Chapter 3

Development and Application of Low-Temperature Curable Isotropic Conductive Adhesive Toward to Fabrication in IoT Generation

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Additional information is available at the end of the chapter

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Abstract

Flexible electronics is the expected technology in the future, and the bonding material may also require flexibility. Silyl terminated poly-ether (STPE) is a promising material that has both flexibility and low-temperature curability. In combination with tri-block polymer-based stretchable conductive paste and artificially formed fillet formed by elastic resin, it can build simple stretchable bonding system. It will be a prominent technology to satisfy the characteristics required by the near future devices.

Keywords: isotropic conductive adhesive, low-temperature bonding, flexible devices, stretchable devices, IoT

1. Introduction

Internet of Things (IoT) means all things are connected to the Internet showing the possibility of changing our lives. With the smartphone market becoming steady once, the explosive popularization of smartphones pushed for the miniaturization of electronic components and the spread of wireless Internet. In response to that, the wearable device approached a more practical device. Then, the role of electronics is becoming different from that of the previous one. For example, the reduction of medical expenses by health-care monitoring, efficient use of energy, assistance of workers and disabled people, and so on is said to be an important social task that electronics can solve. It is a great opportunity for printed electronics to join with the flow of giving an electrical function to various things indicated by IoT and create a light and soft device by printing. Attempts to design interfaces between the Internet world and real society have begun, as sensors and other electronic devices are incorporated all over our lives. In the trend, IoT gives "anywhere anything" according to electric function indicated by IoT, base material has expanded from conventional rigid PCB to heat-sensitive materials, such as plastic, paper, and cloth, which can be formed by flexible circuits. In addition, those materials can be cured by low temperature, which is a major topic and important element technology. In fact, flexible circuits have been created by various materials and have achieved great results. To date, the softening of the wiring materials is largely developed by graphene in [1], carbon nanotubes in [2], silver nanowires in [3], conductive polymers in [4], or metal dispersed elastomers in [5–7]. With the advent of these technologies, flexible electronics can be said to have undergone a dramatic evolution. However, it has been rarely reported about the bonding materials, which coexist with flexibility and low-temperature curability. Furthermore, at present, it is difficult to create ICs, memories, communication modules, and so on by printing; therefore, it is necessary for the next generation devices to use hard parts and flexible substrates together. Additionally, in the connection between flexible substrates and hard components such as a wearable device, the connecting part will bear a large strain (**Figure 1**). As **Figure 2** shows, in Ref. [8], elongation that can occur on human body is around 30%. It is difficult to say that the bonding materials satisfy the requirement of imparting an electrical function to various substrates. In this situation, isotropic conductive adhesives (ICAs) have low-temperature curability and flexibility can be of great potential in creating next generation devices (**Figure 3**).

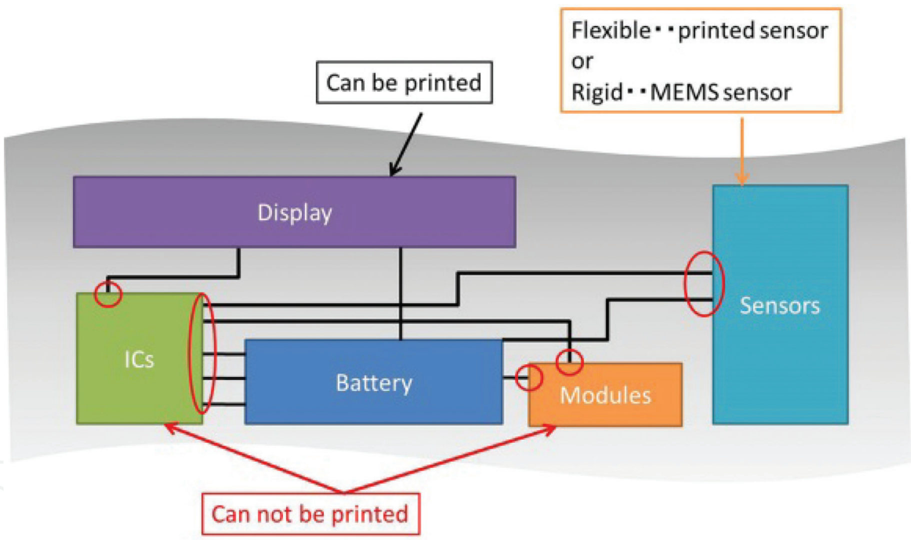

Figure 1. Image of flexible hybrid electronics device in future.

Parts	Elongation(%)
elbow(as flexion)	6-17
shoulder to elbow(as flexion)	13-34
shoulder(as rotation or stretch)	8-36
waist to hip(as flexion)	10-22
knee(as flexion)	2-51

Figure 2. Elongation of each part occurring in the human body.

