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THE ELECTRICAL AND MECHANICAL PROPERTIES OF ELECTRICALLY CONDUCTIVE ADHESIVES IN PIN-THROUGH-HOLE APPLICATIONS

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Electrically conductive adhesives have been used in place of solder for pin-through-hole attachment of dual-in-line IC packages. Joint resistances are much higher than predicted by specified resistivities, but would be adequate for most applications. Shear and fracture strengths are similar to those found for surface mount applications, and boards survive improvised impact testing. Much of the electrical data relates to resistance drifts with thermal cycling, temperature, coefficients of resistance, and dispersion due to small joint geometries.

1. Introduction

The primary motivation for the industry's current interest in electrically conductive adhesives (ECAs) as potential replacement materials for solder is environmental, despite the technology's greater fine pitch capabilities, and eventual processing advantages in manufacturing.[1] Two environmental problems are solved simultaneously by a switch to ECAs: the release of CFC/HCFCs from flux solvents into the atmosphere, and the eventual passage of the Pb content of solders into the world's eco-systems. The current question is whether governments will institute the control legislations, threatened or not, and whether legislation in even one major market could force international compliance in the global economy.

The emphasis in published ECA research is on applications to either advanced devices (e.g. flip-chip attachment for multi-chip modules (MCMs)) or volume printed circuit board (PCB) assembly by surface mount technology (SMT). There is, however, still a significant volume of pin-through-hole (PTH) PCB assembly, particularly in mature or low production volume technologies. For high volume assembly, PTH manufacturers would probably choose to switch to SMT if the move from solder to ECAs should become necessary, given the need to re-tool the appropriate part of the production process anyway. It is the plight of the low-volume producer in this scenario which prompted this work, for a company where PTH PCB circuits are in fact hand assembled, hand soldered, and individually tested. The obvious alternative would be to subcontract the PCB to a commercial assembler, and another is to replace the hand soldering operation with a direct ECA equivalent.

The project reported here was originally conceived as a feasibility study for the hand dispensation of ECAs by syringe at the PTH lead to board interconnection points. The electrical and mechanical test data for such interconnections are presented below. However, the project also expanded into an investigation of the effects of over-curing ECA materials. Prior work has demonstrated that manufacturers' cure schedules are often under-specified,[2–4] and that where this is the case, an increase in cure temperature is more effective than increase in curing time. A secondary objective was therefore

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established to use the project's samples to study thermal stabilities and the effects of exceeding cure temperatures.

2. Materials and Experiments

Three commercial ECA pastes dispensed by 18 gage syringe were used in the study. Relevant properties are listed in Table 1.

Two different types of board were used, both of which were commercial prototyping boards with Ag-plated copper metallizations, which should give best resistances with least interface effects.[5] The component geometry is shown in Fig. 1. Standard 14/16-pin dual in-line (DIL) TTL IC packages were used; the leads are 0.020 in. × 0.015 in. where they pass through the board.

(1) For electrical testing, the conductive tracks are 0.003 in. thick on 0.062 in. thick board; the holes are 0.032 in. in diameter. For the geometry quoted, the lead to track resistance R, can be estimated from the concentric resistor formula

$$R = (\rho/2\pi t)\ln(b/a)$$

as approximately 1.4 mΩ, for resistivity $\rho = 10^{-4}$ Ωcm, $t = 0.003$ in., outer radius $b = 0.032/2$ in., and inner radius, a, approximated for the rectangular lead by 0.016/2 in. The Keithley 580 micro-ohmmeter probes shown in Fig. 1 are configured as Kelvin probes for four-terminal resistance measurements. The current supply and voltage measurement leads are joined very close to the contact points. These lead and track contact points are arranged as close as possible to the adhesive in each case, but there is nevertheless a residual zero error of approximately 10 mΩ which has *not* been subtracted from the data presented below, since for large resistances it is negligible and for very small values its variation is itself significant. Indi-

Table 1. Process parameters and properties of the ECA pastes used.

	A	B	C
Resistivity	6×10^{-5} (Ωcm)	3×10^{-4} (Ωcm)	7×10^{-5} (Ωcm)
Die shear strength	4.5 (kgf/mm^2)	5.1 (kgf/mm^2)	1.4 (kgf/mm^2)
Glass transition, T_g	90 (°C)	125 (°C)	200 (°C)
Cure schedules	30 min/150°C 60 min/130°C	30 min/175°C 60 min/150°C 120 min/125°C	Snap/200°C 2 min/180°C 5 min/170°C 30 min/150°C
Storage life	6 months @ −10°C 1 year @ −40°C	1 year @ −5°C	6 months @ −10°C
Shelf life @ 25°C	2 weeks	2 weeks	2 weeks
Processed:	Upon delivery	Delivery + 7 months	Delivery + 7 months

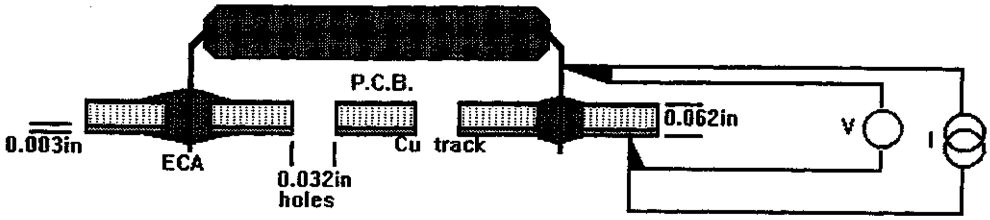


Fig. 1. Pin-through-hole joints and probe points.

vidual joint resistances were measured since it was (correctly) expected that hand dispensation might lead to significant joint-to-joint variations.

(2) The boards used for mechanical tests were similar, but with plated-through holes. For Adhesive A, four adhesive configurations were set up, i.e. adhesive confined to the hole itself, and extending around the hole above and/or below it to provide additional anchoring to the conductive lands. There was no difference in these four cases, since the

Table 2. Thermal testing data.

