

ELECTROTHERMOMECHANICAL ANALYSIS AND ITS APPLICATION TO STUDYING ELECTRICALLY CONDUCTIVE ADHESIVE JOINTS

J. Xiao^{*} and *D. D. L. Chung*^{**}

Composite Materials Research Laboratory, University at Buffalo, The State University of New York, Buffalo, NY 14260-4400, USA

(Received May 24, 2002; in revised form June 5, 2003)

Abstract

Electrothermomechanical analysis (ETMA) is effective for studying electrically conductive adhesive joints. Post curing of an electrically conductive adhesive (silver particle filled epoxy) by heating at an elevated temperature significantly enhances the thermal and mechanical stability of the conductive adhesive joint. The contact electrical resistivity and thickness of a joint tend to decrease cycle to cycle upon thermal cycling between 30 and 50°C and upon compression (up to 0.55 MPa). The effects of compression and thermal cycling are significant in the joint without post curing, but is insignificant after post curing.

Keywords: conductive adhesive, electrical resistivity, epoxy, silver, thermal analysis, thermomechanical analysis

Introduction

Thermal analysis refers to the analysis of a material through measurement of a quantity as a function of temperature. The quantity may be heat (as in the case of calorimetry, usually differential scanning calorimetry, or DSC [1–10]), mass (as in the case of thermogravimetry, i.e., thermogravimetric analysis, or TG [11, 12]), dimension (as in the case of dilatometry, i.e., thermomechanical analysis, or TMA [3, 8, 10]), dynamic mechanical properties such as loss tangent and storage modulus (as in the case of dynamic mechanical analysis, or DMA, i.e., dynamic thermomechanical analysis, or DTMA [3–6, 9, 10, 12–16]), electrical resistivity [17–19], etc. Thermal analysis can provide information on structural transitions, microstructural changes, specific heat, coefficient of thermal expansion (CTE), process kinetics, thermal stability, electrical resistivity and composition.

This paper uses a rather new technique of thermal analysis, hereby called electrothermomechanical analysis (ETMA), which refers to simultaneous electrical resistance

* Permanent address: College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, 29 Yudao Street, Nanjing, 210016, P. R. China

** Author for correspondence: E-mail: ddlchung@eng.buffalo.edu

measurement and TMA. In other words, the electrical resistance and strain (dimension) are simultaneously measured as functions of temperature at various constant stresses. The independent variables in ETMA are temperature and stress; the dependent variables are electrical resistance and strain (dimension). This technique is to be distinguished from measurement of the electrical resistance *vs.* temperature without strain measurement [17–19] and from measurement of the strain (dimension) *vs.* temperature without electrical resistance measurement (i.e., TMA). The electrical resistance component of ETMA is valuable, due to the sensitive dependence of the electrical resistance to defects and the microstructure, and the relevance of the electrical resistance to electronic applications. The ETMA technique has been previously used to study shape memory alloys made by melt spinning [20, 21]. In this work, the ETMA technique is used to study electrically conductive adhesive joints.

Electrically conductive adhesive joints [22–24] are increasingly used for electrical interconnections in electronic packages, although soldered joints still dominate. 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, for some adhesives, room temperature processability (in contrast to the heating 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 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 provide 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 (CTE) 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, thus 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 pores. The contact re-

sistivity 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.

The overall thickness of a substrate–adhesive–substrate joint is the dimension measured in this work as a part of ETMA. The change in joint thickness reflects mainly the change in adhesive thickness.

The most common polymer used in conductive adhesives is epoxy [25–28]. The most common conducting filler used in adhesives is silver particles. This paper addresses silver particle filled epoxy. It 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.

Experimental methods

The conductive adhesive used was silver particle filled epoxy (CW2400 Circuit Works Conductive Epoxy, ITW Chemtronics, Kennesaw, GA). According to the manufacturer, the operating temperature range of the cured adhesive is -91 to 100°C and the volume electrical resistivity of the cured adhesive is less than $0.001 \Omega \text{ cm}$. Adhesive curing was conducted at room temperature for 24 h, with subsequent optional post curing carried out at 80°C for 4 h.

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, as provided by Polyclad Laminates, Inc. (W. Franklin, NH; Product No. PCL-FR-226, tetrafunctional FR-4 laminate, $T_g=140^{\circ}\text{C}$). The glass fibers were E-glass of style 1080. The copper cladding was $13 \mu\text{m}$ thick on one side of the laminate and $48 \mu\text{m}$ thick on the other side. The side with the thinner cladding was used for making a soldered joint. The glass fiber polymer-matrix composite was $76 \mu\text{m}$ thick. The total thickness of the cladded laminate was $137 \mu\text{m}$.