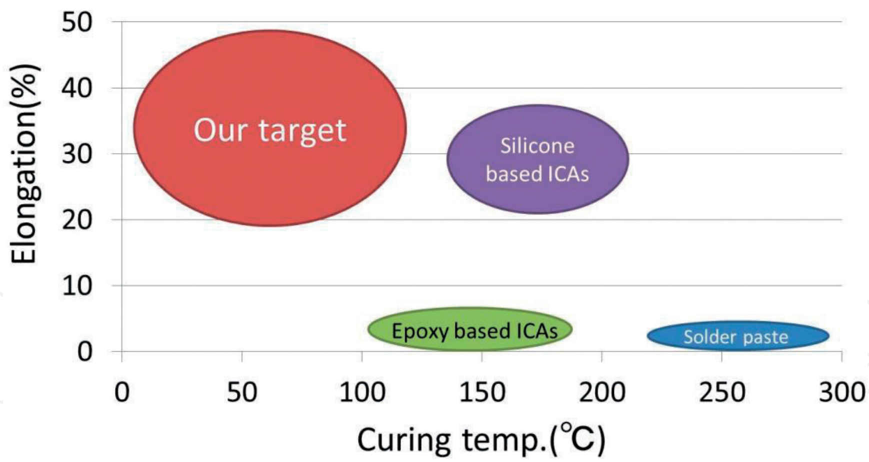

Figure 3. A comparison of this work with conventional conductive materials.

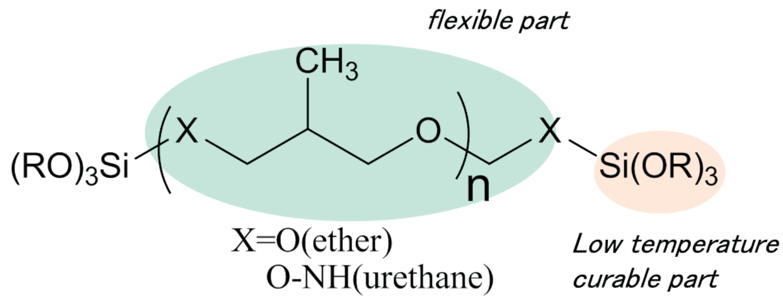

Figure 4. Chemical structure of STPE.

As the types of base materials are expanding, the most important basic property is to ensure adhesion to various base materials, and the adhesion technology is meaningful.

Silyl terminated poly-ether (STPE), as shown in **Figure 4**, is flexible and strong material to repeated strain, such as heat cycle. In present, there are many achievements to sealant for construction and adhesive for electronic components. Conventional conductive adhesives are mainly thermosetting system; the heat energy required for curing itself has disturbed the applications of heat-sensitive substrates and components. The cross-linkable silyl group can react by moisture in the air, even at room temperature, and it is suitable to implement thermally sensitive components. That is, it is possible to assemble the electronic component on the film as well as paper, fabrics, or various materials. We have developed a conductive adhesive having low-temperature curableness and flexibility by distributing the silver microsized to STPE. Here, we describe the characteristics of new isotropic conductive adhesive based on STPE, which has low-temperature curableness and flexibility and its application.

2. Characteristics of the STPE based conductive adhesive

First, we describe the design and characteristics of new conductive adhesives. Next, we describe the low-temperature curability, flexibility, and stretchable conductive paste for flexible devices, and finally, we introduce their application.

2.1. Experimental section

ICAs were fabricated by uniformly dispersing microsized silvers as described later. Uniform dispersion was achieved by a high-speed blender operated at 2000 rpm for 3 min under vacuum conditions (ARV-310, THINKY Company). Epoxy-based ICAs were formulated by Epicote 828 (Mitsubishi Chemical Co., LTD.) and 2-ethyl-4-imidazole (Tokyo Chemical Industry Co., LTD.) as curing agents. ICAs were mask-printed onto glass plate. STPE-based ICAs were cured at 80°C for 2 h, and epoxy-based ICAs were cured at 120°C for 1 h. Their dimensions were 80, 100, and 0.5 mm in width, length, and thickness, respectively. Volume resistivity was measured by MCP-T360 (Mitsubishi Analytec Co., LTD.).

Adhesion strength is tested by die shear tester (Dage 4000) at a shear head speed of 500 μm/s. Epoxy-based ICA (XA-874, FjikuraKasei Co., LTD.) was used as comparison. ICAs were mask-printed onto copper plate on printed circuit board and mounted on 3216-sized chip resistor. Printed thickness was 0.1 mm. The high temperature and high humidity tests were carried out at 85°C and 85% relative humidity (RH), respectively. Heat cycle test was performed at the temperature range between −40 and 105°C. Exposure time was 30 min.

Electrical stability is tested on ISO-16525. ICAs were mask-printed onto copper electrodes, in which dimensions were 2, 4, 8 mm in width, length, interval, respectively, on printed circuit board. Dimensions of ICAs were 4, 100, and 0.1 mm in width, length, and thickness, respectively.

