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Investigation of a Biocompatible Polyurethane-Based Isotropically Conductive Adhesive for UHF RFID Tag Antennas

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As a candidate dispersant for silver-based isotropically conductive adhesives (ICAs), polyurethane (PU) is an environmentally benign material that can withstand a high deformation rate and that exhibits excellent reliability. In this work we investigated methyl ethyl ketoxime (MEKO) blocked isophorone diisocyanate (IPDI) and MEKO blocked hexamethylene diisocyanate (HDI) as dispersant materials, and we characterize the electrical conductivity, mechanical properties, and reliability of these PU-based ICAs with silver-flake filler content ranging from 30 wt.% to 75 wt.%. Results of temperature–humidity testing (THT) at 85°C and 85% relative humidity (RH) and thermal cycling testing (TCT) at −40°C to 125°C show that these ICAs have excellent reliability. Our experimental results suggest that the MEKO blocked PU dispersants are suitable for preparing ultralow-cost, flexible, high-performance ICAs for printing antennas for ultrahigh-frequency radiofrequency identification (RFID) tags. These tags can potentially be used for identifying washable items and food packaging.

Key words: Isotropically conductive adhesives, radiofrequency identification, polyurethane

INTRODUCTION

Isotropically conductive adhesives (ICAs) are a kind of composite material with metallic conductive fillers and a polymeric nonconductive dispersant. They possess many advantages over conventional Sn-Pb eutectic solders, such as the characteristics of good printing resolution, low curing temperature, convenient processing steps for mass production, etc.[1] Therefore, they have wide applications ranging from traditional interconnect applications to the blooming field of flexible printed electronics.[2–5] One of the urgent applications of ICAs is for printing radiofrequency identification (RFID) tag antennas. RFID technology is used for identification and tracking of items using radio waves, and has grown dramatically in recent years. It will gradually replace traditional universal product code (UPC) barcodes in versatile commodity (such as food and garments) supply chains.[6] Thus, there is an increasing environmental concern regarding the massive use of RFID tag materials. Compared with electrochemical etching of copper or aluminum foils for tag antennas, ICA-based RFID antennas are more efficient in mass production and are less polluting;[7] yet, these advantages have to be balanced against the relatively low electrical conductivity. Even though increasing the content of the expensive silver filler can improve the electrical conductivity, the materials cost also increases. To maintain conductivity below 10^{-3} Ω cm (to avoid high loss in high-frequency applications), most ICAs contain very high silver filler content ranging from 70 wt.% to 85 wt.%.[8] To improve the electrical conductivity of ICAs at low silver filler content, for years we have

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conducted a series of surface modification methods.[1,8–11] Such improved ICAs with lower silver content but improved silver percolation would be more competitive when applied in microelectronic devices. In our previous studies,[12] the conductivity of the ICAs reached 10^{-4} Ω cm with 27.5 wt.% silver filler content in the epoxy-based (bisphenol-A type) ICA system. Bisphenol-A-type epoxies such as Shell® EPON 828 are widely used in the electronic packaging industry due to their high Young's modulus, thermal stability, and excellent reliability. However, possible leakage and contamination by bisphenol-A derivatives and their toxic curing agents have been regarded as carcinogenic risks for humans.[13,14] On the other hand, due to their high Young's modulus and the brittleness of the epoxy dispersant, they have limitations in areas requiring high flexibility and stretchability.

Thermal or moisture-curable polyurethanes have vast applications in coating and sealant industries.[15–17] In this work, we investigated –NCO group blocked aliphatic polyurethane (PU) as the dispersant material for preparing ICAs for ultra-high-frequency (UHF) (300 MHz to 3 GHz) RFID applications. Here, two types of methyl ethyl ketoxime (MEKO) blocked aliphatic polyurethane prepolymers were investigated, because they have recently been evaluated by the European Food Safety Authority as a safe material (for applications such as food can coatings).[18] Silver microflakes are used as the conductive filler, with contents ranging from 30 wt.% to 75 wt.%, resulting in optimal conditions in terms of cost-effectiveness. Moreover, as we use the blocked PU prepolymer, the pastes of these ICAs exhibit long shelf-life and stable, moderate viscosity (ranging from about 1000 cPa s to 3000 cPa s, depending on the silver filler content), which is suitable for general screen-printing processes. We evaluate the performance of the PU-based ICAs for printing RFID tag antennas, including their reliability, electrical conductivity, morphology, and mechanical properties. Electric conductivity measurements of the bulk ICA and evaluations of the signal transmittance of the RFID tag using these ICAs both suggest that they are suitable for printed electronic applications. The reliability of these ICAs in temperature–humidity testing (THT) at 85°C and 85% relative humidity condition and thermal cycling testing (TCT) at −40°C to 125°C both showed that these ICAs have excellent reliability.

