Flexible Thermoplastic Conductive Adhesive with High Reliability

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Abstract

Isotropically conductive adhesives (ICAs) have always been a hot spot in producing UHF RFID tag antennas with low cost for mass-production and low conductor loss.[1] As an interesting motif of flexible electronic component, they can also be integrated into sensors or as biocompatible electronic components in tissue engineering applications.[2] Considering the cost-effectiveness and the requirements for making those devices which can remain high conductivity under external stress forces, polyurethane (PU) is an interesting motif for making the dispersant material, as it can provide maximized elongation at break, moisture resistance, and excellent impact resistance and reliability. They are also safe to human health, which have a blooming market in tissue regeneration materials.[3, 4] Severe deformation of the matrix can result in the rearrangement of the conductive silver fillers, which can result in the variation of the electrical resistivity of the elastic ICA. Based on our prior research work on the ultralow silver filling rate of ICAs, we evaluated the electrical performance of the elastic ICA materials and their mechanical properties.[5] From the experimental result, we observed that the ICAs with this elastic polymer dispersant showed stable electrical resistivity after aging for 168 hours and even at low filler content level (e.g. 30%). Read range of the RFID tags showed that these ICAs are feasible for printed antennas.

1. INTRODUCTION:

Herein we present a first study on the characterization of an ultra-low cost flexible isotropically conductive adhesive (ICA). The advance in the development of ICA technique has led to increasing preponderance in electrical packaging industry compared to the current eutectic soldering technique. Meanwhile, people are concerned with the problems such as reducing the use of noble metal (e.g. silver) and improving the environmental benign characters of the ICAs, as this market is growing so rapidly. The titled ICA material is mainly designed for printing electrical circuits and antennas for flexible electronic applications due to its ultra-low cost and easiness for handling. Printable electronics have always been focusing on those materials potentially has low weight, low cost, and feasible to be manipulated in mass production. The flexibility and reliability of printable electronics is one of the requirements with regards to reel-to-reel processing and applications such as radio frequency identity (RFID) tags, light emitting diodes (LED), and thin film solar cells. For example, ICAs have extensive applications as the bonding agent and for the fabrication of vertical structured light-emitting diodes (Flex-LEDs).[6] They are also very competitive than other materials in producing flexible RFID tags.

ICAs are composed of inert polymer dispersant and micron-sized silver fillers. For those ICAs which are suitable for making RFID antennas, the performance of conductivity and the materials cost shall be leveraged. However, traditional ICAs have a threshold of conductance above 70% (by weight) of silver, which maintains a high cost due to the high content of noble metal. In our previous studies,[5] we observed excellent conductivity of the ICAs even at 27.5 % (by weight) of silver fillers in the epoxy-based ICA system (using bisphenol-A type of epoxy as the major dispersant). Bisphenol-A based epoxies such as Shell® EPON 828 has been widely used in electronic packaging industry due to their high Young's modulus, thermal stability, and excellent reliability. However, they have been regarded as mutagenic in recent studies; also, due to their high Young's modulus and hardness, they are quite brittle, which restricts their application in flexible thin film electronics.

In this article, we present our recent study of the polyurethane (PU) based ICAs as the dispersant of the paste for printing RFID tag antennas. Due to the well known excellent mechanical performance of the PU based dispersant, the PU based ICAs can exhibit much better flexibility. As the minimum silver content in the ICA formulation has been demonstrated to be lower than 30% by weight,[5] we characterized the resistivity of the PU based ICAs in the range from 30% to 75%. Herein we demonstrated that the PU dispersed ICAs exhibit controllable electrical conductivity in this filler content range, which can match the different requirements such as antenna read range or others. All samples showed stable conductivity after 168 hours of aging in the condition of 85^{o}C/85 relative humidity. Their mechanical properties at different loading ratio of fillers were also investigated.

2. EXPERIMENTAL SECTION:

2.1 Materials

Polyurethane (PU) adhesive consisting of equal mole of Bayermaterialscience® Desmophen 1380 BT and Desmodur BL 4265 SN were mixed and seasoned with 1% of catalyst (dibutyltin dilaurate, 99%, Aldrich). This dispersant mixture was mixed with silver microflakes and used as a one-component adhesive which has high stability at room temperature. Silver microflakes are from Chengdu Banknote printing complex (SF-01) and activated.[5] The average size of the silver microflakes was 5.6 micron.