Stretchable conductive paste was fabricated by uniformly dispersing microsized silver flakes. Uniform dispersion was achieved by a high-speed blender operated at 2000 rpm for 3 min under vacuum conditions (ARV-310, THINKY Company). Conductive pastes were mask-printed onto various substrates and dried at 100°C for 30 min. Their dimensions were 80, 100, and 0.5 mm in width, length, and thickness, respectively. Cross cut test was performed based on ISO-2649.

Bending resistance test of conductive paste was performed on IEC62715 by DLDMLH-4U (YUASA SYSTEM Co., LTD.). Conductive pastes were mask-printed onto PET film (Lumirror S10, TORAY Co., LTD.) and dried at 100°C for 30 min. Their dimensions were 5, 100, and 0.2 mm in width, length, and thickness, respectively. To investigate the resistance change in real time, copper and lead were connected to both ends, and the resistance was measured in current of 100 mA by the four-terminal method.

Dynamic boding resistance test was similar to the abovementioned test. Copper foiled polyimide was used as circuit. XA-874 and solder paste (FLF01-BZ(L), Matsuo HANDA Co., LTD.) were used as comparison. Artificially formed fillet was formed by SuperXG No.777 (CEMEDINE Co., LTD.).

In stretched resistance test, conductive pastes were mask-printed onto TPU (Platilon VPT9122, Covestro Japan Co., LTD.) and dried at 100°C for 30 min. Their dimensions were 5, 100, and 0.2 mm in width, length, and thickness, respectively.

2.2. Design of STPE-based conductive adhesive

Figure 5 shows formulation and volume resistivity of conductive adhesive. In case of using STPE as base binder, it is understood that combining silver fillers having different shapes and TAP density is important in expressing conductivity. Also, urethane bond in the polymer backbone showed less resistivity. Hard segment derived from a hydrogen bond due to a urethane bond plays strengthening of the interaction and the conductive path between the filler. Otherwise, BPA-based conductive adhesive has higher conductivity when using a single shape. Previously, there are few cases mentioning the TAP density in the formulation of the conductive adhesive, and it has been discussed in the shape of fillers. However, these results show the selectivity of characteristic silver fillers to develop the conductivity to flexible binder as STPE (**Table 1**).

2.3. Curing behavior

Curing behavior of STPE-based conductive adhesive is shown in **Figure 6**. Curing proceeds even at room temperature, the conductivity increased with time. Further, by heating to

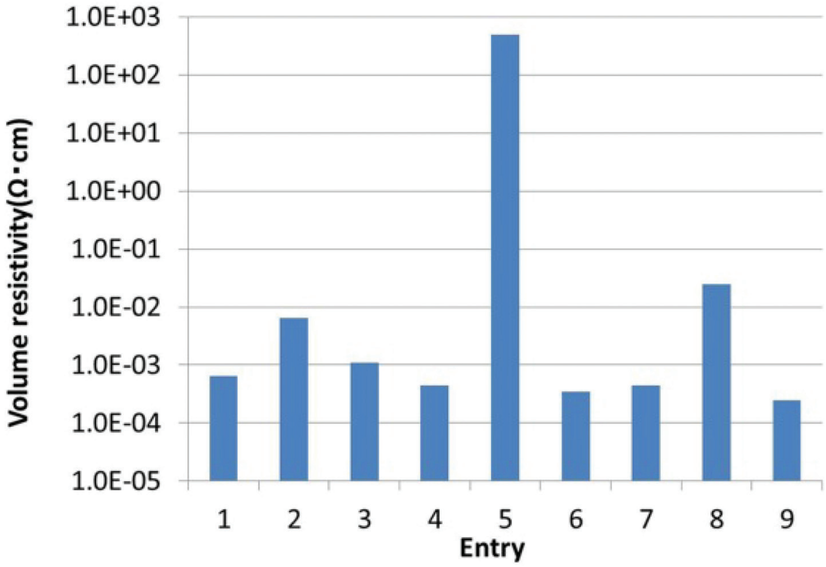

Figure 5. Volume resistivity of designed ICAs shown in **Table 1**.

Entry	TAP density of filler (g/cm³)	3.5	1.0	1.5
	Base resin	Silver flake	Aggregated silver	Spherical silver
1	STPE (ether)	300	200	–
2	STPE (ether)	300	–	200
3	STPE (ether)	300	100	100
4	STPE (ether)	200	300	–
5	STPE (ether)	500	–	–
6	STPE (urethane)	300	200	–
7	BPA	500	–	–
8	BPA	300	200	–
9	BPA	–	500	–

Table 1. Formulation of ICAs, silver weight ratio (per 100 resin).

