

# Thermal and Mechanical Stability of Electrically Conductive Adhesive Joints

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Post curing of electrically conductive adhesives (silver filled epoxy) by heating at an elevated temperature significantly enhances the thermal and mechanical stability of conductive adhesive joints. The contact electrical resistivity and thickness of a joint with epoxy or silicone based adhesive tend to decrease cycle to cycle upon thermal cycling between 30°C and 50°C and upon compression (up to 0.55 MPa), except for the silicone joint in the absence of compression. The effect of compression is significant in epoxy joint without post curing and in silicone joint, but is insignificant in epoxy joint after post curing. The effect of thermal cycling is significant in epoxy joint without post curing, less significant in silicone joint, and insignificant in epoxy joint after post curing.

**Key words:** Conductive adhesive, silver, epoxy, silicone, electrical resistivity

## INTRODUCTION

Electrically conductive adhesive joints<sup>1-3</sup> are increasingly used for electrical interconnections in electronic packages, although soldered joints still dominate. The attractions of conductive adhesive joints compared to soldered joints include the absence of lead, the alleviation of the ozone layer depletion problem related to the use of flux in soldering, the relatively small footprint, and processability at temperatures below that required for soldering. However, due to the relatively low modulus and poor temperature resistance of many adhesives, which are polymers, the effects of heating and stress on conductive adhesive joints is of concern. In general, these effects can be reversible or irreversible. Of particular concern are the effects that impact the electrical performance of the joint. This paper is focused on the reversible and irreversible effects of heating and stress on the electrical performance of conductive adhesive joints. Although irreversible effects are of more concern to the joint performance than reversible effects, the latter provides useful scientific information concerning the origin of the effects.

Heating and stressing relate to the thermal and mechanical abuse that an electronic package often encounters, whether in normal usage or unintended situations. In normal usage, an electronic package can get hot, both due to the heat generated by the electric current and due to the heat present in the ambient (as in automobile electronics). The heat can cause thermal stresses, especially when components with different values of the coefficient of thermal expansion are bonded together. Upon repeated heating, as in the case of turning the electronics on and off repeatedly, thermal fatigue can occur. In both normal usage and unintended situations, mechanical vibrations can occur, resulting in dynamic stresses. This paper addresses the effects of cyclic heating under various levels of mechanical stress on the contact electrical resistivity of adhesive joints.

The most damaging types of mechanical stress on a joint are tensile and shear. However, compressive stresses are as common. This paper is limited to stresses that are compressive.

The contact electrical resistivity of a copper-adhesive-copper joint is used in this work as an indicator of the electrical performance of the joint. This resistivity is given by the product of the joint resistance and the joint area. The joint area is the total area of the joint, including the area that may be occupied by

voids. The contact resistivity characterizes the quality of the overall joint and is a quantity that is independent of the total area of the joint. This resistivity depends on the contact resistance of the copper-adhesive interface and the volume resistance of the adhesive, which are not separately measured in this work. This technique has been previously used in the study of the effect of heating on conductive epoxy and soldered joints.<sup>1</sup> This work differs from Ref. 4 in its address of (1) the effect of post curing of conductive adhesive joints, (2) comparison of epoxy and silicone joints, and (3) the effects of compression and heating on the joints.

The most common polymers used in conductive adhesives are epoxy<sup>5-8</sup> and silicone.<sup>9-12</sup> Epoxy is a stronger and more common adhesive, but silicone has a lower modulus, which is attractive for reducing thermal stress.<sup>13</sup> The most common conducting filler used in adhesives is silver particles. This paper addresses silver particle filled epoxy and silver particle filled silicone. In the case of silver particle filled epoxy, this paper also addresses the effect of post curing at an elevated temperature after curing at room temperature. Post curing allows the cross-linking of the epoxy to reach completion. Post curing is not usually conducted in the electronic packaging industry, due to the possible negative effects of heating on the electronics. Nevertheless, the effect of post curing is relevant to understanding the origin of the changes observed upon heating and stress application.