EXPERIMENTAL PROCEDURES

Materials and Preparation of ICA Pastes

Two series of ICA formulations (series 1 and 2) using two different types of resin were studied. The resin for sample series 1 was a mixture of Bayermaterialscience® Desmodur BL 4265 SN and Desmophen 1380 BT (1:1.10 ratio of –NCO group to –OH group) with 1 wt.% catalyst (dibutyltin dilaurate, 99%, Aldrich). The resin for sample series 2 was a mixture of Bayermaterialscience® Desmodur BL 3175 SN and ethylene glycol (99%, Aldrich) (1:1.10 ratio of –NCO group to –OH group) with 1 wt.% catalyst (dibutyltin dilaurate, 99%, Aldrich). Silver microflakes were from Chengdu Banknote Printing Complex, activated according to the previously reported method.[12] The average size of the silver microflakes was 5.6 μm. The two resin dispersants were mixed with silver microflakes separately in a THINKY AR250 mixer at 2000 rpm for 4 min; the pastes can then be stored at room temperature for over 6 months.

The ICA thin films were printed onto a piece of DuPont Melinex® ST507 polyethylene terephthalate polyester (PET) film (thickness ~30 μm) using a DEK-260 screen-printer at a printing speed of 250 mm/s. The as-printed thin films were cured in a Memmert oven at 140°C for 30 min. The thickness of the printed ICA samples on the PET film was confirmed using a caliper and an Alpha-Step 200 (Tencor) surface profile system to ensure it fell within the range of 25.4 ± 5 μm.

Characterizations

The volume resistivity of the ICA samples was measured according to ASTM F1896-98. The samples were also conditioned in a TERCHY MHU-150L humidity chamber (85°C/85% relative humidity) for 720 h for temperature–humidity testing (THT), and conditioned in an ESPEC chamber (model EGNZ12-6CWL) for thermal cycling testing (TCT) between −40°C and 125°C (according to testing method JESD22-A104). The printed resistor samples with different filler contents were aged for different time periods, and their electrical resistivity was measured and compared with the result before the aging tests. Cross-sections of the bulk ICA samples were prepared using a Leica Ultracut microtome for scanning electron microscopy (SEM) analysis on a JEOL 6390 (Japan). Each sample was sputtered with a layer of gold (20 nm) before SEM observation. To evaluate the high-frequency performance of the antennas, a piece of EPC Class1 Gen2 RFID chip (Alien Technology, Inc.) was adhered to the center of each antenna by a strap. Then the read range of the tags was analyzed by using a commercial UHF RFID system (CS461 RFID reader, Convergence Systems Ltd.; high-speed mode, 640 kbps, powered by Impinj) in an anechoic room at a fixed reader-to-tag distance of 1 m. The reader was able to adjust the power output in steps of 0.5 dBm.[19] Considering the differences in resistivity of each ICA sample, we tentatively adjusted the detailed configuration of the antennas to maximize their signal transmission performance.

The adhesion strength of the ICA samples was determined using an INSTRON 5567 tensile tester. The paste of each sample was sandwiched between two pieces of DuPont Melinex polyethylene terephthalate polyester (PET) film with dimensions of 300 μm thickness, 7.5 $\pm$ 0.05 mm width, and 30 $\pm$ 0.05 mm length. It was clamped with a 15 $\pm$ 0.1 mm overlap, giving a bonding area of 112.5 mm^2. To control the thickness, each pair of PET films was suppressed with a 500 g weight overhead for 30 s to ensure homogeneous paste thickness after fully cured in a Memmert oven, the samples were loaded onto the tensile tester and pulled apart at a pulling rate of 200 mm/min using a pair of numeric crossheads (5 kN load cell limit). For each group of samples, about 15 pieces of bar pairs were tested, and the data were evaluated. The measurement method was based on ISO 4587-1979; the adhesion strength value was obtained as $s = f/a$, where s is the adhesion strength (MPa), f is the pulling force at failure (N), and a is the joint area (mm^2). The adhesion strength of the ICA samples after aging (85°C/85% RH for 168 h) was also evaluated by this method.