50 or 80°C, curing is accelerated and conductivity increases quickly. Conventional epoxy-based adhesives are often unable to exert their performance unless they adhere to the recommended curing conditions. In other words, the curing conditions themselves may cause trouble in bonding process. With STPE-based conductive adhesive, even if heating is stopped halfway, the reaction proceeds, so that, a flexible production process can be constructed. Also, die shear strength increased with time, curing is accelerated and die shear strength increased quickly. On the other hand, the expression of adhesion strength does not match with the conductivity; this is because the adhesion is rate-limiting between electrode and adhesive interface.

2.4. Adhesion durability

Figure 7 shows adhesion durability at high temperature and high humidity, and heat cycle (−40–105°C) compared with thermosetting epoxy resin-based electrical conductive adhesive that is conventionally used. Initial adhesion strength of the STPE-based ICA is smaller than the epoxy resin system, since STPE has a lower elastic modulus than conventional epoxy resin. For this reason, it is better to consider a device having a slightly different design philosophy such as a flexible device than a simple replacement for solder. In particular, STPE-based ICA exhibits excellent bonding strength retention under heat cycle environment. On the other

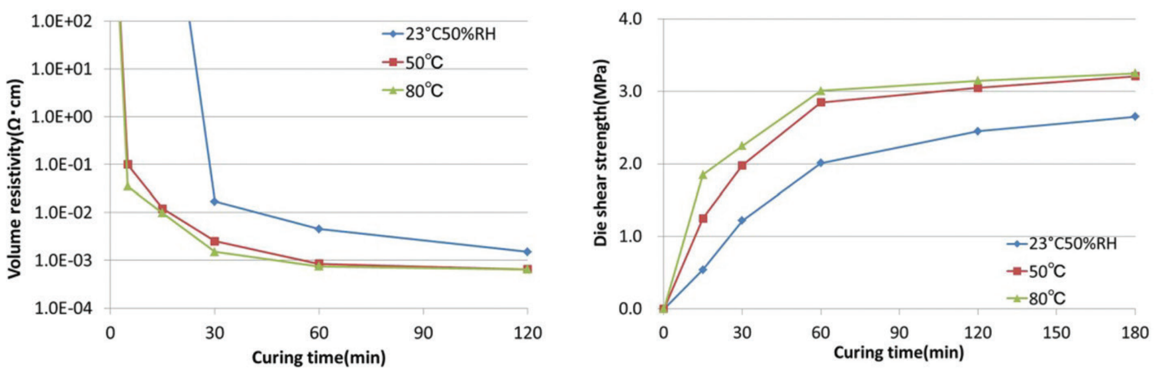

Figure 6. Curing behavior of STPE-based ICA. Left: curing behavior of volume resistivity. Right: curing behavior of adhesion strength.

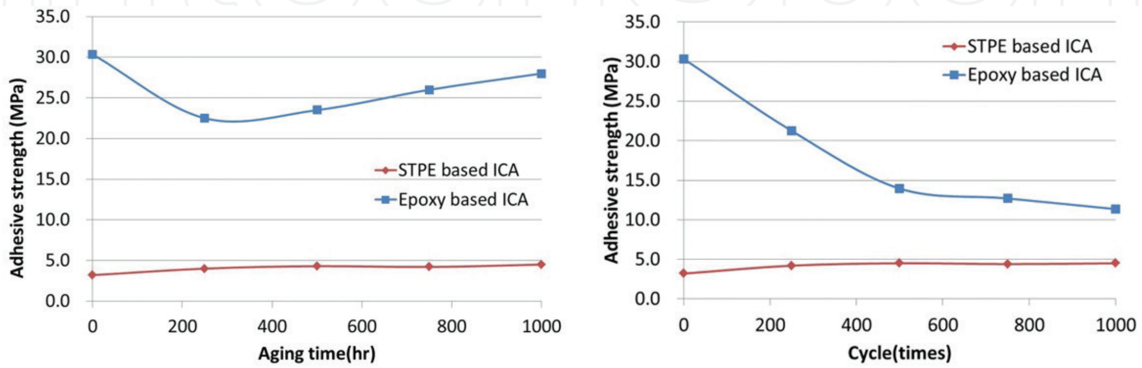

Figure 7. Adhesion strength at durability test. Left: 85°C and 85% RH. Right: heat cycle (−40–105°C).

