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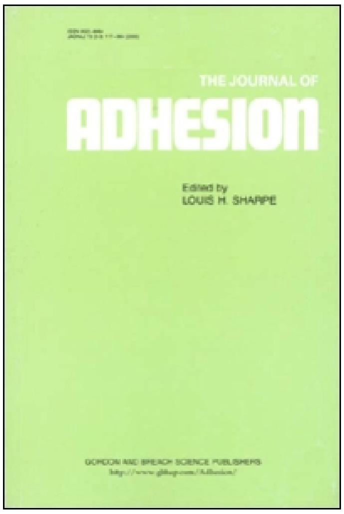

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A Solder Alloy Filled Z-Axis Conductive Epoxy Adhesive

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A Solder Alloy Filled Z-Axis Conductive Epoxy Adhesive*

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Epoxy adhesives filled with four different volume fractions of eutectic tin-bismuth solder alloy were prepared and the effect of filler content on the electrical and mechanical properties of these anisotropic electrically conductive adhesives was investigated. The results show that the adhesive containing the lowest amount of the filler alloy had the best combination of conductivity, insulation resistance and shear strength. The DSC-measurements suggested that the filler melts before the cure of the resin begins which allows the filler to wet and bond well to the conductors. This was verified by SEM/EPMA examinations. A temperature cycling test and high humidity, high temperature treatment were conducted on the best composite adhesive. The temperature variation had no effect on conductivity of the joints while humid and hot environment decreased the conductivity.

KEY WORDS: anisotropically conductive adhesive; solder filler; heat curing epoxy; lead free interconnection; microstructures; reliability testing.

1. INTRODUCTION

Increasing use of compact and lightweight electronic equipments such as portable telephones and notebook computers sets new requirements for component packaging and interconnections. Advanced surface mounting and direct chip attachment solutions are needed to increase the level of integration and to decrease the size of equipment.[1,2] Consequently, the interconnection density will be high and more attention will be paid to reducing the risk of bridging when soldering components to circuit boards. When the lead pitch is below 0.5 mm the process yield and reliability of reflowed solder joints may become a problem.[2-4] In addition, high soldering temperatures may damage components and flux removal can present further problems. These difficulties can be diminished by using anisotropic electrically conductive adhesives.

The curing temperatures are relatively low and commercially-available adhesives are utilised in production of 7 to 10 lines/mm interconnections.[5,6] In addition, environmental problems are avoided because neither fluxes nor lead-based alloys are needed. The adhesive is a composite material consisting of polymer matrix and conductive filler material, for example silver, graphite, nickel or metal-coated polymer particles. The

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amount of filler used is typically 10–15 vol%. The anisotropically-conductive adhesives are available in film form or as a paste suitable for screen printing. All anisotropic adhesives need bonding under pressure at elevated temperature. The temperature and pressure needed depend on the adhesive used, typical values being 150–180°C and 2–45 kg/cm^2, respectively. Generally, curing times vary between 20 and 60 seconds. When the pressure and heat are applied, the filler particles are trapped between the mating interconnection pads of each substrate in the compressed direction of the adhesive. This provides electrical conductivity through the thickness of the otherwise isolating polymer layer. The maximum number of interconnection pads per unit length depends on the average size, amount and distribution of conductive particles.

In this study, heat curable adhesive resins were filled with tin-bismuth solder alloy powder (5 to 20 vol%) to produce anisotropically-conductive adhesives. The effects of filler loading and bonding parameters on properties of joints were evaluated. The microstructures of the joints were examined by optical microscopy and the Scanning Electron Microscope/Electron Probe Microanalysis (SEM/EPMA) technique. The reliability of joints produced by the adhesive with optimum filler loading was tested by temperature cycling and high humidity, high temperature treatments.

