modulus and Poisson ratio of the epoxy resin, and filler content[18]. Stress measurements and determination of these factors are necessary to give the final mechanism. Further work is under consideration.

CONCLUSIONS

Siloxane modifiers with carboxyl end groups increase the linear thermal expansion coefficient of epoxy resins, while they decrease the thermal expansion coefficient of epoxy moulding compounds. The degree of change is dependent on the molecular weight of the siloxane modifier. The effect is greatest when the siloxane carboxyl equivalent weight is 1400 g mol^{-1} eq. For higher siloxane carboxyl equivalent weights the effect is small.

Two factors influence the thermal expansion behaviour of siloxane-modified epoxy resins. First, the degree of miscibility after cure between the epoxy resin and the siloxane modifier determines this behaviour. A higher degree of miscibility after cure results in a higher intrinsic thermal expansion of the network chains as a result of building siloxane molecules into the network structure. Second, thermal stresses, which develop in the epoxy matrix as a result of phase-separated particles that tend to have a higher degree of shrinkage than the epoxy

matrix after cooling from the cure temperature to r.t., result in an increased local free volume in the epoxy matrix. This results in a higher thermal expansion coefficient.

For the lowest molecular weight siloxane modifier, the miscibility effect dominates, whereas the thermal stress effect dominates for the siloxane modifiers having carboxyl equivalent weights higher than 2420 g mol^{-1} eq, since they are completely phase separated. For these modifiers, the adhesion at the particle–matrix interface seems to decrease with increasing siloxane carboxyl equivalent weight, resulting in lower free volumes and thus lower thermal expansion coefficients. These lower free volumes can also explain the increase in the dynamic modulus as a function of the siloxane carboxyl equivalent weight for these materials. When the carboxyl equivalent weight of the siloxane modifier is 1400 g mol^{-1} eq, both effects might occur, resulting in an extraordinarily high thermal expansion coefficient of this material.

This thermal expansion behaviour of epoxy resin seems to have an effect on that of epoxy moulding compounds. It is likely that the increased difference of the thermal expansion coefficient between the resin and the filler leads to the development of thermal stresses near the filler–polymer interface. This is one factor determining the thermal expansion behaviour of epoxy moulding compounds.

ACKNOWLEDGEMENTS

The authors thank Toray Dow Corning Silicone for the supply and synthesis of siloxane modifiers, and gratefully acknowledge M. Inoue, F. Furusawa, S. Ichimura and K. Kinashi of Hitachi Chemical Company for helpful discussions and for supplying siloxane.

REFERENCES

1 Kinjo, N., Ogata, M., Nishi, K. and Kaneda, A. 'Advances in Polymer Science 88', Springer-Verlag, Berlin, 1989
2 Kuwata, K., Ikoh, K. and Tabata, H. *IEEE Trans. Components Hybrids Manuf. Technol.* 1985, **CHMT-8** (4), 486
3 Shoraka, F., Kinsman, K., Natarajan, B. and Gealer, C. 'Proceedings of the Technical Conference', International Electronics Packaging Society Inc., Wheaton, 1986
4 Tomiyoshi, K. Internal Report, Shin-Etsu Chemical Co. Ltd, Annaka, Japan, 1990
5 Takada, K. *Nikkei New Mater.* 1987, **25**, 25
6 Kinjo, N., Ogata, M., Eguchi, S., Hozoji, H., Nishi, K. and Horie, O. 'Proceedings of the 1st Japan International SAMPE Symposium', The Nikkan Kogyo Shinbun Ltd, Tokyo, 1989, p. 521
7 Hozoji, H., Horie, O., Ogata, M., Numata, S. and Kinjo, N. *Kobunshi Ronbunshu* 1990, **47**, 483
8 Yorkgitis, E. M., Eiss, N. S., Tran, C., Wilkes, G. L. and McGrath, J. E. *Adv. Polym. Sci.* 1985, **72**, 79
9 Bucknall, C. B. 'Toughened Plastics', Applied Science Publishers, London, 1977
10 Bucknall, C. B. and Partridge, I. K. *Polym. Eng. Sci.* 1986, **26**, 54
11 Butta, E., Levita, G., Marchetti, A. and Lazzeri, A. *Polym. Eng. Sci.* 1986, **26**, 63
12 Gazit, S. and Bell, J. P. *J. Am. Chem. Soc.* 1983, **85**, 55
13 Riffle, J. S., Yilgor, I., Tran, C., Wilkes, G. L., McGrath, J. E. and Banthia, A. K. *J. Am. Chem. Soc.* 1983, **85**, 21
14 Romanchick, W. A., Sahn, J. E. and Geibel, J. F. *J. Am. Chem. Soc.* 1983, **85**, 85
15 Inoue, M., Furusawa, F., Ichimura, S. and Kinashi, K. personal communication, 1991
16 Low, I. M. *J. Appl. Polym. Sci.* 1990, **39**, 759
17 Nielsen, L. E. 'Mechanical Properties of Polymers and Composites' Vol. 2, Marcel Dekker, New York, 1974, pp. 434–438
18 Wang, T. T. and Kwei, T. K. *J. Polym. Sci., Part A-2* 1969, **7**, 889
19 Burton, B. L. '19th International SAMPE Technical Conference', 1987, p. 653
20 Beck, R. H., Gratch, S., Newman, S. and Rush, K. C. *Polym. Lett.* 1968, **6**, 707
21 Newman, S. and Strella, S. *J. Appl. Polym. Sci.* 1965, **9**, 2297