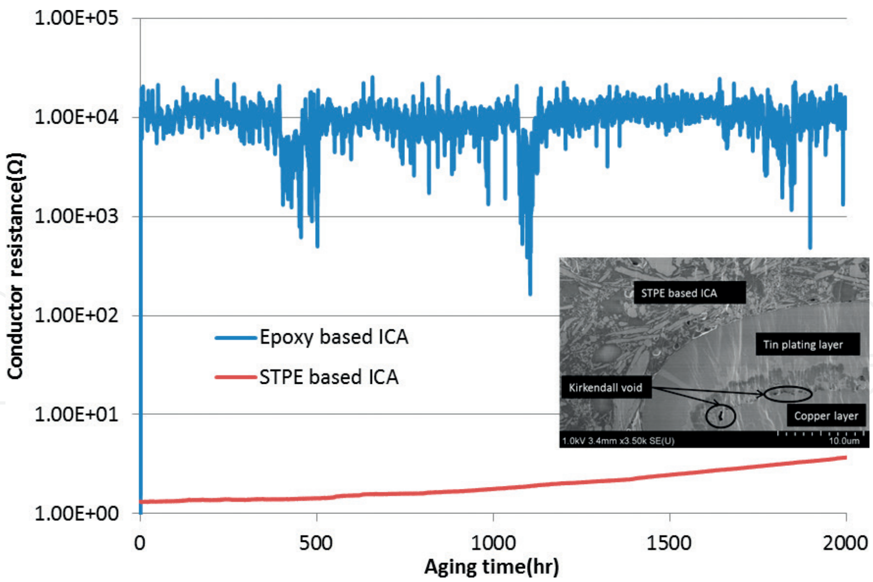

Figure 8. Conductor resistance of STPE-based ICA (red) and epoxy-based ICA (blue) at 85°Cand 85% RH on tin plated-copper electrode. SEM images show sectional view of PCB in the test of STPE-based ICA after 2000 h.

hand, the adhesion strength of epoxy-based ICA has decreased in every cycle. This phenomenon is induced by internal stress generated at the bonding interface when the temperature change occurs across the glass transition point in Refs. [9–11]. In this situation, rigid base resin cannot reduce the internal stress at bonding interface. STPE has low modulus and flexibility that induce stress relaxation characteristics, and it leads to ensure long-term reliability.

2.5. Electrical stability

The excellent characteristics of STPE-based ICA are shown in **Figure 8**. Galvanic corrosion between tin electrode and silver fillers in a high-temperature and high-humidity environment has become a long-standing problem of the epoxy-based ICAs. Therefore, in order to put the conductive adhesive into practical use, an increase in parts' cost has become a problem due to the use of a gold electrode or the like. Corrosion of the tin electrodes is said to be accelerated by the chloride ion in epoxy resin in Ref. [12]. In contrast, STPE is not containing chloride ion, and STPE-based ICA does not occur corrosion on tin electrode. A slight increase is observed in the conductor resistance after 1000 h, and it is found that it was generated by Kirkendall void between tin plating layer and copper used as electrode from SEM observation.

3. Characteristics of conductive paste

3.1. Design of flexible/stretchable conductive paste

As stated earlier, securing adhesion to enlargement of applied base material is an important factor, and adhesion technology is a key point. Conventional conductive paste does not have

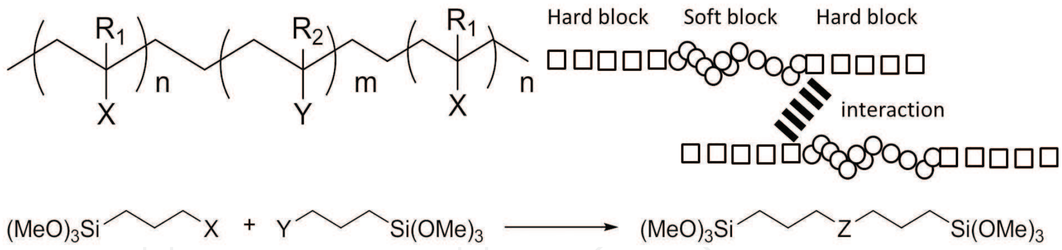

Figure 9. Schematic image of tri-block elastomer and pre-cured silane coupling agents.

Base polymer	Acrylic	SIS	SEBS
Volume resistivity	3.50E − 04	8.50E − 05	7.50E − 05
Adhesion to PET	100/100	70/100	75/100
Adhesion to PEN	100/100	60/100	70/100
Adhesion to TPU	100/100	50/100	70/100
Adhesion to excimer laser treated SR	100/100	0/100	0/100

Table 2. Test results of block polymer-based conductive paste.

extensive adhesion property. Therefore, we have to choose conductive paste according to substrates. To solve it, we choose tri-block elastomer as binder and pre-cured silane coupling agents (**Figure 9**).

Adhesion test results by cross cut test is shown in **Table 2**. Hydrocarbon polymers such as SIS and SEBS show high conductivity, but they do not exhibit extensive adhesion property. On the other hand, it was found that the acrylic polymer has good adhesion to various substrates and is excellent in balance with conductivity. In subsequent experiments, the conductive paste based on an acrylic polymer is used.

3.2. Dynamic durability of conductive paste

Figure 10 shows real time resistance change due to bending on PET film. The resistance change due to bending is smaller than that of conventional epoxy-based flexible conductive paste. In addition, the resistance fluctuation when bending once is also small, which is considered to be based on polymer with hard segment and soft segment coexisting.