2. MATERIALS AND METHODS

A one-component, solventless epoxy resin (LID 1408, supplied by Loctite Int.) was used as a matrix for the conductive composite adhesive. The filler material was a powdered eutectic tin-bismuth solder alloy of commercial purity having the melting temperature of 139°C. Formerly, solder alloys were employed as filler materials.[7–9] However, the filler alloys used in those adhesives contain lead as the main component. Furthermore, the adhesive studied here has some fluxing action itself, which is due to the amine curing agent used. The particle size was between 25 and 40 μm. Adhesives containing 5, 10, 15 and 20 vol% of solder filler were prepared. The solder filler was added to the polymer matrix under nitrogen atmosphere in order to prevent further oxidation of the solder particles. Then the composite was mixed carefully from five to ten minutes and the completeness of mixing was checked by optical and scanning electron microscopy.

The materials to be joined were polyimide flexible circuit and polyester foil connector. The conductor test pattern was fabricated on the polymide substrate. The test pattern consists of gold/nickel coated copper conductors (0.330 mm pitch, thickness of metallization being 35 μm) and the pattern contains a total of 240 interconnection pads, the area of each pad being $0.165 \times 2.5\,\text{mm}^2$. Half of the interconnection pads form a daisy chain for contact resistance measurements and the other half is a finger pattern for insulation resistance measurements. On the polyester foil the conductors are flash-Au coated copper and they are 15 μm thick. The adhesive was screen printed on the substrate. In addition, copper-to-copper joints were prepared for mechanical tests. The copper substrates were pickled for 30 seconds in a solution of 30 ml of concentrated nitric acid in 50 ml of water before bonding.

The bonding was conducted with a heat seal bonder (Shin-Etsu HS-002). The polymide and polyester substrates were cleaned carefully with acetone before bonding. The substrates were aligned under stereomicroscope. Two different temperature settings were employed and the measured adhesive temperatures were 180°C and 220°C. Three different loads (12.5, 25.0 and 37.5 kg/cm^2) were used at the lower bonding temperature for evaluating the effect of pressure on the properties of the joints. At the upper temperature only 25.0 kg/cm^2 was used. Nine circuits per parameter combination were bonded and the contact resistances were measured from the daisy chain with a multimeter (Keithley 195A). In addition, insulation resistance values were measured from the finger pattern of the test circuit with a Keithley 617 Programmable Electrometer.

The shear tests were performed with an Instron 4204 testing machine. The nominal joint dimensions were 2 × 5 mm^2 and the thickness of the copper substrate was 0.5 mm. The crosshead speed was 1.5 mm/min. Ten specimens for mechanical testing were bonded at 180°C with pressure 37.5 kg/cm^2 for each adhesive composition to compare the mechanical strength of the different adhesive compositions.

Thermal characterisation of the composite adhesive included separate DSC measurements of the resin, the filler alloy and the composite adhesive. The measurements were carried out under nitrogen atmosphere with a DSC device (PL Thermal Sciences) with heating rates ranging from 5 to 40°C/min.

The effect of temperature variation on the reliability of the joints was tested in temperature cycling procedure. Cycling was conducted in a cycling chamber (Vötsch GmbH) in which the temperature was altered between the limits: + 100°C and -40°C, in such a way that the specimens were held at the limiting temperatures for 15 minutes. Heating rate was 3°C/min and cooling rate was 1.3°C/min, giving rise to a total cycle of three hours. The joint resistances were measured during the test at room temperature. High temperature (85°C) and high humidity (85%RH) testing was conducted on the circuits after temperature cycling (Arctest ARC – 400/ – 40 + 100/RH chamber). The contact resistance values were measured during the test at the temperature of 85°C.

Cross-sectional samples for optical and electron microscopy were mounted in resin and then ground with 1200 grit wet SiC paper and polished with diamond paste. The scanning electron microscope (JEOL JSM-840A) equipped with x-ray spectrometer (Tracor Northern 5500) was used for studying the distribution of metallic elements in the cross-sectional areas of the joints.