Adhesives	A	B	C
Initial Cure	30 min @ 150°C*	30 min @ 175°C*	3 min @ 175°C*
Elec Sample Set #1	All	Chips 1 & 2	Chips 1 & 2
Thermal Cycle #1	25 ↔ 125°C*	25 ↔ 150°C*	25 ↔ 150°C*
Thermal Cycle #2	25 ↔ 125°C (2 hr)*	25 ↔ 200°C	25 ↔ 200°C
Thermal Cycle #3	25 ↔ 125°C (2 hr)*	25 ↔ 150°C	25 ↔ 150°C
Thermal Cycle #4	25 ↔ 125°C (2 hr)*	25 ↔ 200°C	25 ↔ 200°C*
Thermal Cycle #5	25 ↔ 125°C*	—	—
Elec Sample Set #2	—	Chips 3–5	Chips 3–5
Thermal Cycle	—	25 ↔ 150°C (30 min)*	25 ↔ 150°C (30 min)*
Mech Sample Set #1	No further treatments after initial cure		
Mech Sample Set #2	—	5 min @ 200°C	5 min @ 200°C

Notes: (1) * indicates all pin resistances measured after this procedure.
(2) Adhesive A: all pins also tested 5 days after cure, before thermal cycling.

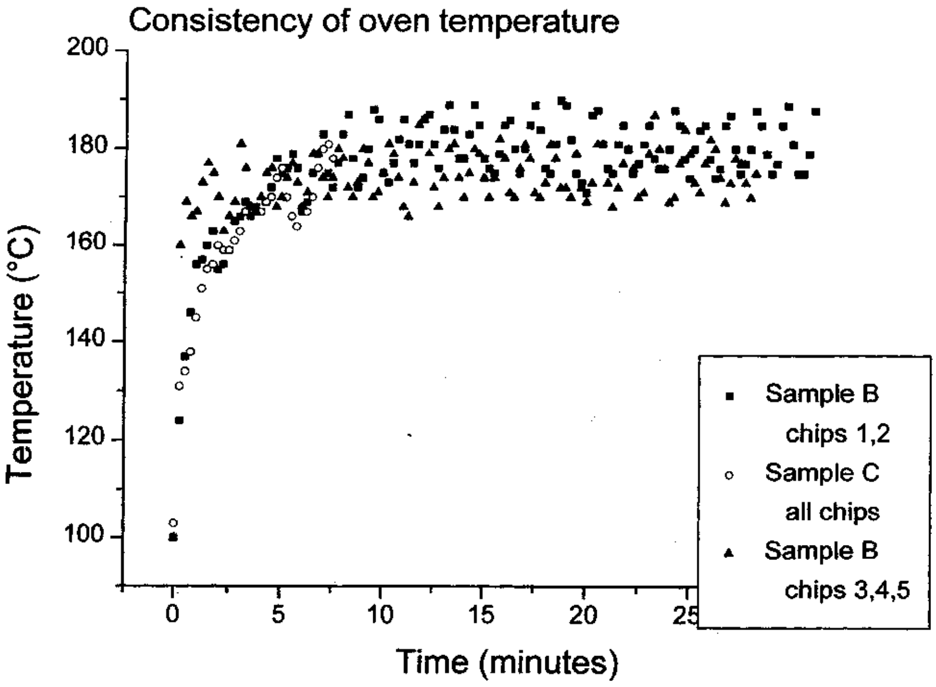


Fig. 2. Temperature characteristics of the oven.

adhesive never ever pulled out of the holes, so the only control exercised for Adhesives B and C was that the adhesive extended fully through the hole with minimum excess. After curing, the IC/PCB assemblies were sliced by a diamond saw into samples for pull-testing on an Instron 1122. Each mechanical sample consisted of a sliver of the board and another of the IC package, coupled by the IC leads and ECA attachment. Conventional fracture samples were also made of Adhesive A. The Instron was calibrated directly by standard weights.

The thermal treatments are summarized in Table 2. During thermal treatments, one ECA resistance was monitored, along with the oven temperature (measured with a thermocouple). After the initial cure, all ECA resistances were measured, and one was selected as representative of the batch for subsequent testing. Its behavior may not necessarily continue to be typical, however.

Note that initial cures were performed according to the manufacturers' specifications, but the single temperature specifications in Table 2 can be a little misleading; in practice a significant hysteresis was noticed in the oven temperatures (typically ±5°C about nominal, as shown in Fig. 2). Thermal cycling of Adhesive A does not exceed the cure temperature (even with the hysteresis). For Adhesives B and C, thermal cycles alternate higher and lower temperatures.

3. Results

3.1. *Mechanical strengths*

Measured fracture strengths for Adhesive A as listed in Table 3 are very consistent, unlike the shear strength data in Fig. 3 which shows considerable scattering. In all shear cases, the failure mode was adhesion failure at the IC pin surface, with the pin pulling *relatively* cleanly from the adhesive in the hole. To normalize the data to shear force per unit area, the effective pin lead area in contact with the adhesive can be estimated between 2.8 mm^2 (for the hole filled precisely, with no adhesive above either board surface) to about twice that for cases with excess adhesive. There is some correlation between the measured values in Fig. 3 and variations in contact area, but it can only account for a little of the scatter. Re-curing the materials does not seem to degrade the mechanical strengths.

Table 3. Fracture strengths for Adhesive A samples.

Sample	Working area (mm^2)	Fracture load (kgf)	Fracture strength (kgf/mm^2)
Aa	4.87	14.2	2.92
Ab	5.02	14.6	2.91
Ac	4.29	13.5	3.15
Ad	3.94	11.4	2.89
Ae	5.47	17.0	3.10
Af	3.65	11.5	3.15

The magnitudes of the shear strengths are not unlike those published by others,[6–9] but the real problem for mechanical attachment by ECAs comes with impact testing — the drop test. In the PTH case, sharply rapping the edge of the board against a table, for example, has no effect on the components which remain firmly in place. Similarly, striking the table surface with the top (component) side of the PCB does not dislodge the ICs either.

3.2. *Electrical resistances*

The first point about the resistance measurements is that the values are all at least of an order of magnitude higher than the calculated 1.4 mΩ. Most ran around two orders higher, i.e. on the order of 100 mΩ after first cure. The second noteworthy point is the scatter in resistance values. For Adhesive A, the lowest measured resistance following initial cure is 37 mΩ (which includes the estimated 10 mΩ zero error), with about 4% exceeding 1 Ω; for B the lowest value is 100 mΩ, with about 20% over 3 Ω; and for C, 40 mΩ with 11% over 1 Ω. The ratios of these minimum values roughly matches the ratios of the manufacturers' specified resistivities.