2.2 Methods

The mixing process was carried out in a THINKY ARE 250 mixer at 2000 rpm for 4 minutes. Then we loaded the silver paste onto a piece of DuPont Melinex® ST507 polyethylene terephthalate polyester (PET) film (~30 μm in thickness) using a DEK-260 screen printer at a printing speed of 250 mm/sec. Then the paste samples were cured at 140°C for 15 minutes. The thickness of the printed ECA samples on the PET film was confirmed using a caliper and a Surface Profile System, Model Alpha-Step 200 (Tencor) to ensure the range is within 25.4 ± 5 μm. The volume resistivities of the ECA samples were measured according to ASTM F1896-98. The ICA samples were conditioned in a TERCHY MHU-150L humidity chamber (85°C/85%RH) for 168 hours to examine they performance in reliability. The antenna samples with different filler content were aged for different period of time and measured with their electrical resistivity. The data were also compared with their original ones before aging. Cross sections of the bulk ICA samples were prepared on a Leica Ultracut microtome machine for scanning electron microscopy (SEM) analysis on a JEOL 6390 (Japan). Each sample was sputtered with 20 nm of gold before SEM observation. A piece of Class 1 Gen 2 RFID chip (Alien Technology Inc.) was adhered to the center of the antenna. Then the tags were analyzed with their read range by using a commercial UHF RFID system (CSL CS461) (mode: High Speed 640k bps, powered by Impinj) in an anechoic room with a fixed reader-to-tag distance of 1 meter.

2.3 Adhesion strength analysis

We carried out the experiment to determine the adhesion properties of adhesive on an INSTRON 5567 tensile tester. The ICA is bonded between two pieces of Dupont Melinex polyethylene terephthalate polyester (PET) film with the dimension of 300 μm in thickness, 7.5 ± 0.05 mm width and 30 ± 0.05 mm in length. The surfaces of the PET films did not experience any treatment before they were adhered together by the paste and examined. The paste was applied between the PET films and clamped with a 15 ± 0.1 mm overlap, giving a bonding area of 112.5 mm^2. To control the thickness, each pair of the PET films was stuck with a 500-gram weight overhead for 30 seconds to allow for the homogeneity of the paste thickness. After curing, the cooled samples were pulled apart at a pulling rate of 200 mm/min using a pair of numeric crossheads (5 kN). Two groups of specimens were prepared for the test. In each group about 15 pieces of bar pairs were prepared for each kind of ICA. One group was tested after left for 24 hours at room temperature; the other group was tested after the samples were conditioned at 85°C/85%RH for 168 hours. The measurement method refers to ISO 4587-1979, and the adhesion strength value can be obtained by $s = f / a$, where s is the adhesion strength (MPa), f the pulling force at failure (N) and a the joint area (mm^2).

3. RESULTS AND DISCUSSIONS:

3.1 Electrical resistivity

Bayermaterialscience Desmodur BL 4265 SN is a kind of blocked isophorone diisocyanate (IPDI) based prepolymer. It can couple with Desmophen 1380 BT to form a low viscosity, transparent paste for preparing light-stable colorless flexible coatings. Their mixture (with the existence of catalyst) is stable at room temperature due to the blocked isocyanate group. After mixing with different content of silver filler, the pastes were screen-printed onto PET films and cured. Figure 1 shows the photographic images of the printed antennas using these pastes. We can observe that the color of the ICAs with low silver content show dark colors even though the PU dispersant is transparent, which is due to the low content of the silver microflakes scatter the incident light to other directions. These antenna samples were measured with their electrical resistivity and aged for 168 hours before their resistivity was measured again. The changes of the resistivity are listed in figure 2.

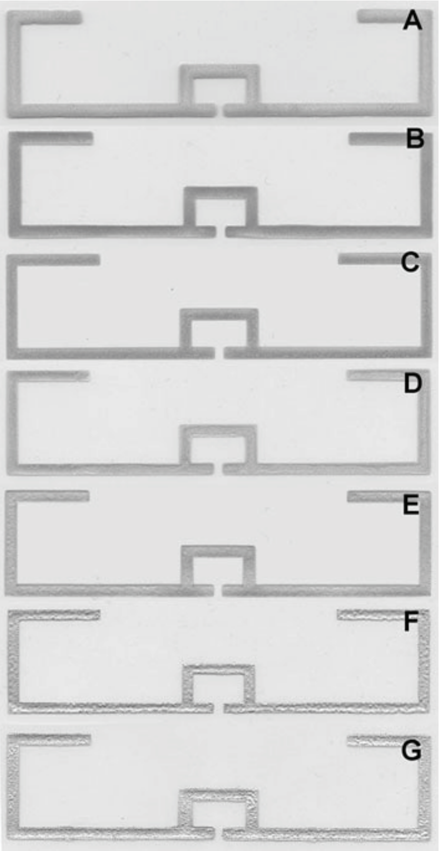

Figure 1: Photographic images of the ICA printed RFID antennas with different silver content. (A) 30% of filler; (B) 40% of filler; (C) 47.5% of filler; (D) 55% of filler; (E) 62.5% of filler; (F) 70% of filler; and (G) 75% of filler.