3. RESULTS AND DISCUSSION

The contact resistance and insulation resistance values are shown in Figure 1. The contact resistance values decreased slightly with the filler content but the differences between the adhesives were quite insignificant. The insulation resistance values of the 5, 10 and 15 vol% adhesives were close to each other but the number of test vehicles having short circuits increased dramatically when the 15 and 20 vol% compositions were measured (Figure 2). The high filler loading and circuit misalignment during the bonding process caused the high number of short circuits of these two adhesives. The insulation resistance values for the 20 vol% adhesive were orders of magnitude lower (few tens of ohms) than the values for the other adhesive compositions, indicating poor electrical insulation in the xy-plane of the adhesive. The shear strength values shown in Figure 3 did not differ remarkably but the adhesives with the lowest amounts of the filler alloy were slightly better than those containing above 10 vol% of the filler. In

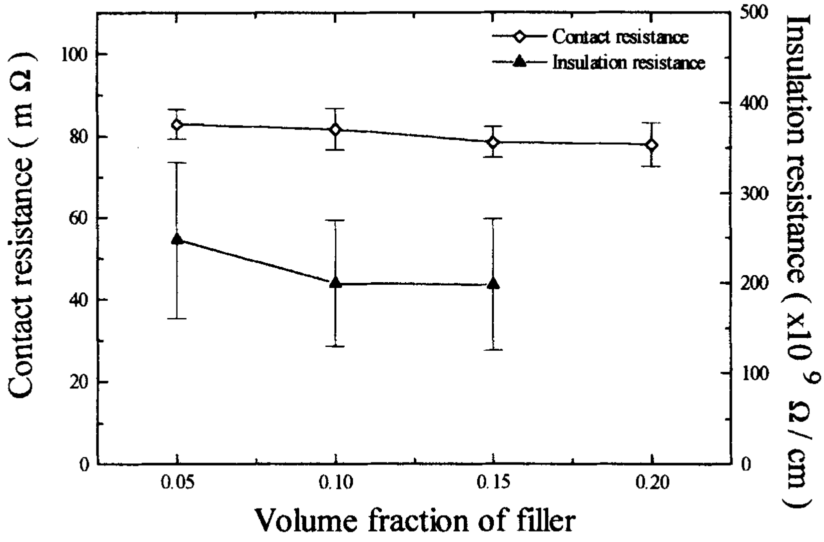

FIGURE 1 Contact resistance and insulation resistance values measured on the test structures.

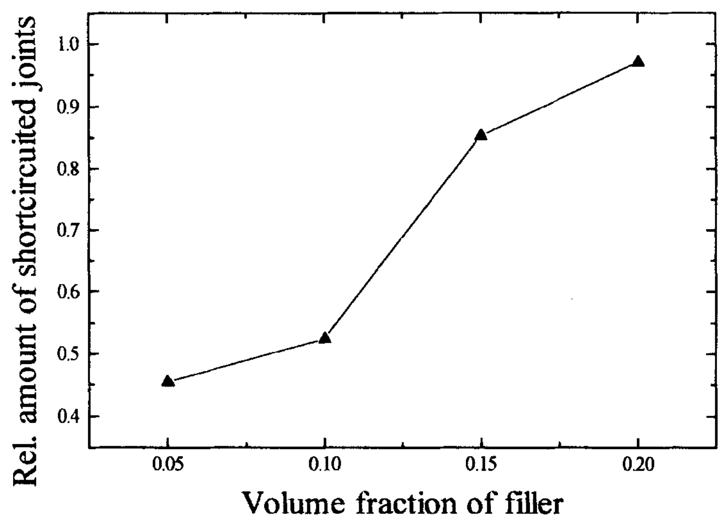

FIGURE 2 Relative amount of short circuited test structures.

Figure 4 is shown a fracture surface of a copper-to-copper joint. The joint fractured cohesively and the rough surface indicates that the polymer matrix was deformed noticeably during the testing. This, and the dependence of strength on filler fraction, suggest that the filler has only minor effect on the mechanical strength of the composite adhesive. As far as the results of electrical and mechanical tests are concerned it is obvious that the lower filler volume adhesives are more viable for producing high density interconnections. Furthermore, no risk of open circuits was observed when