Thermal cycling plots are shown in Fig. 4. The general trend seen is for all resistances to increase steadily with heat treatments, even if previous high temperatures or the cure temperature are not exceeded. But the trend is not invariate; for Adhesive A, there is a sudden decrease (following a very noisy phase) while cooling on the first cycle, and the resistance also dropped markedly between the fourth and fifth cycles. For sample B/2/2 [Fig. 4(b)] there is a period at high temperature on the fourth cycle when resistance begins to fall, before reverting to the common trend. For sample C/1/15, note the jump while cooling on cycle 2, and the temporary drop at

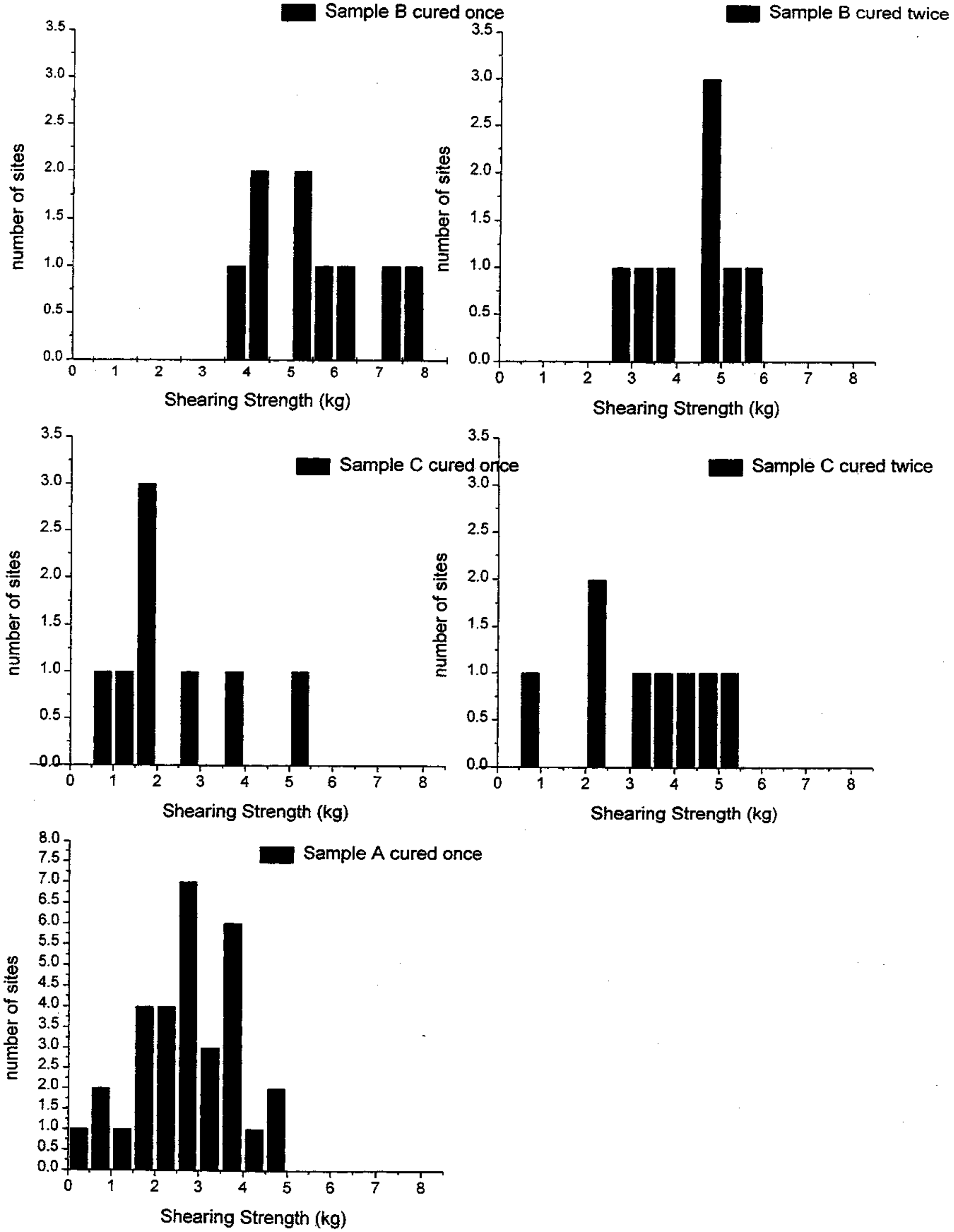
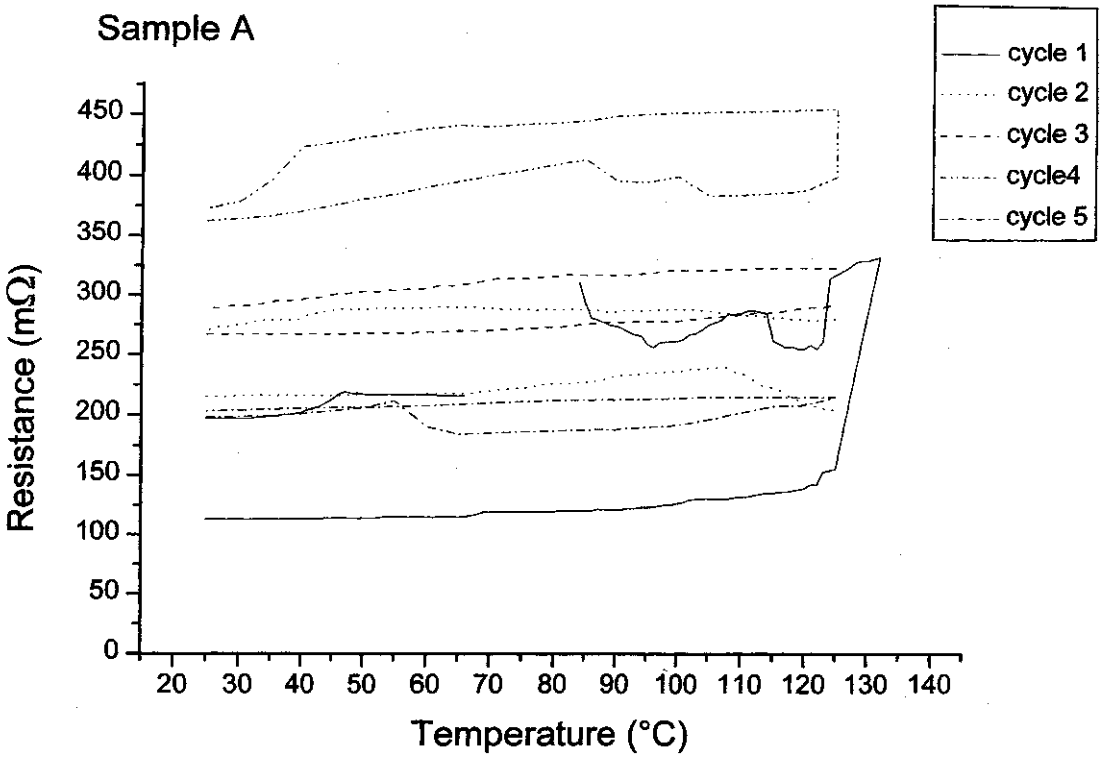
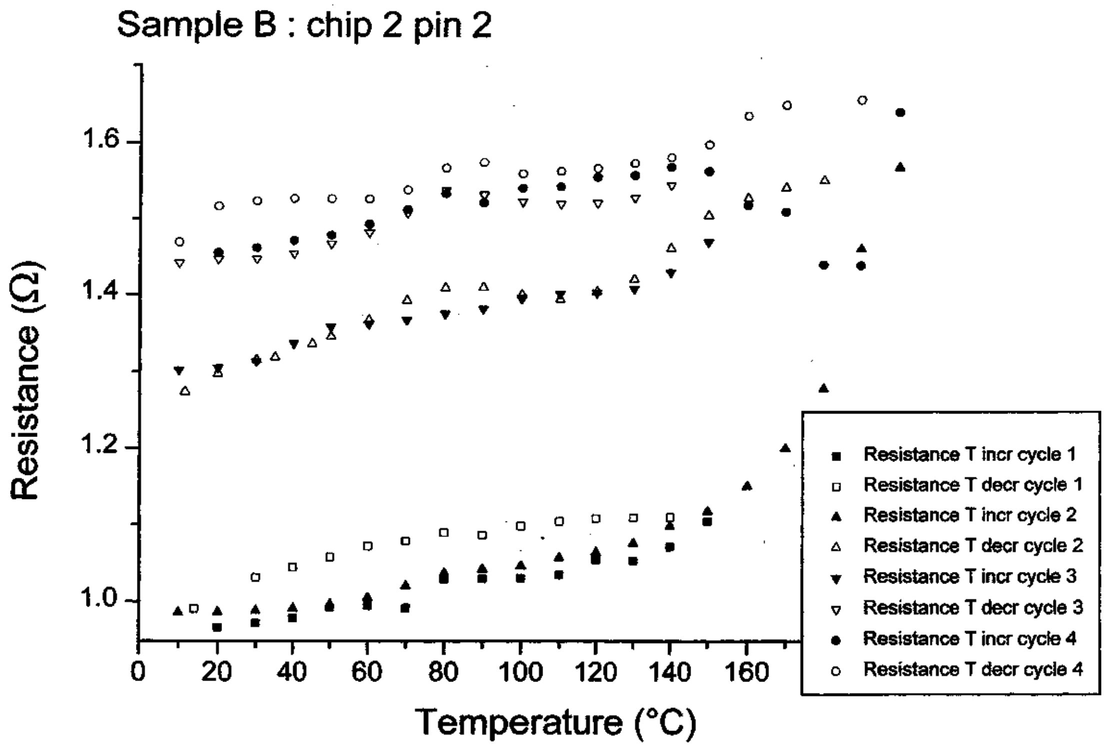