Adhesive joining was conducted by (i) mixing equal amounts of Part A (epoxy) and Part B (hardener) for at least 2 min, (ii) applying the mixture within 5 min on the surface of one of the components to be joined (width=3.0 mm), (iii) placing the other component to be joined (width=3.0 mm) on the adhesive (Fig. 1), (iv) applying a mass on the joint area ($3.0 \times 3.0 \text{ mm}$) to give a compressive stress of 55 kPa, (v) allowing the epoxy to cure at room temperature under the compressive stress for 24 h, and (vi) optionally allowing the epoxy to post cure at 80°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 $300 \mu\text{m}$.

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

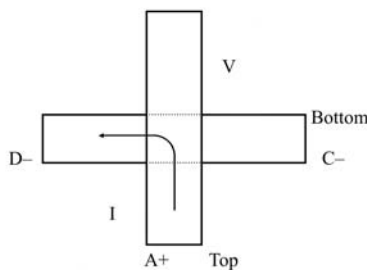


Fig. 1 Specimen configuration. Current I is passed from A to D, while voltage V is measured between B and C

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 square junction; the voltage at C was essentially that at the bottom of the square 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 (not necessarily square) gave the contact resistivity. A Keithley 2001 multimeter was used.

For investigation of the effect of heating and compression, a thermomechanical analyzer (Perkin Elmer Corp., TMA7) was used to provide controlled heating from 30 to 50°C at 5°C min⁻¹, controlled cooling from 50 to 30°C at 2°C min⁻¹, and a constant compressive stress from 0 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 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

Joint without post curing

Figure 2 shows the effect of thermal cycling at different compressive stresses on the contact resistivity for the 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 crosslinking.

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

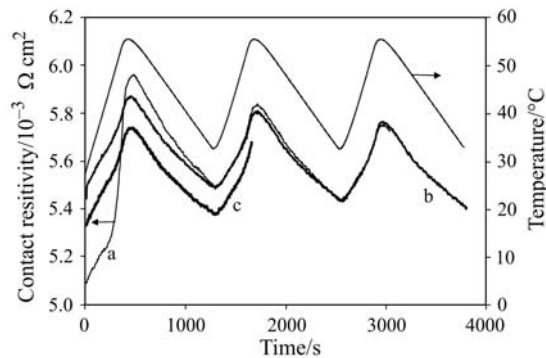


Fig. 2 The contact resistivity of joint without post curing during thermal cycling at a constant compressive stress of a – 0 MPa; b – 0.33 MPa and c – 0.55 MPa

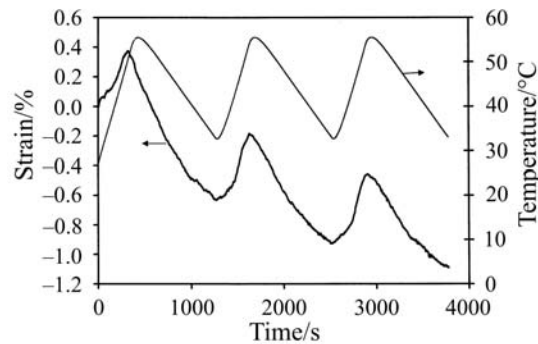


Fig. 3 The strain (fractional change in thickness) of joint without post curing during thermal cycling at a constant compressive stress of 0.33 MPa

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

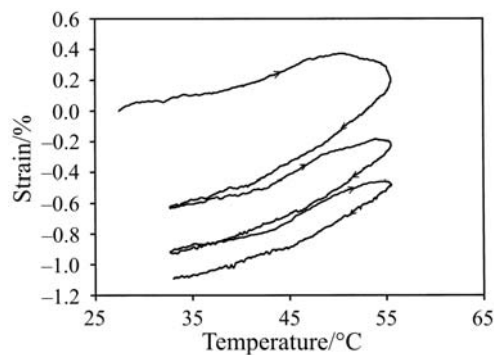


Fig. 4 The strain (fractional change in thickness) of joint without post curing vs. temperature during thermal cycling at a constant compressive stress of 0.33 MPa. a – 1st cycle; b – 2nd cycle; c – 3rd cycle