RESULTS AND DISCUSSION

Bayermaterialscience Desmodur BL 4265 SN is a kind of MEKO blocked isophorone diisocyanate (IPDI) trimer, while Desmodur BL 3175 SN is a kind of MEKO blocked hexamethylene diisocyanate (HDI) trimer. Both of them can couple with polyols to form a transparent, low-viscosity, long-shelf-life paste for preparing light-stable, colorless, flexible, and weather-stable stoving coatings. After mixing the dispersants with silver filler, the resulting ICA pastes were subsequently screen-printed onto PET films and cured. The structure of the blocked polyurethane prepolymers is shown in Fig. 1. To prepare the ICAs, silver flakes with dimensions of about 5.6 μm diameter and 500 nm thickness were mixed into the resin dispersants at different filler contents. As shown in the SEM images in Fig. 2, which show cross-sections of ICA samples prepared using a Leica ultramicrotome, we can observe that the silver microflakes had a good distribution in the PU dispersant over a wide range of filler content from 30 wt.% to 75 wt.%.

Figure 3 shows the measurement results for the electrical resistivity of the printed ICA samples containing different silver filler contents. From this figure, we can observe that the electrical resistivity of these ICAs was in the range from about 2×10^{-5} Ω cm to 2×10^{-3} Ω cm, showing a close relationship to the silver filler content; i.e., with increasing silver content there is a trend towards improved electrical conductivity. It is noted that the resistivity of the PU-based ICAs are slightly higher than those dispersed by epoxy previously reported,[11,12] which may be related to the different intrinsic properties between the PU and epoxy dispersants. At 75 wt.% silver content, sample series 1 exhibits an electrical resistivity of 1.51×10^{-5} Ω cm and sample series 2 exhibits an electrical resistivity of 2.52×10^{-5} Ω cm. When the silver content is reduced to 30 wt.%, the electrical resistivity of sample series 1 and 2 drops to 1.88×10^{-3} Ω cm and 1.64×10^{-3} Ω cm, respectively.

Figure 4a, b shows the correlation between electrical resistivity and aging time in a TERCHY MHU-150L humidity chamber (85°C/85% RH) for up to 720 h for the two series of ICA samples. From this figure, we can observe that, compared with the original values without aging, most of the electrical resistance data show a slight decrease. For the ICA samples with low filler contents (30% and 40%),