Fig. 3. Shear strength histograms for Adhesives A, B and C.

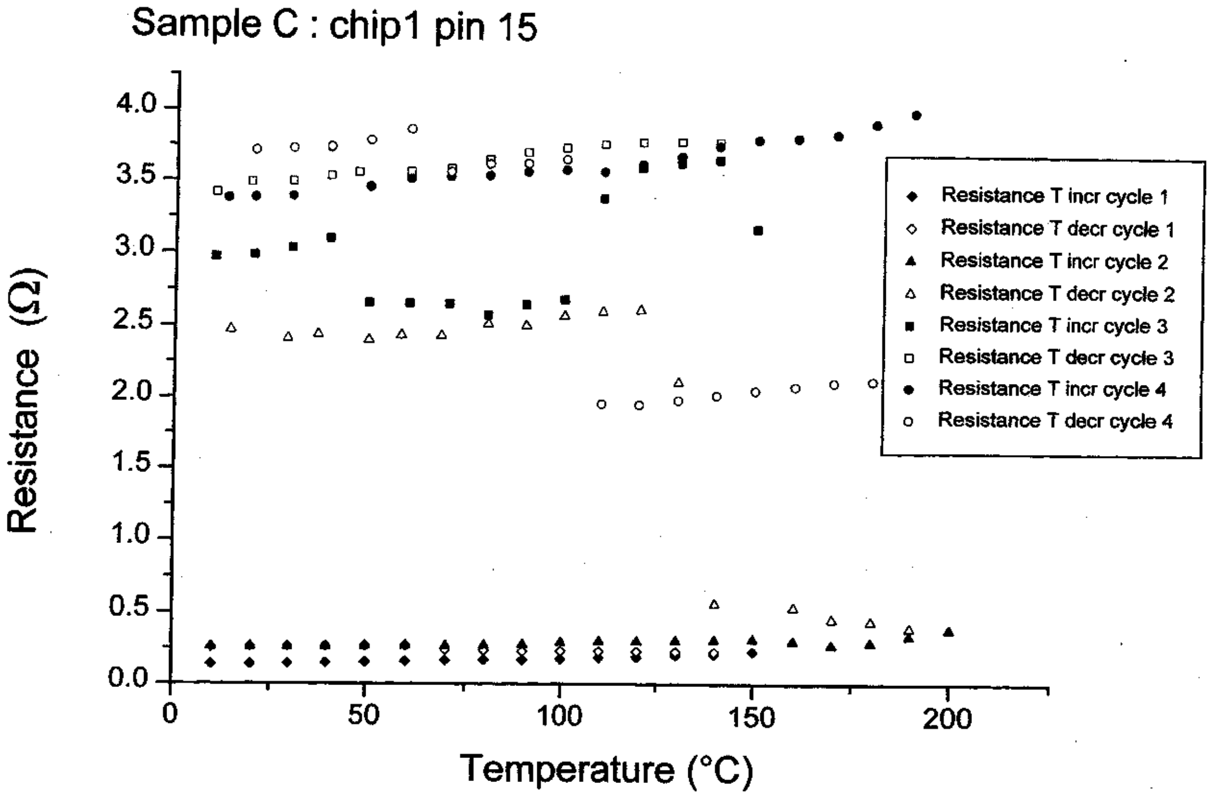


(a)



(b)

Fig. 4. Thermal cycling plots: (a) Adhesive A, (b) Adhesive B, (c) Adhesive C.



(c)

Fig. 4. (*Continued*)

high temperature on cycle 4. These sudden, major transitions are typical of the "make and break" of individual conduction paths in metal-insulator systems near the percolation threshold where there would be relatively few parallel paths. The steady upward drift of resistances with successive heating cycles is shown for Adhesive A in Fig. 5. It must be emphasized, however, that a few individual ECA joints do run counter to the general trend, and show decreases in resistance. The relative proportions can be found in Fig. 6 for Adhesives B and C, and in Fig. 7 for A. In Fig. 7, there is a six-month delay between cycles #3 and #4, during which resistances generally decrease.

Following the experiments in thermal cycling described above, fresh samples of B and C were prepared, with the resistance tracked throughout the curing process (call these Elec Sample Set #3). The general form of the resistance versus time or temperature is as reported elsewhere,[4,10] (except for the snap-cure Adhesive C for which the resistance drop was too rapid to track), but the observation of interest here is that once the resistances reached their minimum values, they began to increase immediately regardless of whether the temperature was still rising or had already begun to fall.

Temperature coefficients of resistance (TCRs) were measured by varying temperatures over a limited range to minimize further changes during the cycle. The first point that emerged from these tests is that the TCR for a given material is reasonably constant as the resistances themselves vary much more. Some measured values are cited in Table 4. Two TCR examples are shown in Fig. 8; the straight lines represent $\mathrm{TCR}_{\mathrm{Ag}}$, with the absolute zero intercepts indicated. On a simple model:

$$R = R_{\mathrm{metal}} + R_{\mathrm{contact}}$$

with the contact resistance TCR ~ 0 between metal particles for either a constriction resistance or tunneling, etc., the TCR should decrease from a maximum value of $\mathrm{TCR}_{\mathrm{Ag}}$ as resistance increases with larger contact contributions. In Fig. 8(a), the hysteresis shown by Adhesive B is not uncommon, and suggests some reversible change in contact resistances at high temperatures.