The objectives of this paper are (1) to study the reversible and irreversible effects of heating and compression on the electrical performance of conductive adhesive joints, (2) to compare these effects in epoxy and silicone joints, and (3) to study the effect of post curing on a conductive epoxy joint.

For the purpose of understanding the effects on the electrical performance, this paper includes measurement of the joint thickness during repeated heating and compression. The change in joint thickness reflects mainly the change in adhesive thickness.

## EXPERIMENTAL METHODS

A conductive adhesive was silver particle filled epoxy. According to the manufacturer, the operating temperature range of the cured adhesive is  $-91^{\circ}\text{C}$  to  $100^{\circ}\text{C}$  and the volume electrical resistivity of the cured adhesive is less than  $0.001\ \Omega\cdot\text{cm}$ .

Another conductive adhesive was silver particle filled silicone. According to the manufacturer, the operating temperature of the cured adhesive is up to  $230^{\circ}\text{C}$  and the volume electrical resistivity of the cured adhesive is  $0.001\ \Omega\cdot\text{cm}$ .

For epoxy joints, adhesive curing was conducted at room temperature for 24 h, with subsequent optional post curing carried out at  $80^{\circ}\text{C}$  for 4 h. For silicone joints, adhesive curing was conducted at  $120^{\circ}\text{C}$  for 20 min.

Both of the components to be joined by the use of the conductive adhesive were a copper-cladded

continuous glass fiber epoxy-matrix composite in the form of a laminate (tetrafunctional FR-4 laminate,  $T_g = 140^{\circ}\text{C}$ ). The glass fibers were E-glass of style 1,080. The copper cladding was  $13\text{-}\mu\text{m}$  thick on one side of the laminate and  $48\text{-}\mu\text{m}$  thick on the other side. The side with the thinner cladding was used for making a joint. The glass fiber polymer-matrix composite was  $76\text{-}\mu\text{m}$  thick. The total thickness of the cladded laminate was  $137\ \mu\text{m}$ .

Adhesive joining using silver epoxy as the adhesive was conducted by (1) mixing equal amounts of part A (epoxy) and part B (hardener) for at least 2 min, (2) applying the mixture within 5 min on the surface of one of the components to be joined (width = 3.0 mm), (3) placing the other component to be joined (width = 3.0 mm) on the adhesive (Fig. 1), (4) applying a weight on the joint area ( $3.0 \times 3.0\ \text{mm}$ ) to give a compressive stress of 55 kPa, (5) allowing the epoxy to cure at room temperature under the compressive stress for 24 h, and (6) optionally allowing the epoxy to post cure at  $80^{\circ}\text{C}$  under no applied stress for 4 h. The thickness of the sandwich was  $600\ \mu\text{m}$ . The thickness of the silver epoxy in the sandwich was around  $300\ \mu\text{m}$ .

Adhesive joining using silicone as the adhesive was conducted by (1) applying the silicone on the surface of one of the components to be joined (width = 3.1 mm), (2) placing the other component to be joined (width = 3.0 mm) on the adhesive, (3) applying a weight on the joint area ( $3.1 \times 3.0\ \text{mm}$ ) to give a compressive stress of 55 kPa, and (4) allowing the silicone to cure at  $120^{\circ}\text{C}$  under the compressive stress for 20 min. The adhesive thickness after curing (but before heat or stress application) was  $320\ \mu\text{m}$ .

An electrical contact in the form of silver paint in conjunction with copper wire was applied to the copper cladding of each of the four legs of the crossed bars (Fig. 1). The length of each of the four legs is not important and is limited by the size of the furnace used in providing temperature variation. In the four-probe method, two of the electrical contacts (A and D in Fig. 1) were for passing current; the remaining two contacts (B and C) were for measuring voltage. The voltage at B was essentially that at the top of the junction; the voltage at C was essentially that at the bottom of the junction. The voltage difference between B and C, divided by the current, gave the contact resistance of the joint. The resistance multiplied by the contact area gave the contact resistivity.