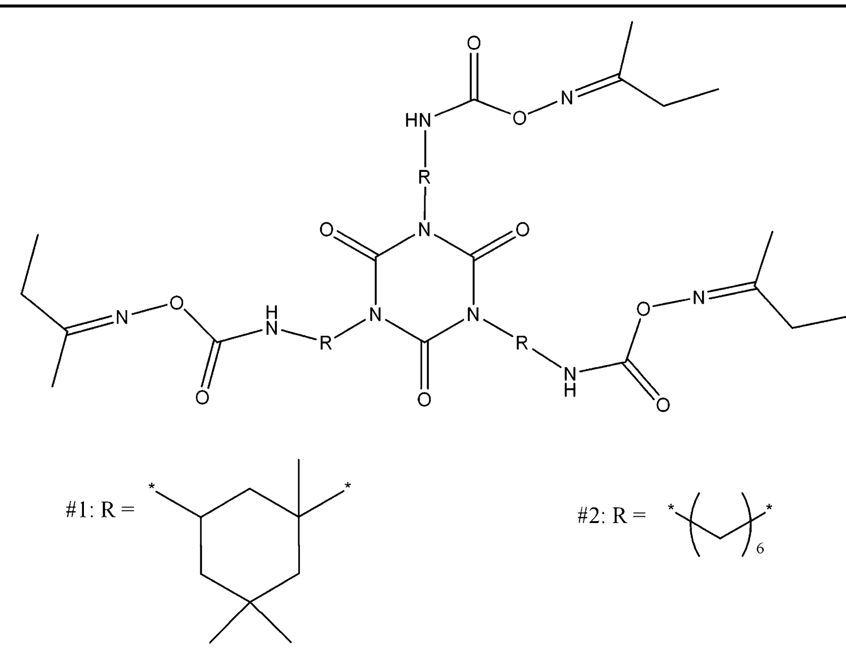

Fig. 1. Structure of the blocked polyurethane prepolymers for series 1 and 2.

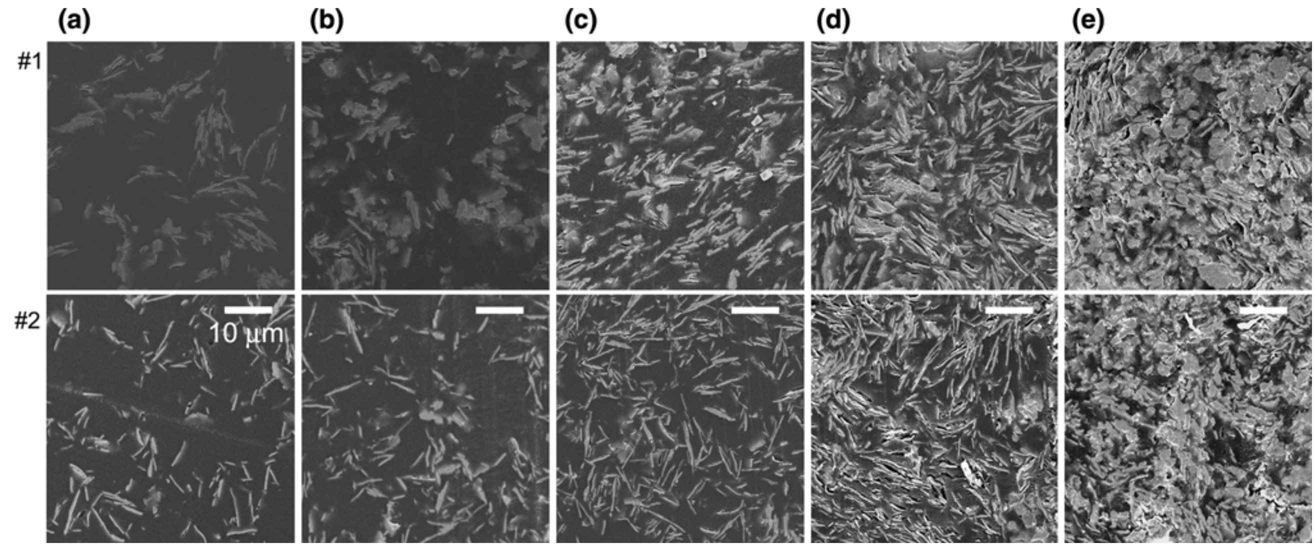

Fig. 2. SEM images of cross-sections of some of the ICA bulk samples: (a) 30% filler, (b) 40% filler, (c) 55% filler, (d) 70% filler, and (e) 75% filler (*scale bars* = 10 μm).

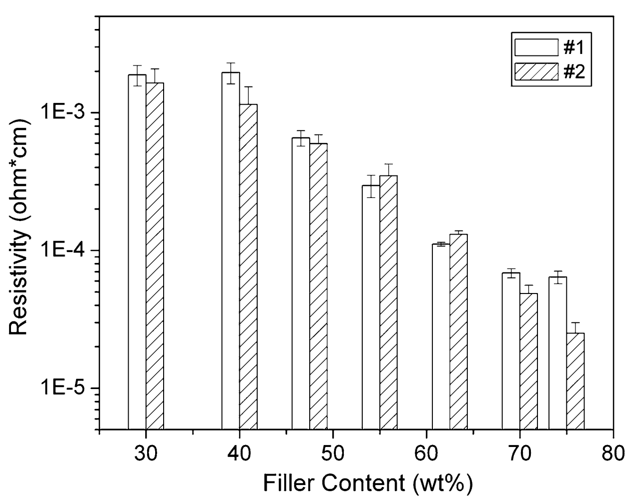

Fig. 3. Resistivity of printed resistors of ICAs (series 1 and 2) with different silver filler contents.