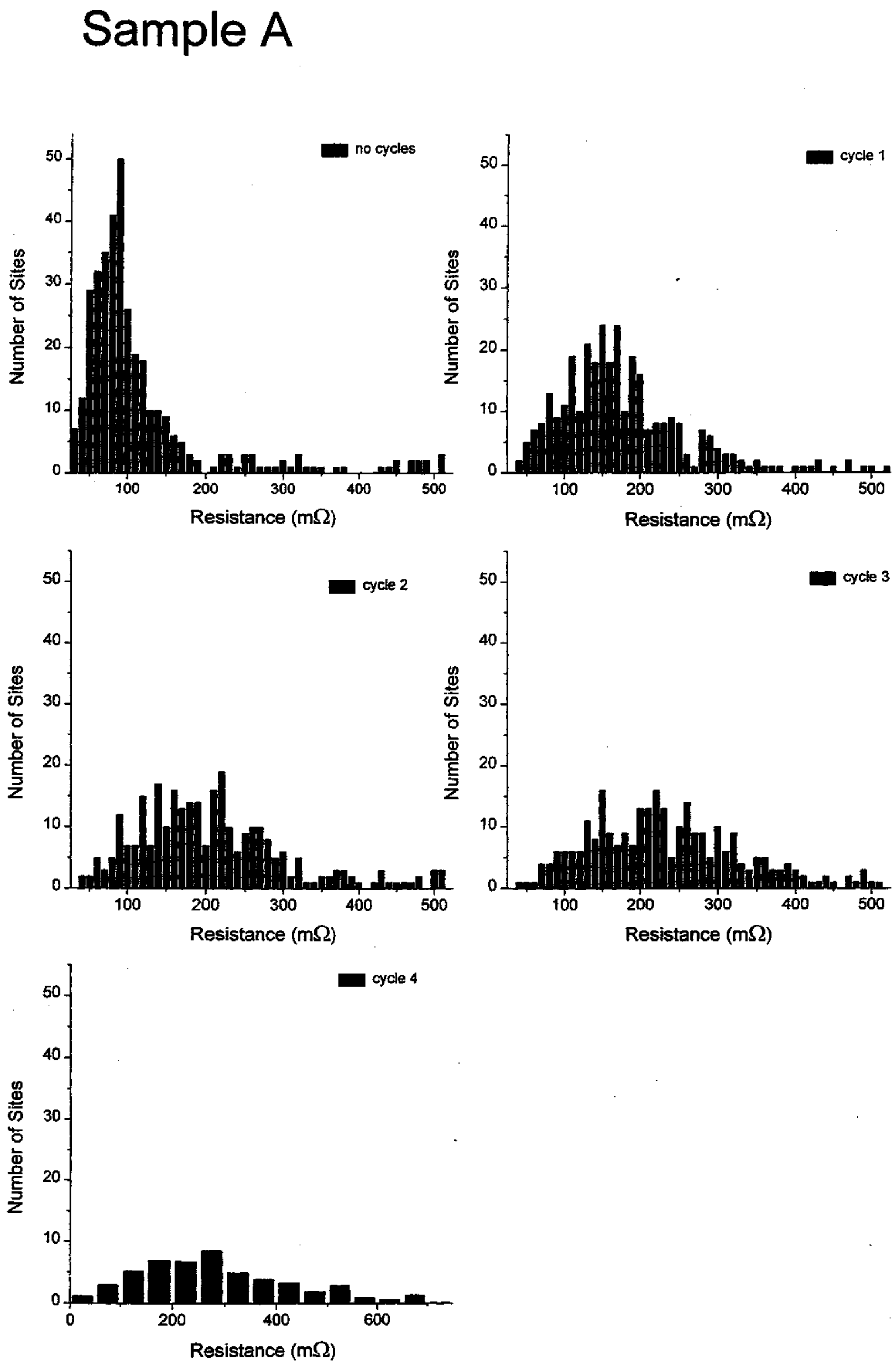
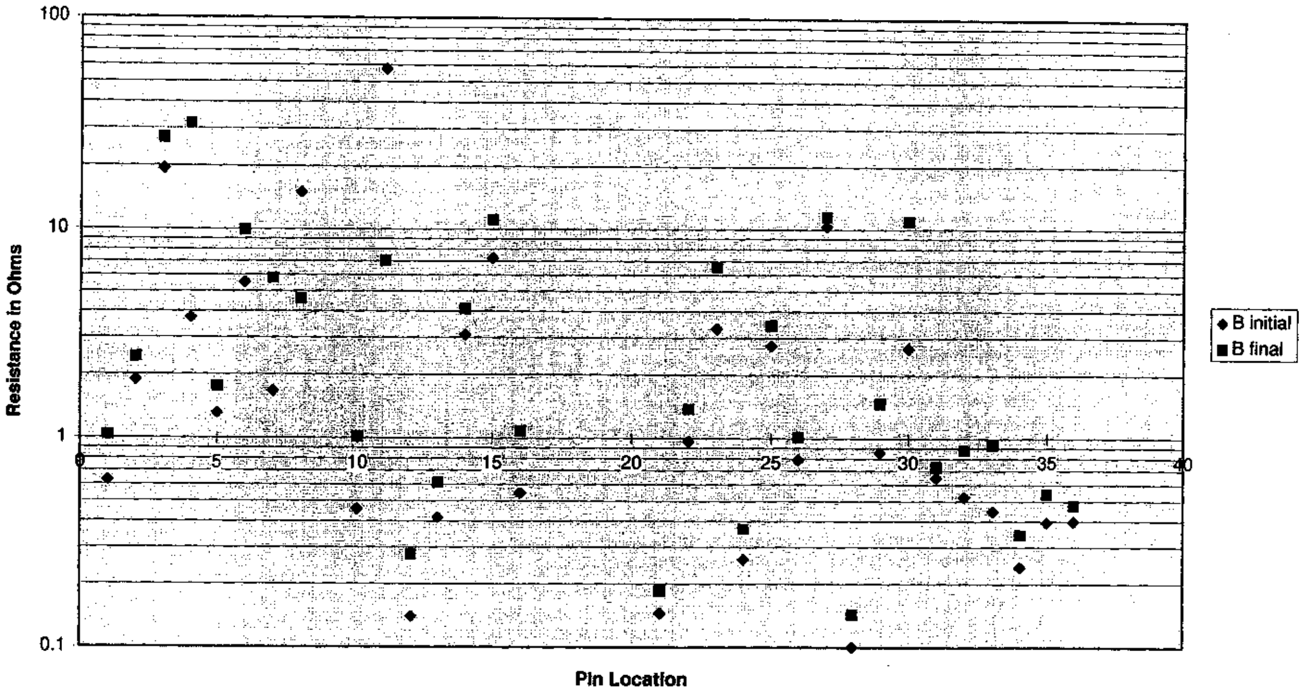


Fig. 5. Adhesive A histograms of resistance distributions following thermal cycles.