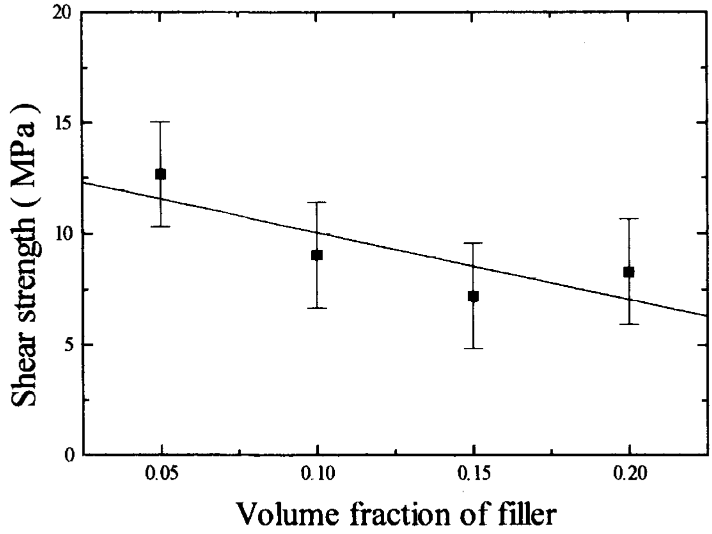

FIGURE 3 Shear strength values of copper-to-copper joints.

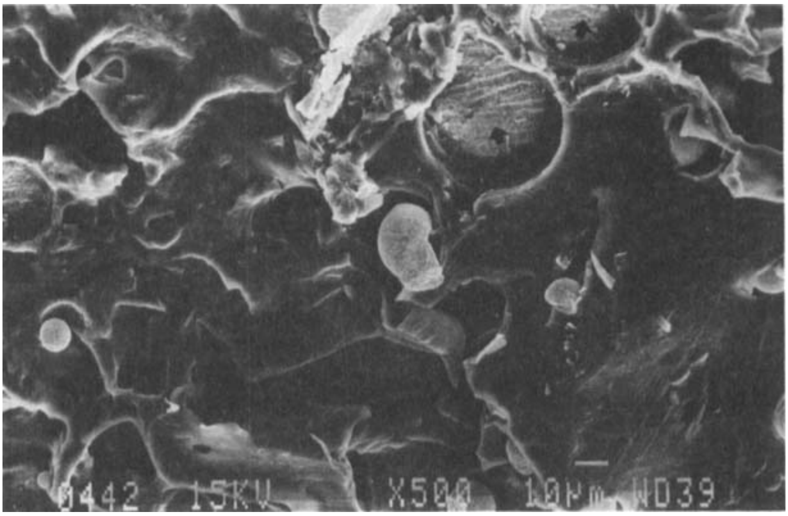

FIGURE 4 Cohesively fractured surface of shear test specimen: the polymer was deformed. Arrows show places where the filler particles attached to copper were sheared away.

using low filler fractions with this kind of configuration of the test circuit. This results from the large area of the interconnection pads compared with the size of particles and, therefore, several particles were found in every case between the conductors to be joined. The particle density and distribution was examined with SEM/EPMA using x-ray absorption from samples where the polyester was stripped off the polyimide. This study showed that the contact area is much larger than with conventional anisotropic adhesives. This is due to the fact that the filler alloy melts during the process and flows over a relatively large area as compared with the average particle size.

The process parameters had only a minor effect on joint resistance values when the effects of different temperatures (in the range 180°C–220°C) and loads varying from 12.5 kg/cm^2 to 37.5 kg/cm^2 were tested (Figure 5). This results from the fact that the temperatures used were high enough to cure the epoxy, as verified by the DSC measurements. Furthermore, the DSC showed that addition of the filler does not affect the cure of the resin (Figure 6). Because the heating rate in the actual bonding process is much higher than that of the DSC measurements it is likely that the start of the cure reaction is delayed in such a way that the filler melts and flows, wetting the electrodes before the resin is cured and solidified.