Figure 2 lists the measurement results of the electrical resistivity of the antenna samples containing different silver content in the ICAs. From this figure, we can observe that with different content of silver fillers, the electrical resistivity of the ICAs showed different resistivity ranging from the order of 10^{-5} Ω·cm to 10^{-3} Ω·cm. Considering the different intrinsic properties from PU and epoxy dispersant, the resistivity of the PU based ICAs are a little higher than those with epoxy as dispersant.[5] Currently, we are still conducting fundamental research work to understand the detailed mechanism of the effects of dispersants. In figure 2, we can observe that, at high silver content levels, e.g. 70% and 75% of silver, the resistivity of the ICAs shows similar level. This demonstrates that the silver content above 70% can show stable and low resistivity; further increasing the silver content may not significantly improve the electrical performance. When the silver content is lowered to 40% and 30%, we observed that the resistivity reaches a plateau. As previously reported,[5] the further lowering down the filler content may result in unstable conductivity when the silver content is lower than 30%,[5] and we also noted that the resistivity at this silver content (above 10^{-3} Ω·cm) limits its performance in RFID antennas, so we do not discuss about the situation when the silver content is further lowered down in this article.

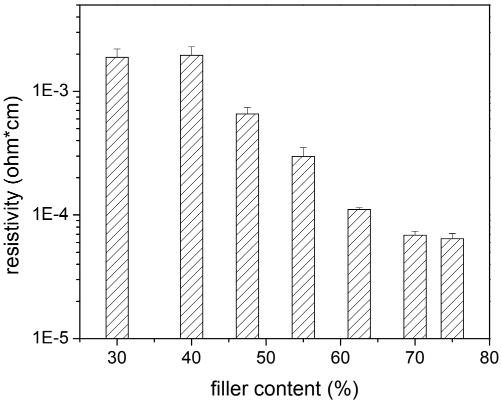

Figure 2: Electrical resistivity of the ICA printed antennas with different filler contents.

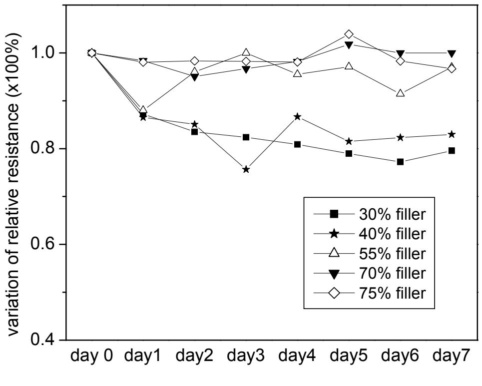

Figure 3: Resistance changes at different aging periods (up to seven days).

Figure 3 shows the change of resistivity versus the aging time in a TERCHY MHU-150L humidity chamber (85°C/85%RH) for up to 168 hours. From this figure, we can observe that after taken out from the chamber and immediately measured with the resistance and compared to the original one before aging, most of the resistances are lower than their resistance in day 0. For ICA samples with low filler content (30% and 40% of the filler content), the resistance even dropped about 20% after aging for two days or longer. For the other samples, the variation of resistance is lower than 10%, which suggest that the electrical resistivity of the ICAs is quite stable in this aging condition. The decrease of the resistance of the ICAs at low filler contents may due to the further crosslinking of the PU prepolymers, which were not fully cured prior to this aging test. As the samples were fully cured during the aging condition, it results in a further improvement of the percolation of the fillers.

3.2 Adhesion strength measurement

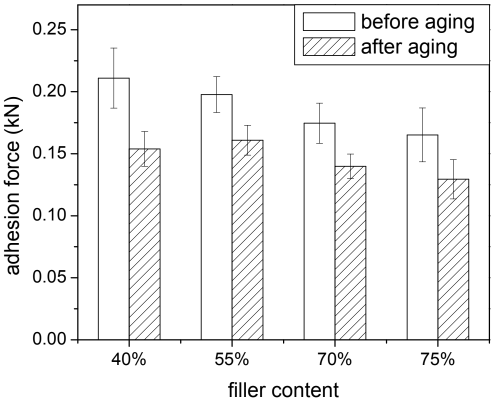

Figure 4: Adhesion force towards PET film (before and after aging for 168 hours) versus filler content in the ICAs.