For investigation of the effect of heating and compression, a thermomechanical analyzer was used to provide controlled heating from  $30^{\circ}\text{C}$  to  $50^{\circ}\text{C}$  at  $5^{\circ}\text{C}/\text{min}$ , controlled cooling from  $50^{\circ}\text{C}$  to  $30^{\circ}\text{C}$  at  $2^{\circ}\text{C}/\text{min}$ , and a constant compressive stress from 0 MPa to 0.55 MPa in the direction perpendicular to the joint area (as exerted by a probe on the top surface of the specimen throughout the measurement). The contact resistivity and the thickness of the joint were simultaneously measured during thermal

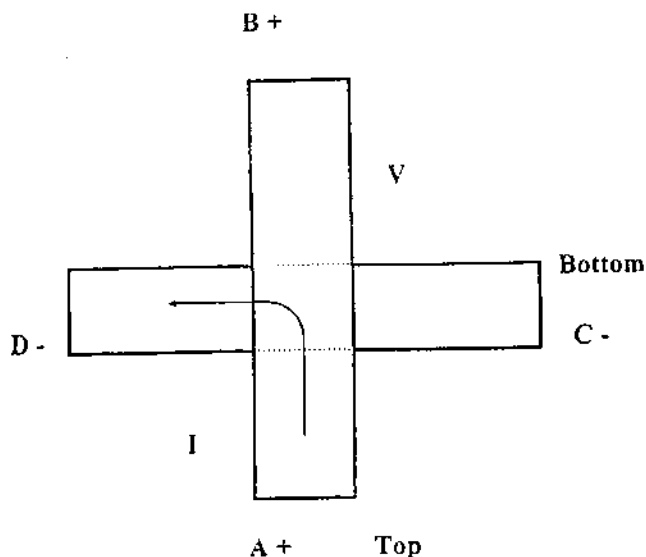


Fig. 1. Specimen configuration. Current  $I$  is passed from A to D, while voltage  $V$  is measured between B and C.

cycling at various constant compressive stresses. For each specimen, the compressive stress was progressively increased, such that, at each stress level, measurement was conducted during thermal cycling for up to three cycles.

### EXPERIMENTAL RESULTS

#### Epoxy Joint without Post Curing

Figure 2 shows the effect of thermal cycling at different compressive stresses on the contact resistivity for an epoxy joint without post curing. The resistivity increases upon heating and decreases upon subsequent cooling in every thermal cycle, such that the resistivity is lower for a higher compressive stress (applied during thermal cycling). The effect of compressive stress diminishes as thermal cycling progresses. By the third thermal cycle, the compressive stress has essentially no effect on the resistivity. During heating in the first cycle, the resistivity increases particularly sharply. This is believed to be due to the occurrence of cross-linking.

Figure 3 shows the effect of thermal cycling on the strain, i.e., fractional change in sandwich thickness, for a constant compressive stress of 0.33 MPa. The strain increases upon heating in every cycle, due to thermal expansion. The coefficient of thermal expansion was not determined, due to the small and insufficiently accurate value of the initial thickness of the adhesive. The strain decrease during subsequent cooling is more than that during heating. As a result, the thickness diminishes cycle by cycle. The corresponding relationship of strain with temperature is shown in Fig. 4. The corresponding relationship of contact resistivity with temperature is shown in Fig. 5. Although there is considerable reversibility in the effect of heating on the resistivity, the resistivity decreases cycle by cycle (Fig. 5). The increase in resistivity upon heating in every cycle is

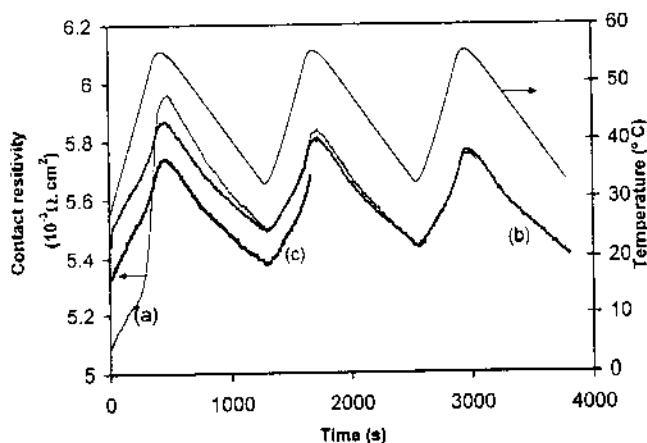


Fig. 2. The contact resistivity of epoxy joint without post curing during thermal cycling at a constant compressive stress of (a) 0 MPa, (b) 0.33 MPa, and (c) 0.55 MPa.