A scanning electron micrograph and EPMA of the cross section of a typical joint show clearly that the solder filler wets the conductor materials well and forms a metallurgical bond (Figures 7a and 7b). However, due to the miscibility gap, i.e. very low solubility of bismuth in copper (as well as in Ni), there occurs a phase separation: tin is found on the surfaces of Cu and Ni as thin layers of intermetallic compound (most probably Cu_3Sn and Ni_3Sn) while bismuth remains between the reaction layers (Figure 8). This same behaviour is also found in the Sn/Pb alloys but, as compared with lead, bismuth is inherently brittle due to its rhombohedral crystal structure. In addition, when tin reacts with conductor metals, the composition of the solder alloys changes towards bismuth-rich alloy which leads to the enrichment of practically pure bismuth in the center and, therefore, the formation of a eutectic microstructure is prevented during the solidification. The phase separation tendency is reinforced kinetically due to

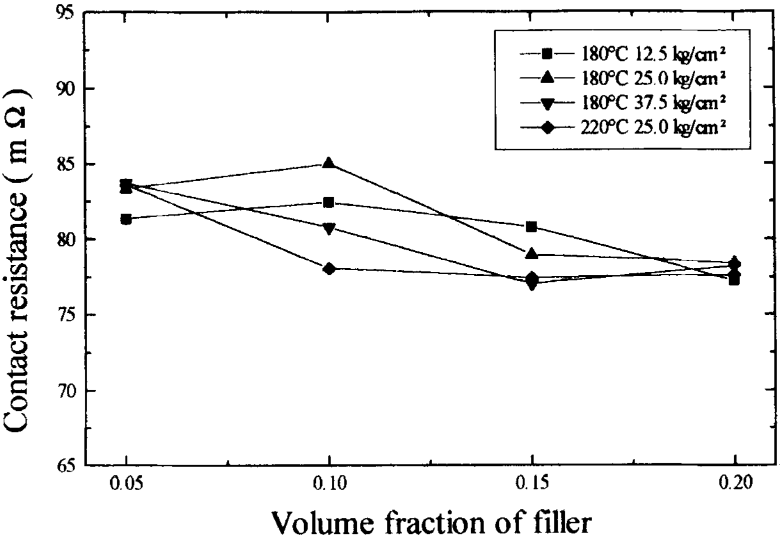

FIGURE 5 The effect of bonding temperature and pressure on contact resistance values. Bonding time was one minute for all specimens.

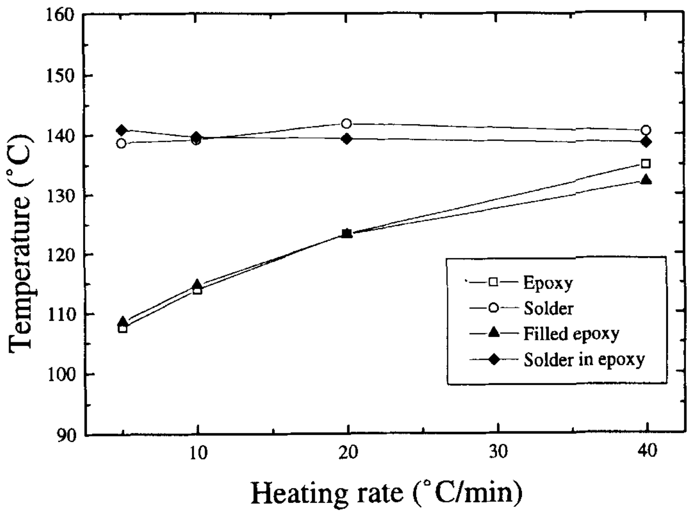

FIGURE 6 Effect of heating rate on the reaction peak temperatures of unfilled epoxy, filled epoxy, solder alloy in epoxy as well as solder powder. The shift of cure to higher temperatures is caused by thermal lag.