(a) Adhesive B: Initial & Final Resistances



(b) Adhesive C: Initial & Final Resistances

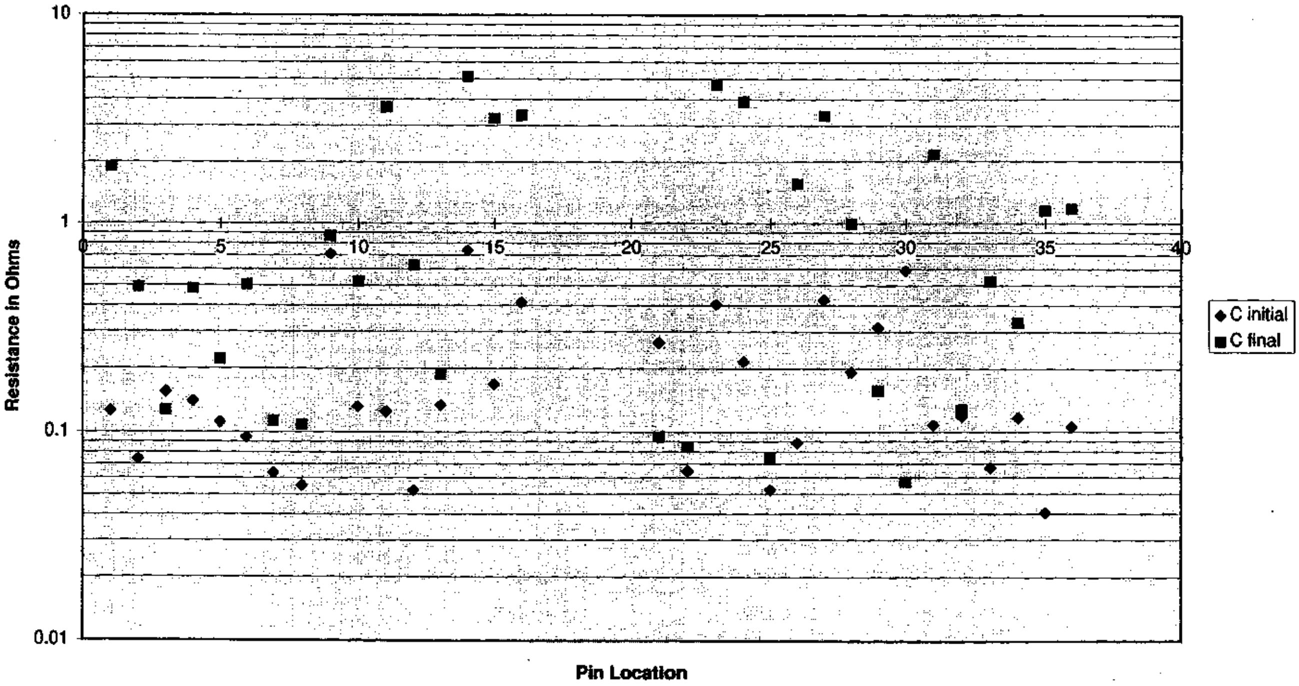


Fig. 6. Initial and final resistances for (a) Adhesive B and (b) Adhesive C. (Chip 1: pins 1–16; chip 2: pins 21–36).

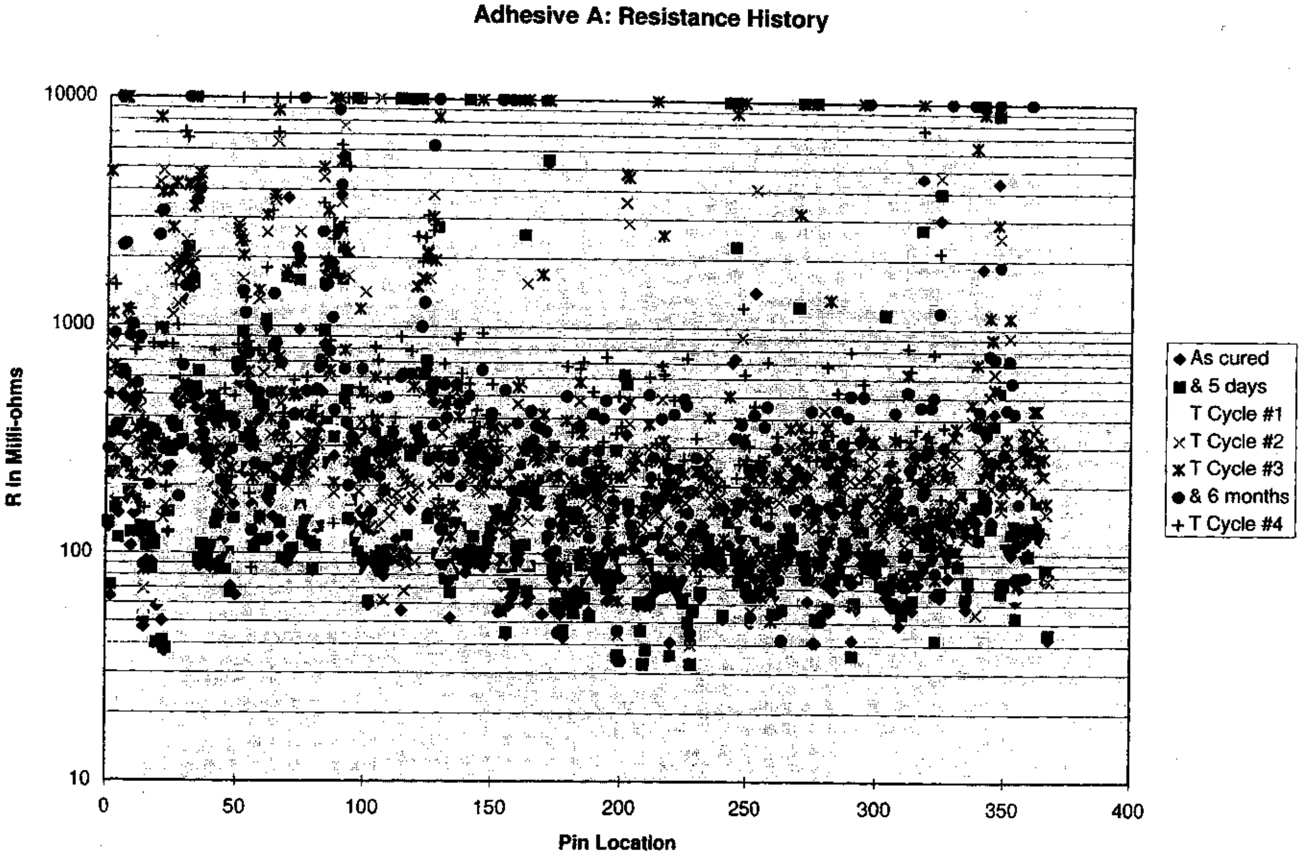


Fig. 7. Resistance history of Adhesive A samples. (10 Ω points include higher values & opens)

Table 4. Measured temperature coefficients of resistance.

Adhesive B		Adhesive C	
Resistance (Ω)	TCR (/°C)	Resistance (Ω)	TCR (/°C)
0.25	9.6×10^{-4}	0.05	1.6×10^{-3}
0.6	1.8×10^{-3}	2.0	1.8×10^{-3}
1.3	3.3×10^{-3}	3.0	8.7×10^{-4}