Figure 11 shows the resistance change at elongation on TPU. For example, the strain accruing on the human body is about 50% at the maximum. It is thought that the hysteresis of resistance is small, and it functions as strain sensor, which is capable of detecting elongation of about 50%. Also, by utilizing high adhesion and flexibility, it is possible to form circuits for various substrates.

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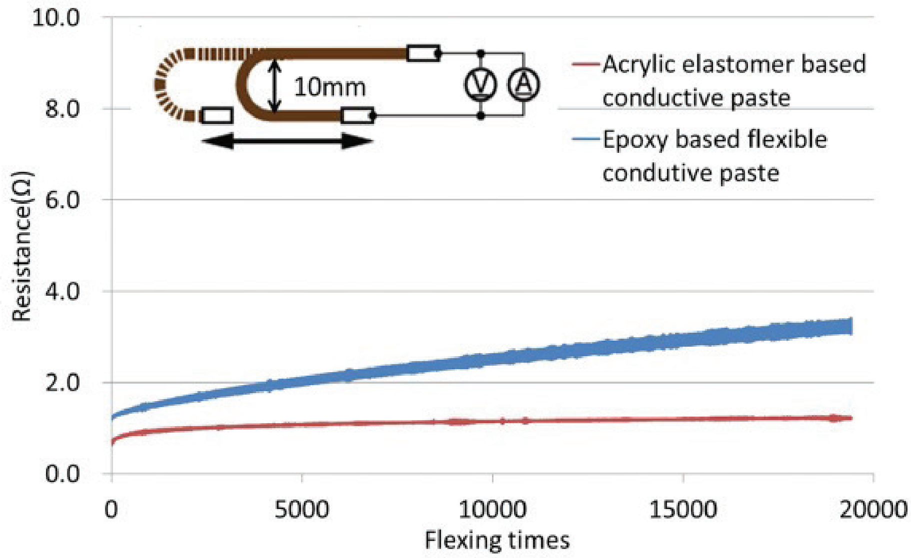

Figure 10. Conductor resistance change of acrylic elastomer-based conductive paste in bending test.

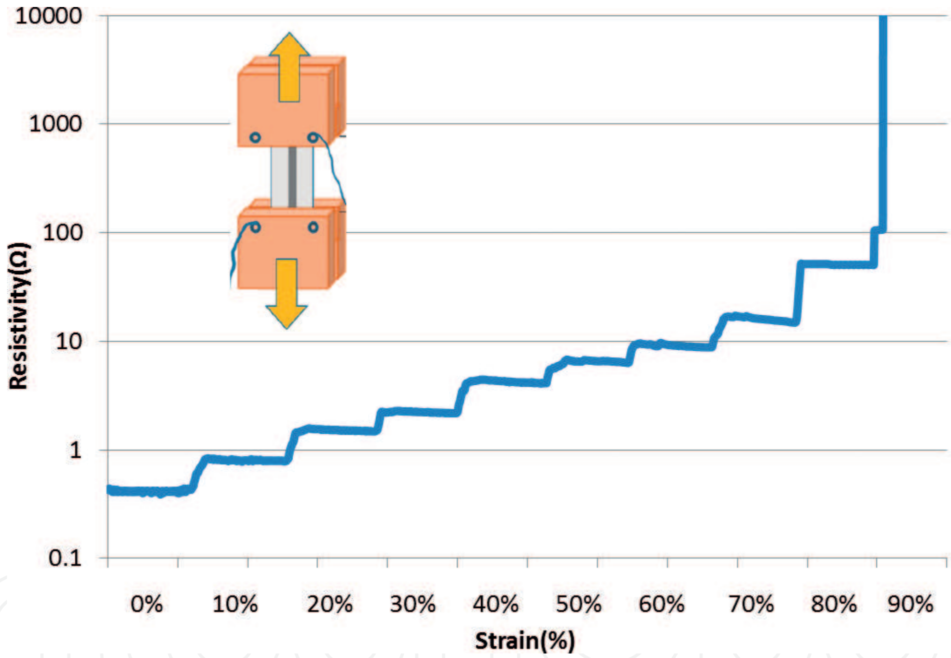

Figure 11. Conductor resistance change of acrylic elastomer-based conductive paste at elongation. Circuit size width: 5 mm, length: 100 mm, and thickness: 30 μm.