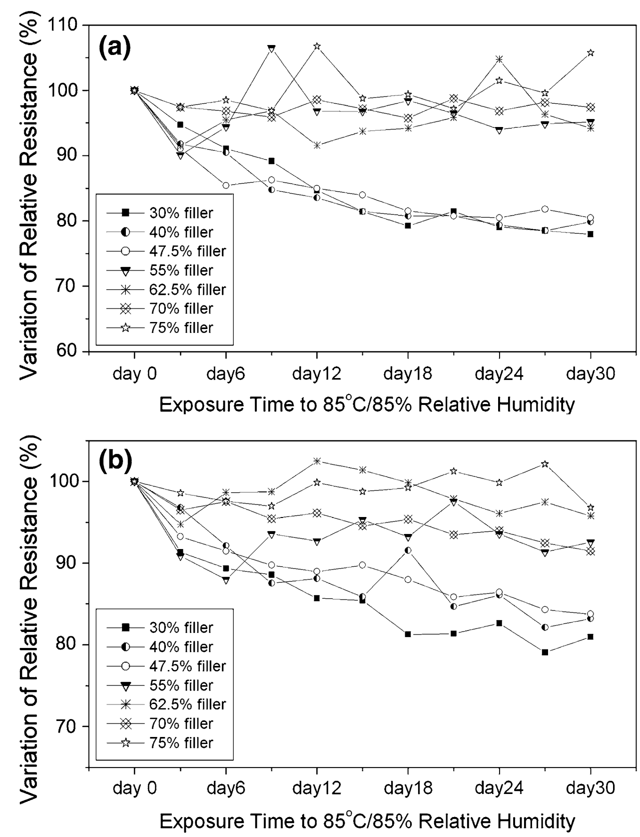

Fig. 4. 85°C/85% relative humidity reliability analysis of the ICAs (resistance measurement). (a) Variation of the relative resistance of the printed resistors of ICA series 1. (b) Variation of the relative resistance of the printed resistors of ICA series 2.

after aging, the electrical resistance even dropped by about 20%. For the other samples, the variation of the electrical resistance value is less than 10%, which suggest that these PU-based ICAs have good reliability up to 720 h. Figure 5 shows the 720 h thermal cycling analytical results for the two series of ICA samples. In this figure, the variations in the electrical resistance of all samples were less than 10% after aging. Both Figs. 4 and 5 suggest that the two series of ICA samples with different silver filler contents exhibit reliable electrical performance under the above-described testing conditions. These samples exhibit a drop of electrical resistance after the aging test, which is supposed to be a characteristic feature of these PU-based ICAs. As the blocking agent (MEKO) has a boiling point at 152°C, it may resume evaporating after the ICA curing process (only at 140°C for 30 min) during the aging process. This process consequently causes shrinkage of the total volume of the PU matrix, which may provide a condition of better percolation through the