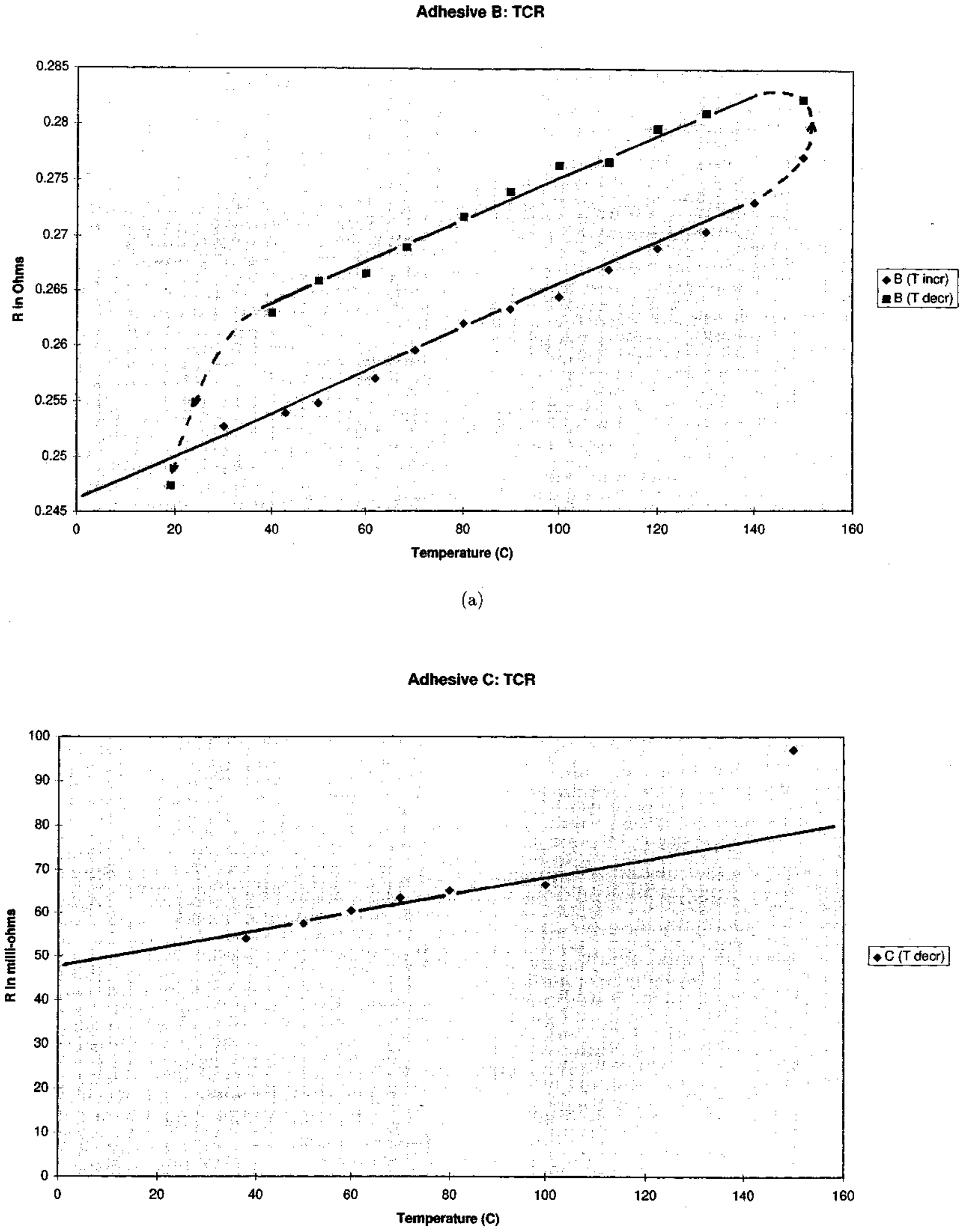
4. Conclusions

The mechanical results are encouraging. Although shear strengths are less than manufacturers' quoted values, they are on the same order, and the survival of the improvised impact tests is also satisfying.

Although most of the resistances would be satisfactory for most applications, the comparison with expectations based on manufacturers' specifications, the scatter, and the changes with time and temperature would all present problems in commercial applications. The TCR data provides a possible interpretation, taken in conjunction with the observation of large jumps in resistances, some of which reverse upon further treatments.

We can consider the conduction to take place by multiple parallel percolation paths, each consisting of a series combination of the resistance of the silver flakes along the path (with the TCR of silver at approximately 3.75×10^{-3} °C) and of the contact resistances between flakes. The contact resistance may be from tunneling through the intervening polymer, by conduction through a degenerate semiconducting silver oxide layer, or by the constricton resistance of point contacts between grains, but all these mechanisms can be considered to have zero or negligibly small (or negative) TCRs. So measured TCRs are always less than that of silver, but typically of the same order for low resistivity materials [e.g. Fig. 8(b)].

It is noted that the critical dimension in the electrical measurement is the 0.003 in. (75 μm) track thickness, which is less than ten times the typical ECA particulate dimensions (10 μm). At this ratio, resistivities are known to increase.[1,11] In effect, the percolation threshold moves to a higher metal content, which means that the system is moved closer to



(a)

(b)

Fig. 8. Examples of TCR measurements for (a) Adhesive B and (b) Adhesive C. (The straight lines represent $\mathrm{TCR}_{\mathrm{Ag}}$ with resistances at $T = 0$ K of (a) 190 and 200 mΩ, and (b) approx. 0 Ω.)

the threshold, i.e. towards (or even into) the transition region characterized by fewer parallel conduction paths, increased scatter, high resistivities, etc.

Now, if the component which varies is the particle contact resistance, then the slopes of the resistance versus temperature plots would remain constant as resistances increased (and TCRs would decrease steadily as resistances rose). Adhesives A [in Fig. 4(a)] and B [in Figs. 4(b) and 8(a)] look like they might fit this model.

The alternative mechanism of resistance change, particularly of discrete changes, is the abrupt removal (and perhaps addition) of parallel percolation paths. For this model, there should be no consistent TCR changes (if all paths had the same ratio of metal to contact resistances, there would be *no* change in TCR. There could be a consistent shift if the probability of path removal correlated with its metal:contact resistance ratio). For the loss of a percolation path to have a significant effect upon the resistance, there must be only a few of such paths, as expected here with a sample dimension on the order of the percolation coherence length.

In conclusion, the system shows all the characteristics of being closer to the percolation threshold than intended, and is correspondingly more sensitive to process parameters. It is believed that this problem is exacerbated by the paste dispensation by syringe, a hypothesis supported by the localization of major resistance changes in Fig. 7 which indicate compositional fluctuations in the syringe.

Obviously, some problems need to be solved before syringe dispensing for PTH boards is viable for mass production. A thicker syringe needle, which would go over the end of the protruding pin on the rear of the board, could force adhesive more neatly and uniformly into the hole around the pin, but the interaction of the two-phase paste viscosity with syringe gage and possible phase separation needs due consideration. Plated-through holes are necessary to eliminate the dimensional dependence on PCB track thickness, in order to reduce both the resistivity and its scatter.

Acknowledgments

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