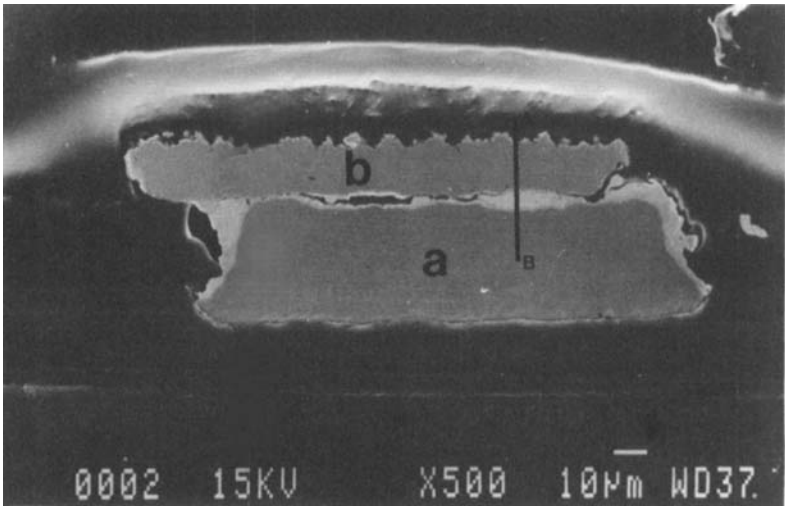

FIGURE 7(a) A typical SEM micrograph of a cross section of one pair of mating conductors: a = copper on polyimide, b = copper on polyester.

the thin gold coating since gold dissolves readily in the liquid solder and exposes practically unoxidized surfaces of copper and nickel for tin to react with.

The contact resistance values measured during temperature cycling are presented in Figure 9. The resistivity of the joints remained constant through the temperature

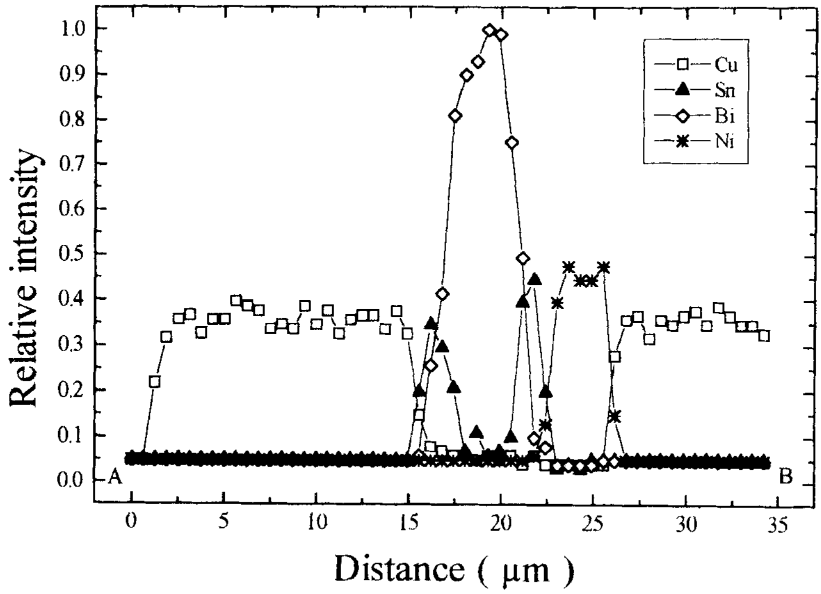

FIGURE 7(b) EPMA profile across the joint (line A-B) in Figure 7(a) demonstrates the phase separation of bismuth and tin.

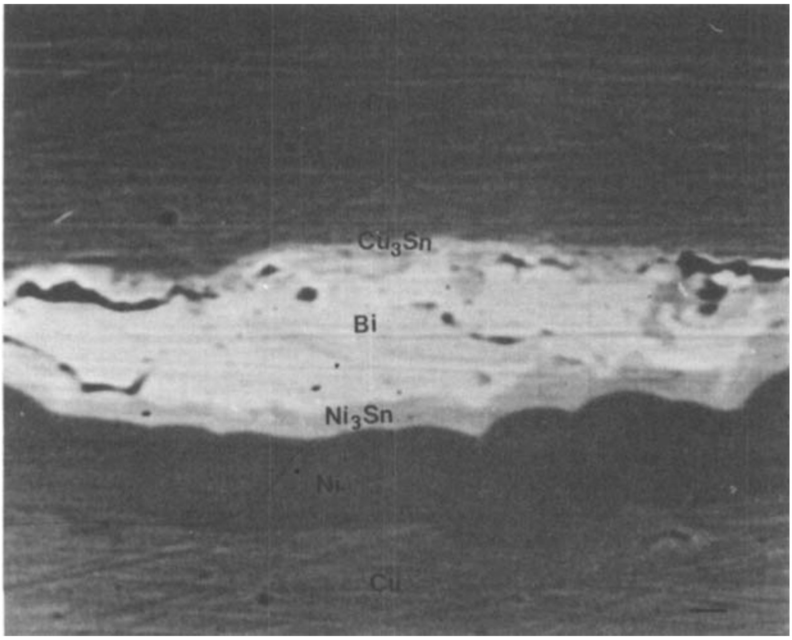

FIGURE 8 A detail of Figure 7(a) showing clearly the thin reaction layers and the bismuth-rich phase in the middle (scale bar = 1 μm).