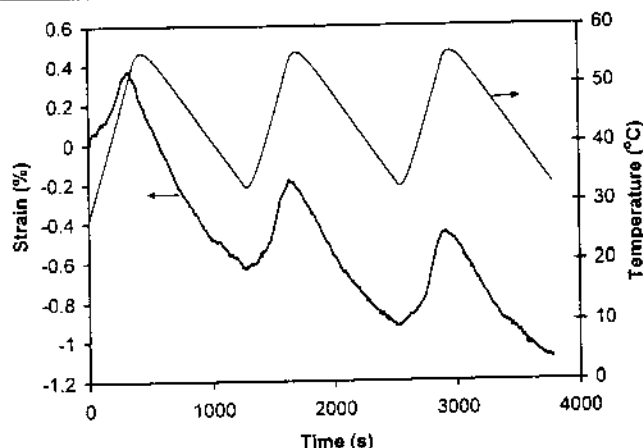


Fig. 3. The strain (fractional change in thickness) of epoxy joint without post curing during thermal cycling at a constant compressive stress of 0.33 MPa.

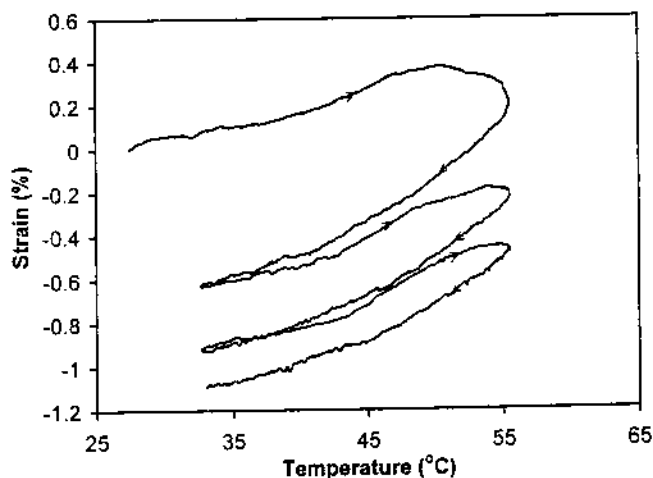


Fig. 4. The strain (fractional change in thickness) of epoxy joint without post curing versus temperature during thermal cycling at a constant compressive stress of 0.33 MPa: (a) 1st cycle, (b) 2nd cycle, and (c) 3rd cycle.

mainly due to thermal expansion and the consequent decrease in proximity between adjacent silver particles.

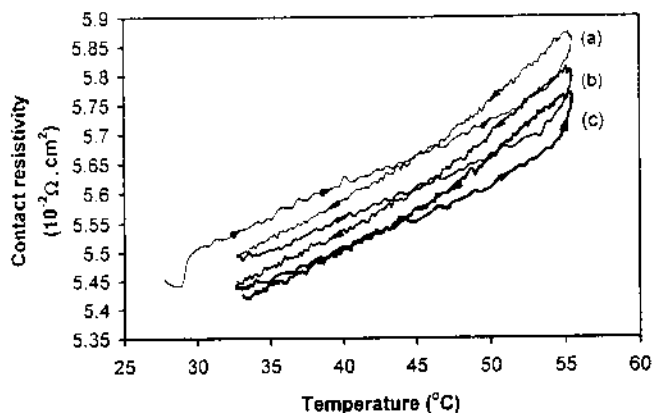


Fig. 5. The contact resistivity of epoxy joint without post curing versus temperature during thermal cycling at a constant compressive stress of 0.33 MPa: (a) 1st cycle (b) 2nd cycle, and (c) 3rd cycle.