Besides electrical conductivity, the performance in mechanical property of the ICAs is another critical parameter for their potential applications. We carried out the adhesion strength measurement of these ICAs on smooth PET thick films (300 μm) and evaluated the adhesion force both before and after aging. Different ICA formulations were tested and the adhesion strength of these specimens is reported (figure 4). In figure 4, we can observe that, after aging for 168 hours, the adhesion strength of all the ICA samples decreased about 15% to 20% compared to their peers before the aging process. This observation suggests that the high humidity and high temperature can deteriorate the interfacial bonding of the PET film. But this process does not significantly affect the electrical resistivity of the ICAs, as observed in the resistivity measurement. From figure 4, we can also observe that the adhesion strength of the ICAs over PET film decreases as there is more filler content in the samples. When increasing the filler content from 40% to 75%, the adhesion force decreased from 211.0 N to 16.5 N, which means that the higher silver filler content, the lower adhesion force. The decrease of the adhesion force suggests that the efficient contact area between the dispersant and the PET substrate is the major issue in the interfacial adhesion strength. With the increase of the silver content, the contact area between the ICA and the PET film is suffered from the additional inert silver microflakes, which decreases the adhesion force. Meanwhile, when increasing the silver filler content, the filler-dispersant interface gets more vulnerable and the overall mechanical property is deteriorated due to the weak boundary and mismatch of the mechanical properties of the filler and the dispersant.

From the SEM analysis (figure 5) of the cross sections of the ICA samples which were cut on a microtome machine, we can observe that the silver microflakes are homogeneously distributed inside the PU dispersant. This observation demonstrates supportive evidence of the adhesion force measurement result, that the higher silver filler content, the lower efficient contact area between the PU dispersant and the PET film.

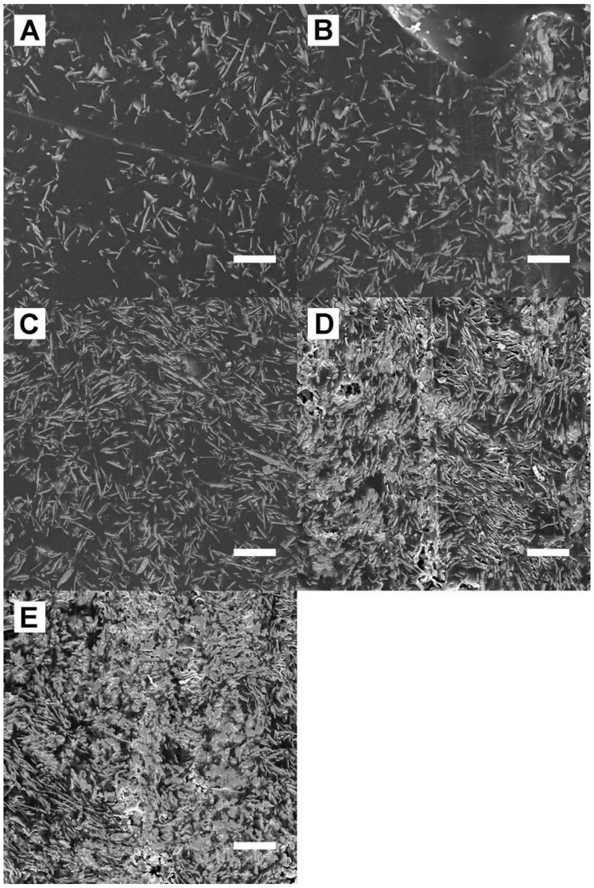

Figure 5: SEM images of some of the ICA bulk samples. (A) 30% of filler; (B) 40% of filler; (C) 55% of filler; (D) 70% of filler; and (E) 75% of filler. (Scale bar = 25 μm)

Figure 6 shows the crack interface of the ICA samples which were peeled off from the PET substrate. From this figure, we can observe that the fillers can homogeneously distribute in the PU matrix and there is some variation of antenna thickness, especially for those with higher filler contents, which is due to the increase of viscosity of the ICA pastes. At high filler contents (e.g. 70% and 75%), the surface of the antenna is getting rougher and there is increased number of voids, which are both harmful to the electrical property of the ICA antenna.

3.3 Read range test

In order to evaluate the performance of the flexible ICA printed RFID tag antennas, we conducted the read range examination of these antenna samples (a piece of EPCglobal Class 1 Gen 2 RFID Chip is adhered to the center of each antenna). The minimum turn-on power of the reader is recorded to demonstrate the antenna performance. The reader is located one meter in distance towards the RFID tag. From the read range observation which is listed in figure 7, we can observe that the minimum turn-on power of the reader is consistent with electrical resistivity of the ICA samples; when the resistivity of the ICA antenna is higher, the reader needs a higher power out-put to detect the tag. Therefore, using the same antenna design, we can adjust the content of silver filler in the ICA to cater for different requirement of read range. As for the real application of RFID technique, the power out-put of the reader is often fixed to a certain value. Controlling the resistivity of the ICA can probably be a convenient way to cater for the different requirement of read range requirement.