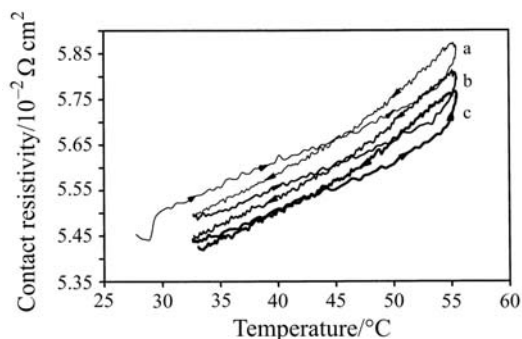


Fig. 5 The contact resistivity of joint without post curing vs. temperature during thermal cycling at a constant compressive stress of 0.33 MPa. a – 1st cycle; b – 2nd cycle; c – 3rd cycle

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

Joint after post curing

Figure 6 shows that, 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

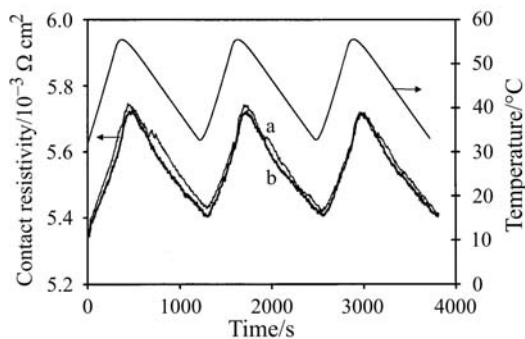


Fig. 6 The contact resistivity of joint after post curing during thermal cycling at a constant compressive stress of a – 0 MPa, and b – 0.55 MPa

contrast to the joint without post curing, Figs 2 and 5) and it decreases slightly with increasing compressive stress (also in contrast to the joint without post curing, Fig. 2).

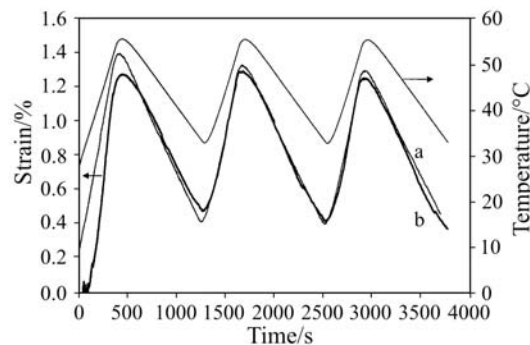


Fig. 7 The strain (fractional change in thickness) of joint after post curing during thermal cycling at a constant compressive stress. a – 0 MPa; b – 0.55 MPa

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 joint without post curing (Fig. 3), the thickness does not decrease cycle by cycle.

Discussion

The 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 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 and/or thermal cycling is due to the fact that the epoxy is rather soft when the crosslinking is incomplete.

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

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.

As ETMA can be performed using a conventional TMA instrument, it does not require special instrumentation. However, electrical leads need to emanate from the specimen to the multimeter located outside the TMA furnace. The quality of the electrical contacts on the specimen should be maintained during temperature variation. Because of the limited temperature resistance of electrical contacts, the maximum temperature of ETMA is limited (about 150°C in the case of contacts made from conductive paint or solder and about 850°C in the case of brazed contacts). Moreover, the four-probe method rather than the two-probe method is preferred, as the former excludes the contact resistance from the measured resistance and thus allows the measured resistance to be more accurate and allows the contact quality to be less critical.

Conclusions

The ETMA technique of thermal analysis is effective for studying electrically conductive adhesive joints.

Post curing of a conductive adhesive in the form of silver particle filled epoxy by heating at 80°C significantly enhances the thermal and mechanical stability of the adhesive joint, as shown by the effects of thermal cycling (between 30 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 a joint increases 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 tend to decrease cycle by cycle. Upon compression, the resistivity and thickness tend to decrease. The effect of compression is significant in the joint without post curing, but is insignificant after post curing. This is because of the relative softness of epoxy without post curing, and the relative stiffness of epoxy after post curing. The effect of thermal cycling is significant in the joint without post curing, but is insignificant after post curing.