### Epoxy Joint after Post Curing

Figure 6 shows that, for an epoxy joint after post curing, the contact resistivity increases reversibly in every thermal cycle, due to thermal expansion, such that it does not decrease cycle by cycle (in contrast to the epoxy joint without post curing, Fig. 2 and 5) and it decreases slightly with increasing compressive stress (also in contrast to the epoxy joint without post curing, Fig. 2).

Figure 7 shows that the strain (thickness) increases reversibly in every thermal cycle, such that the thickness is slightly less at a higher compressive stress. In contrast to the epoxy joint without post curing (Fig. 3), the thickness does not decrease cycle by cycle.

### Silicone Joint

Figure 8 shows that, for a silicone joint, the contact resistivity increases reversibly in every thermal cycle, such that it decreases significantly with increasing compressive stress (more so than for an epoxy joint without post curing, Fig. 2). Moreover, it decreases cycle by cycle (as for an epoxy joint without post curing, Fig. 2), but only when a compressive stress is present.

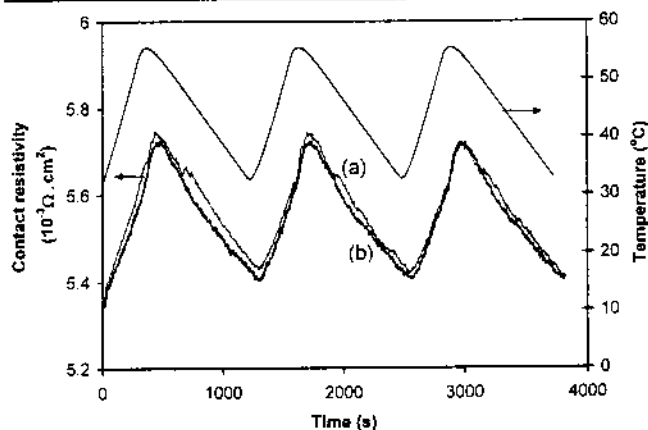


Fig. 6. The contact resistivity of epoxy joint after post curing during thermal cycling at a constant compressive stress of (a) 0 MPa and (b) 0.55 MPa.

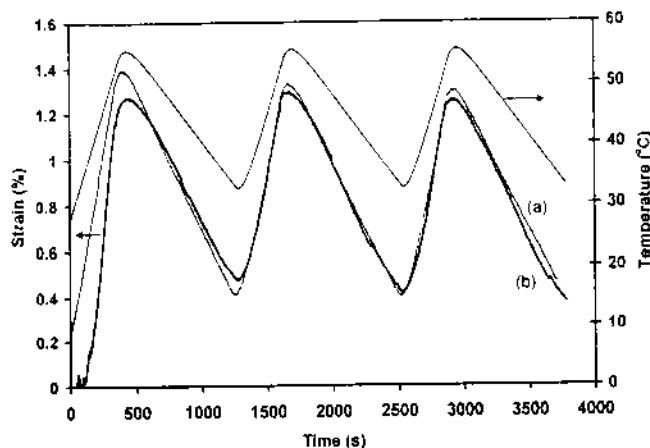


Fig. 7. The strain (fractional change in thickness) of epoxy joint after post curing during thermal cycling at a constant compressive stress: (a) 0 MPa and (b) 0.55 MPa.

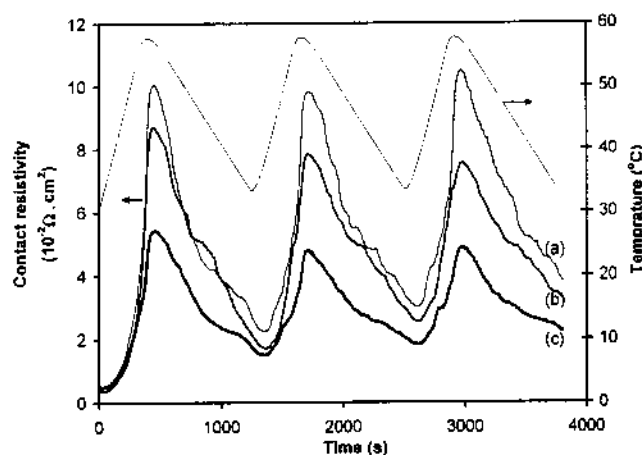


Fig. 8. The contact resistivity of silicone joint during thermal cycling at a constant compressive stress of (a) 0 MPa, (b) 0.33 MPa, and (c) 0.55 MPa.