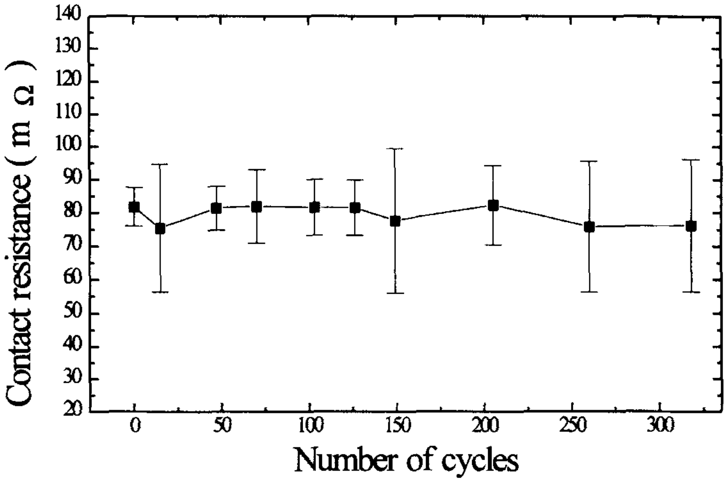

FIGURE 9 Contact resistance values during temperature cycling test.

cycling. Small variation of the average values was due to varying measuring temperature, from 20 to 24°C. By measuring the contact resistance during one cycle a noticeable temperature dependence of contact resistance was observed. Moreover, the insulation resistance values increased remarkably which is likely due to postcuring of the adhesive. The hot and humid environment had quite a strong effect on contact resistance values (Figure 10) during 300-hour ageing. It is likely that water diffused into the joints. The swelling of the polymeric materials decreased the integrity of the joints thus increasing the joint resistivities.

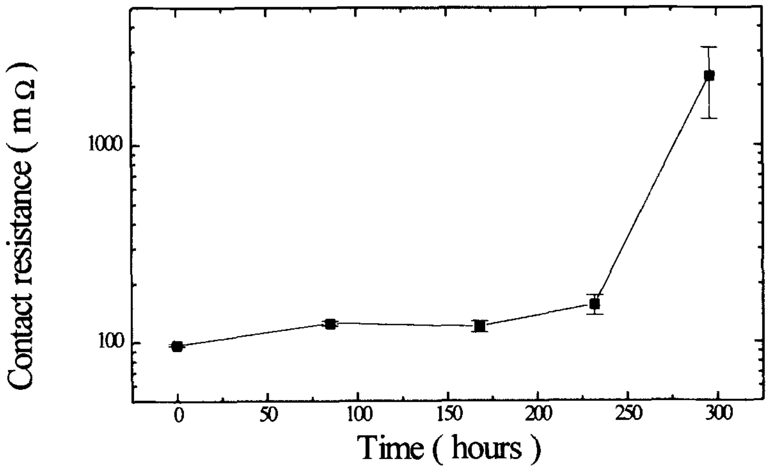

FIGURE 10 Contact resistance values during 85°C/85% RH-test.

4. CONCLUSIONS

Sn-Bi alloy filled composite adhesives with various filler contents were prepared and tested. The measured contact resistance values of the adhesives differed only slightly. On the other hand, the low filler volume adhesives were superior as regards the insulation properties and shear strength. With the aid of optical and scanning electron microscopic techniques it was shown that the eutectic Sn-Bi alloy bonds well to the conductors but the mechanical integrity of the joints is reduced by the microsegregation of bismuth. The effect of bonding pressure and temperature on the electrical properties was negligible. The contact resistance values remained constant during the temperature cycling test but hot and humid environment caused a noticeable increase in resistance values.

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