References

- 1 J. Mijovic and T. C. Gsell, SAMPE Quarterly – Society for the Advancement of Materials and Process Engineering, 21 (1990) 42.
- 2 K. C. Cole, D. Noel, J.-J. Hechler, A. Chouliotis and K. C. Overbury, Polym. Compos., 10 (1989) 150.
- 3 W.-D. Emmerich and E. Kaisersberger in Materials Science Monographs, Vol. 35, Elsevier, Amsterdam, Neth and New York, 1986, p. 289.
- 4 W. J. Sichina and P. S. Gill in Tech. Sessions of the 41st Annual Conf. – Reinforced Plastics/Composites Institute, SPI, New York, NY, Sess. 24, 1986, p. 4.
- 5 J. N. Leckenby, D. C. Harget, W. J. Sichina and P. S. Gill in Carbon Fibers: Technology, Uses and Prospects, Noyes Publ., Park Ridge, NJ 1985, p. 86.
- 6 J. N. Leckenby, D. C. Harget, W. J. Sichina and P. S. Gill in Carbon Fibers III, Plastics & Rubber Inst., London 1985, p. 11.1.
- 7 T. W. Johnson and C. L. Ryan in Proc. 31st International SAMPE Symposium and Exhibition 1986, Materials Sciences for the Future, SAMPE, Azusa, CA 1986, p. 1537.
- 8 D. Wong, J. Jankowsky, M. DiBerardino and R. Cochran in Proc. 38th Int. SAMPE Symp. and Exhibition, SAMPE, Covina, CA, Part 2, 38 (1993) 1552.
- 9 K. E. Atkinson and C. Jones, J. Adh., 56 (1996) 247.
- 10 J. L. Jankowsky, D. G. Wong, M. F. DiBerardino and R. C. Cochran in ASTM Special Technical Publication, no. 1249, Proc. Symp. on Assignment of the Glass Transition, ASTM, Philadelphia, PA 1994, p. 277.
- 11 P. Olivier, J. P. Cottu and B. Ferret, Composites, 26 (1995) 509.
- 12 A. Licea-Claverie and F. J. U. Carrillo, Polymer Testing, 16 (1997) 445.
- 13 B. Harris, O. G. Graddell, D. P. Almond, C. Lefebvre and J. Verbist, J. Mater. Sci., 28 (1993) 3353.

- 14 M. Akay, J. G. Cracknell and H. A. Farnham, *Polym. & Polym. Compos.*, 2 (1994) 317.
- 15 J. W. E. Gearing and M. R. Stone, *Polym. Compos.*, 5 (1984) 312.
- 16 J. R. Sarasua and J. Pouyet, *J. Thermoplastic Compos. Mater.*, 11 (1998) 2.
- 17 D. D. L. Chung, *J. Therm. Anal. Cal.*, 65 (2001) 153.
- 18 V. Chellappa, Z. W. Chiou and B. Z. Jang, *J. Mater. Sci.*, 30 (1995) 4263.
- 19 Z. Mei and D. D. L. Chung, *Cem. Concr. Res.*, 30 (2000) 799.
- 20 G. Airoidi, S. Piredda, M. Pozzi and A. V. Shelyakov, *Mater. Sci. Forum*, 327 (2000) 135.
- 21 G. Gomasca, G. Airoidi and A. V. Shelyakov, *J. de Physique. IV:JP*, 11 (2001) Pr8339.
- 22 S. K. Kang and S. Purushothaman, *J. Electron. Mater.*, 28 (1999) 1314.
- 23 D. Lu, Q. K. Tong and C. P. Wong, *IEEE Transactions on Electronics Packaging Manufacturing*, 22 (1999) 223.
- 24 T. Inada and C. P. Wong, *Proc. 1998 4th Int. Symp. & Exhib. On Advanced Packaging Materials, Properties & Interfaces*, (1998) 268.
- 25 T. W. Giants, *J. Adh. Sci. & Tech.*, 12 (1998) 593.
- 26 K. Feldmann and R. Luchs, *Surface Mount Tech.*, 12 (1998) 74,76,78.
- 27 C. P. Wong, D. Lu, L. Meyers, S. A. Vona Jr. and Q. K. Tong in *Proc. 1997 1st IEEE Int. Symp. on Polymeric Electronics Packaging*, IEEE, Piscataway, NJ 1997, p. 80.
- 28 M. Zwolinski, J. Hickman, H. Rubin, Y. Zaks, S. McCarthy, T. Hanlon, P. Arrowsmith, A. Chaudhuri, R. Hermansen, S. Lau and D. Napp, *IEEE Transactions on Components, Packaging, & Manufacturing Technology. Part C: Manufacturing*, 19 (1996) 241.