Figure 9 shows that the strain (thickness) increases with partial reversibility upon heating in every thermal cycle. The tendency for the thickness to decrease cycle by cycle increases as the compressive stress increases. This tendency is clear in Fig. 10, which shows the corresponding relationship between strain and temperature for a compressive stress of 0.55 MPa. As shown in Fig. 9, the effect of thermal cycling is only significant when the stress is high (0.55 MPa).

In the absence of compressive stress, the thickness increases cycle by cycle, in contrast to the decrease in the presence of stress (Fig. 9). This increase is believed to be due to the loosening of the molecular packing in the polymer matrix of the adhesive as thermal cycling progresses.

### DISCUSSION

The epoxy joint without post curing has its contact resistivity and thickness decreasing with increasing compressive stress and decreasing cycle by cycle upon thermal cycling at a fixed compressive stress. The effects on resistivity and thickness are related, as a

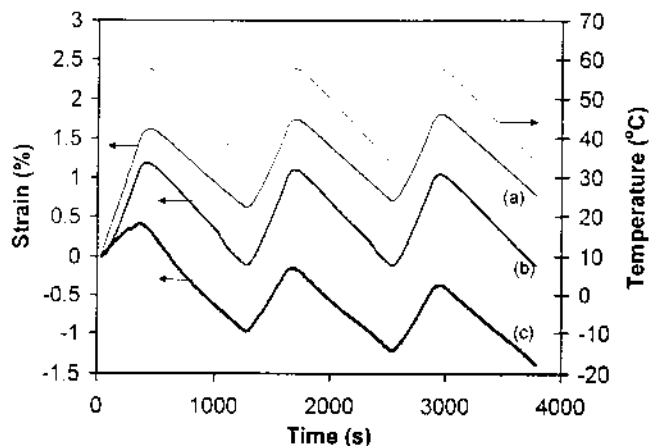


Fig. 9. The strain (fractional change in thickness) of silicone joint during thermal cycling at a constant compressive stress. (a) 0 MPa, (b) 0.33 MPa, and (c) 0.55 MPa

thickness decrease causes the volume electrical resistivity of the adhesive to decrease, due to the increase in proximity between adjacent silver particles in the adhesive. The thickness decrease upon compression or thermal cycling is due to the fact that the epoxy is rather soft when the cross-linking is incomplete.

After post curing, the effect of thermal cycling is absent and the effect of compression is slight. Hence, the completion of cross-linking during post curing greatly enhances the thermal and mechanical stability of the epoxy joint.

Silicone is even softer than epoxy without post curing. Thus, the effect of compressive stress is even more significant. However, in contrast to epoxy without post curing, silicone has been cross-linked by curing at an elevated temperature. As a result, the silicone joint exhibits little change upon thermal cycling, unless the compressive stress is high (0.55 MPa).

For the purpose of attaining thermal and mechanical stability in conductive adhesive joints, thorough curing of the adhesive is recommended, even though this involves heat treatment.

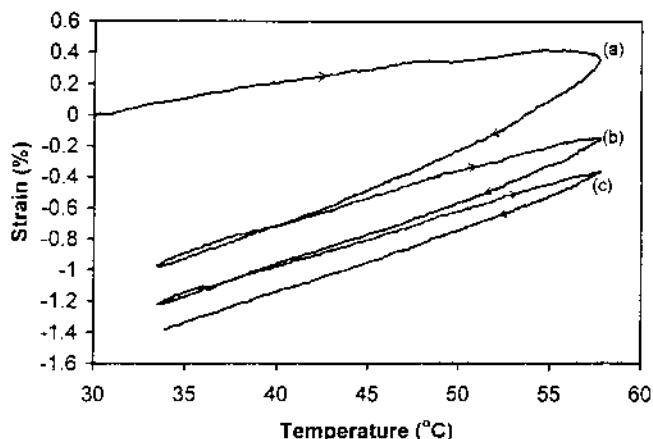


Fig. 10. The strain (fractional change in thickness) of silicone joint versus temperature during thermal cycling at a constant compressive stress of 0.55 MPa: (a) 1st cycle, (b) 2nd cycle, and (c) 3rd cycle.