4. Application for flexible/stretchable bonding system

As mentioned earlier, STPE-based ICA does not have strong bonding strength as conventional materials. Therefore, in order to take advantage of this material, it is necessary to construct reinforcing structure. Solder or thermosetting conductive adhesive forms a fillet at the time of curing, and it becomes a reinforcing layer against dynamic strain. On the other hand, since STPE-based ICA is a low-temperature curable, it is difficult to form fillets. **Figure 12** shows bending resistance of mounting on FPC by STPE-based ICA and conventional materials and the effect of artificially formed fillet. Although the bonding resistance of solder is stable, bonding resistance of STPE-based ICA does not form a fillet, which has a considerable resistance variation. Even in the case of a thermosetting epoxy-based ICA, a slight resistance

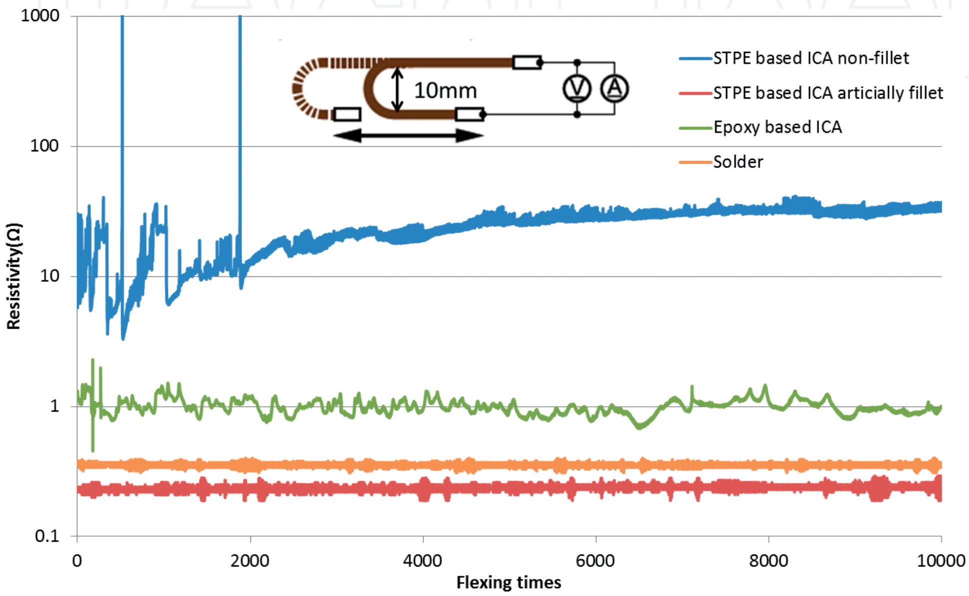

Figure 12. Bonding resistance change of various materials on FPC in bending test.

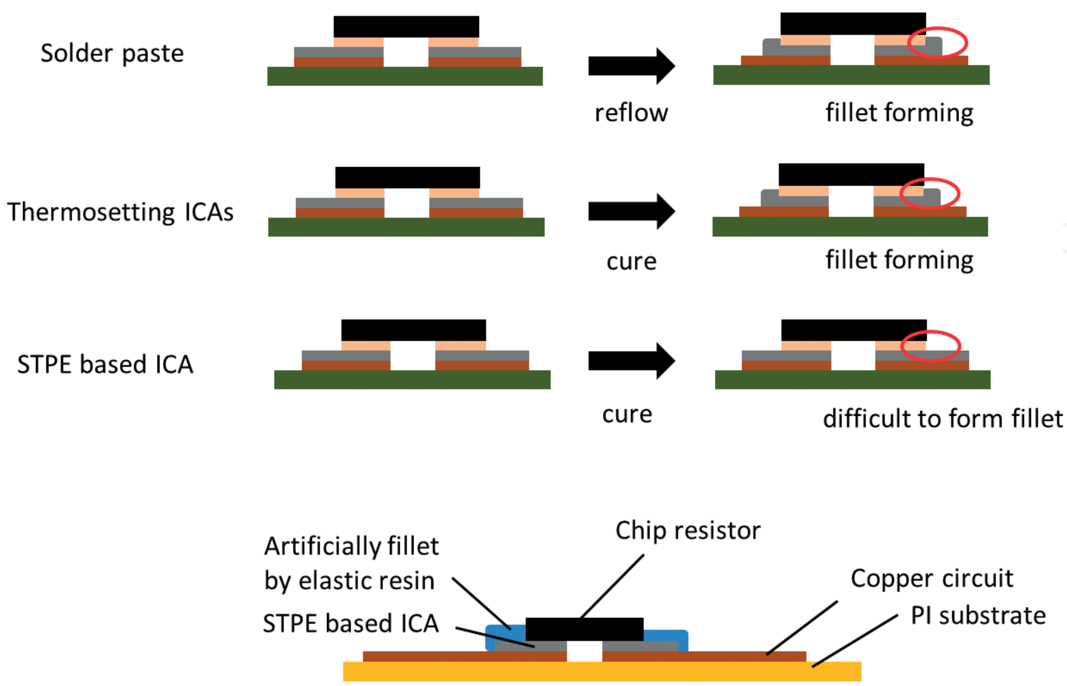

Figure 13. Images of fillet forming at bonding process and detailed image of reinforced STPE bonding structure.

(a) (b)

Figure 14. Pictures of implementation of LED on stretchable substrate. Left: stretched. Right: crumpled.

change is observed. On the other hand, fillet formed STPE-based ICA get bending resistance similar to solder connection.