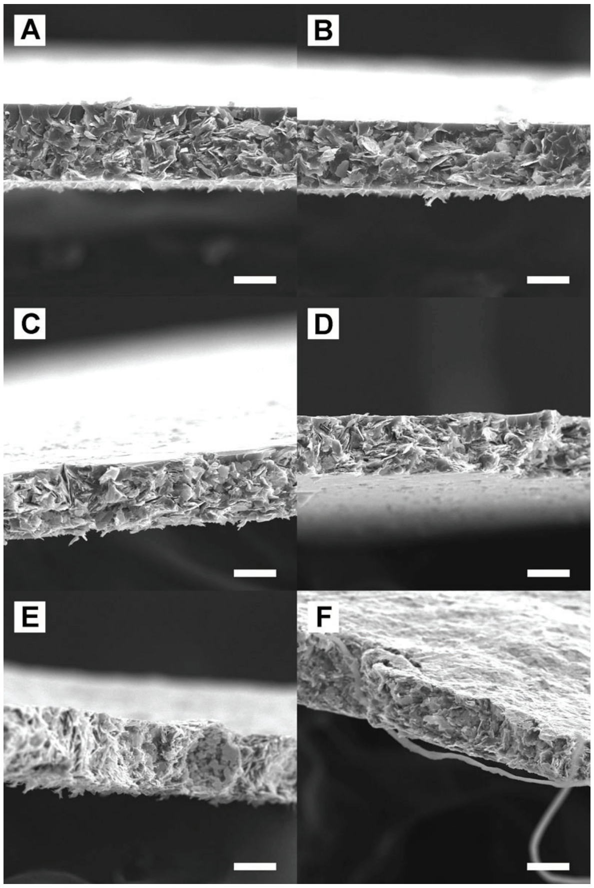

Figure 6: SEM images of some of the ICA printed RFID tag antennas. (A) 30% of filler; (B) 40% of filler; (C) 47.5% of filler; (D) 55% of filler; (E) 70% of filler; and (F) 75% of filler. (Scale bar = 25 μm)

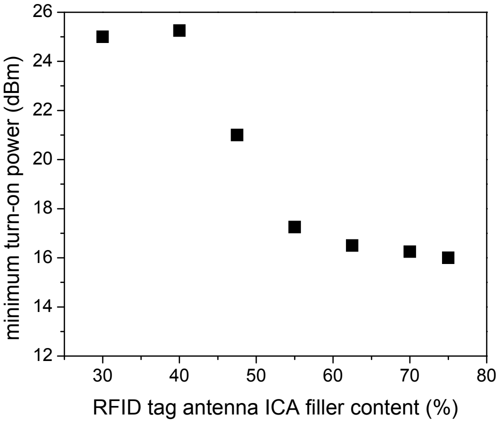

Figure 7: Minimum turn-on power of the reader in detecting the RFID tags with the antenna printed using the ICAs. (The filler content of each ICA formulation is listed as the x-axis.)

4. CONCLUSION:

In this study, we present the study on a new kind of flexible ICA material which is suitable for printing RFID tag antennas. The ICA samples with different silver content were prepared, printed into pre-designed geometries and their performances such as electrical resistivity, adhesion strength to PET film (substrate material for the tag antenna), reliability, and antenna performances were studied. From the experimental results, we observed that the silver content plays a key role, which is very useful in adjusting the electrical and mechanical properties of the ICAs. We observed that the ICA samples with ultra-low silver content still exhibit stable conductivity and the silver filler content at 30% and 40% showed similar conductivity. We also observed that the silver content at 70% showed similar conductivity to those with higher silver content, which is meaningful for saving the noble silver microflakes in making ICAs. In a 168-hour 85^{o}C/85%RH aging test, we observed that in a large range of silver contents from 30% to 75%, the electrical resistivity of this PU based ICA was very stable after aging for 168 hours. The lap-shear test was carried out to measure the adhesion strength of these ICA materials towards PET film. With the increase of the silver content, there is a decrease of adhesion force towards PET film. After all, we have developed a low-cost, flexible, material, which has also been demonstrated feasible in the application of RFID tag antenna uses. We are still characterizing the other properties of this material and we believe it would have a vast application in printing ultra-low cost antenna materials.

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