## CONCLUSIONS

Post curing of a conductive adhesive in the form of silver particle filled epoxy by heating at an elevated temperature significantly enhances the thermal and mechanical stability of the adhesive joint, as shown by the effects of thermal cycling (between 30°C and 50°C) and compression (in the direction perpendicular to the joint interface at a stress up to 0.55 MPa) on the contact electrical resistivity and thickness of the joint. The resistivity and thickness of joints with epoxy or silicone based adhesives increase upon heating, with at least partial reversibility, due to thermal expansion, which in turn causes decrease in proximity between adjacent silver particles in the adhesive. Upon thermal cycling, the resistivity and thickness of joints with epoxy or silicone based adhesives tend to decrease cycle by cycle, except for the silicone joint in the absence of compression. Upon compression, the resistivity and thickness of joints with epoxy or silicone based adhesives tend to decrease. The effect of compression is significant in epoxy joint without post curing and in silicone joint, but is insignificant in epoxy joint after post curing. This is because of the relative softness of epoxy without post curing and of silicone, and the relative stiffness of epoxy after post curing. The effect of thermal cycling is significant in epoxy joint without post curing, less significant in silicone joint, and insignificant in epoxy joint after post curing.

## REFERENCES

1. S.K. Kang and S. Purushothaman, *J. Electron. Mater.* 28, 1314 (1999).
2. D. Lu, Q.K. Tong, and C.P. Wong, *IEEE Trans. Electron. Packaging Manufacturing* 22, 223 (1999).
3. T. Inada and C.P. Wong, *Proc. 1998 4th Int. Symp. Exhib. on Advanced Packaging Materials, Properties & Interfaces* (1998), pp. 268-271.
4. K.-D. Kim and D.D.L. Chung, *J. Electron. Mater.* 31, 933 (2002).
5. T.W. Giants, *J. Adh. Sci. Technol.* 12, 593 (1998).
6. K. Feldmann and R. Luchs, *Surface Mount Technol.* 12, 74 (1998).
7. C.P. Wong, D. Lu, L. Meyers, S.A. Vona, Jr., and Q.K. Tong, *Proc. 1997 1st IEEE Int. Symp. on Polymeric Electronics Packaging* (Piscataway, NJ: IEEE, 1997), pp. 80-85.
8. M. Zwolinski, J. Hickman, H. Rubin, Y. Zaks, S. McCarthy, T. Hanlon, P. Arrowsmith, A. Chaudhuri, R. Hermansen, S. Lau, and D. Napp, *IEEE Trans. Components, Packaging, Manufacturing Technol. Part C: Manufacturing* 19, 241 (1996).
9. K.F. Schoch, Jr. and A.I. Bennett, *Proc. 17th Electrical/Electronics Insulation Conf.* (Piscataway, NJ: IEEE Service Center, 1985), pp. 291-293.
10. M.A. Lutz and R.L. Cole, *39th Electronic Components Proc.-Electronic Components Conf.* (Piscataway, NJ: IEEE Service Center, 1985), pp. 291-293.
11. R.L. Keusseyan, J.L. Dilday, and B.S. Speck, *Int. J. Microcircuits Electron. Packaging* 17, 263 (1994).
12. S.W. Wilson, A.W. Norris, E.B. Scott, and M.R. Costello, *Nat. Electron. Packaging Production Conf.-Proc. Techn. Program* 2, 788 (1996).
13. J.C. Bolger, *Proc. ACS Division of Polymeric Materials Science and Engineering* (Washington, DC: ACS, Books & Journals Division, 1988), pp. 502-506.