Detailed structure is shown in **Figure 13**. This structure can also be applied to elastic substrates. Previously, there have been various reports on mounting of rigid parts on stretchable base materials, but it is mainly focused on design of base substrates and how to use rigid bonding materials [13, 14]. By combining STPE-based ICA and flexible reinforcing material, it is not necessary to design a complicated base material and it is possible to simply mount on a flexible base material such as **Figure 14**. In **Figure 14**, a wiring is drawn on a stretchable substrate with a stretchable conductor, and LED chip is mounted with STPE-based ICA and reinforced by elastic resin. Even without constructing a complicated mounting structure, disconnection is not observed, and LED chip continued to light up during repetition of expansion.

5. Conclusion

Characteristics of the conductive adhesive having both low-temperature curability and flexibility, which is based on STPE shows a great advantage compared with conventional conductive adhesive. In addition, it showed dynamic durability rivaled to conventional solder connection. Namely, the bonding system which is almost constructed by elastic resin and highly reliable is a promising technology for electronics in the next generation. Fabrication in IoT and wearable devices still has room for improvement. STPE-based ICA is developed as one solution for the future electronics society and we expect that innovation will happen.

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References

[1] Qin Y, Peng Q, Ding Y, Lin Z, Wang C, Li Y, et al. Light weight, superelastic, and mechanically flexible graphen/polyimide nano composite foam for strain sensor application. ACS Nano. 2015;**9**:8933-8941. DOI: 10.1021/acsnano.5b02781

[2] Yu Y, Luo S, Sun L, Wu Y, Jiang K, Li Q, et al. Ultra stretchable conductors based on buckled super-aligned carbon nano tube films. Nanoscale. 2015;**7**:10178-10185. DOI: 10.1039/C5NR01383F

[3] Kim KK, Hong S, Cho HM, Lee J, Suh YD, Ham J, et al. Highly sensitive and stretchable multidimensional strain sensor with prestraind anisotropic metal nanowire percolation network. Nano Letters. 2015;**15**:5240-5247. DOI: 10.1021/acs.nanolett.5b01505

[4] Bandodkar AJ, Nuñez-Flores R, Jia W, Wang J. All-printed stretchable electrochemical devices. Advanced Materials. 2015;**27**:3060-3065. DOI: 10.1002/adma.201500768

[5] Araki T, Nogi M, Suganuma K, Kogure M, Kirihara O. Printable and stretchable conductive wiring comprising silver flakes and elastomer. IEEE Electron Device Letters. 2011;**32**:1424-1426. DOI: 10.1109/LED.2011.2161663

[6] Sekitani T, Noguchi Y, Hata K, Fukushima T, Aida T, Someya T. A rubberlike stretchable active matrix using elastic conductors. Science. 2008;**321**:1468. DOI: 10.1126/science.1160309

[7] Matsuhisa N, Kaltenbrunner M, Yokota T, Jinno H, Kuribara K, Sekitani T, et al. Printable elastic conductors with a high conductivity for electronic textile applications. Nature Communications. 2015;**6**:7461. DOI: 10.1038/ncomms8461

[8] Aratani Y, Kojima T. Stretch fabrics. Sen-ito Kogyo. 1984;**40**(4-5):318-321. DOI: 10.2115/fiber.40.4-5_P318

[9] Devroy DRE, Homma M. Blends of silyl-terminated polyethers and epoxides as elastic adhesives. International Journal of Adhesion and Adhesives. 2001;**21**(4):275-280. DOI: 10.1016/S0143-7496(00)0035-X

[10] Berzins R, Meri RM, Zicans J. Compatibilizers effect on silyl-terminated polyether/epoxy resin system mechanical ans rheological properties. Key Engineering Materials. 2017;**721**:441-445. DOI: 10.4028/www.scientific.net/KEM.721.441

[11] Hashimoto K, Imaya K. Silyl-terminated polyethers for sealant use: Performance updates. Adhesives Age. 1998;**41**(8):18-22. ISSN: 0001-821X

[12] Kim S-S, Kim K-S, Lee KJ, Kim S, Suganuma K, Tanaka H. Electrical resistance and microstructural changes of silver-epoxy isotropic conductive adhesive joints under high humidity and heat. Journal of Electronic Materials. 2011;**40**(2):232-238. DOI: 10.1007/s11664-010-1421-z

[13] Kubo M, Li X, Kim C, Hashimoto M, Wiley BJ, Ham D, Whitesides GM. Stretchable microfluidic radiofrequency antennas. Advanced Materials. 2010;**22**:2749-2752. DOI: 10.1002/adma.200904201

[14] Hu X, Krull P, de Graff B, Dowling K, Rogers JA, Arora WJ. Stretchable inorganic-semiconductor electronic systems. Advanced Materials. 2011;**23**:2933-2936. DOI: 10.1002/adma.201100144

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