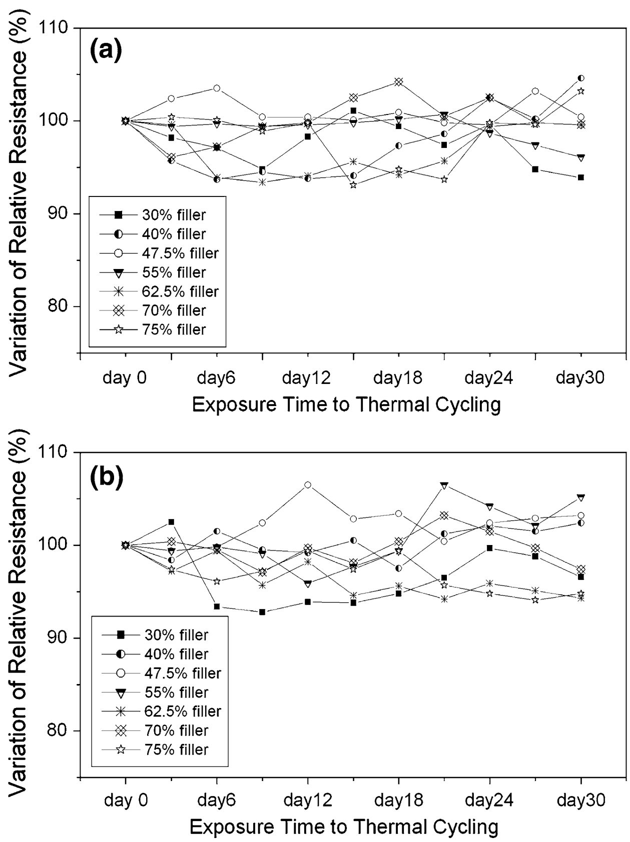

Fig. 5. Thermal cycling analysis of the ICAs. (a) Variation of the relative resistance of the printed resistors of ICA series 1. (b) Variation of the relative resistance of the printed resistors of ICA series 2.

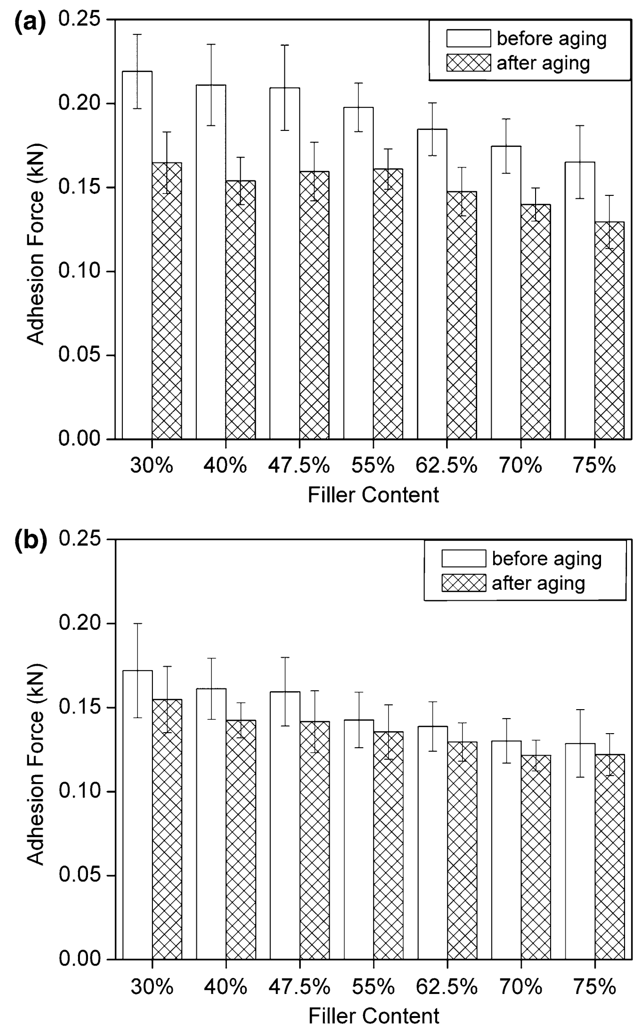

Fig. 6. 85°C/85% RH reliability analytical result of the ICAs (lap shear mechanical force measurement). (a) Variation of the lap shear adhesion force of ICA series 1 onto PET substrates. (b) Variation of the lap shear adhesion force of ICA series 2 onto PET substrates.

silver filler particles.[20] The detailed mechanism of this process deserves further investigations, which is still ongoing in our group.

Besides electrical conductivity, the mechanical performance of the ICA is another critical parameter for real applications. We carried out measurements of adhesion (lap shear) strength of these ICAs on smooth PET films (300 μm thick) and evaluated the adhesion force both before and after aging for 168 h. From Fig. 6, we can observe that, after aging, the adhesion strength of all the ICA samples decreased as compared with before aging. This phenomenon suggests that the 85°C/85% RH aging condition is harmful to the interfacial bonding with the PET film. However, it appears that this process does not significantly affect the electrical resistivity of the ICAs, as observed in the electrical resistance measurements above. When increasing the filler content in series 1 from 40% to 75%, the adhesion force decreased from 211 N to 165 N, which illustrates the sharp decrease in adhesion force when increasing the silver filler content. For series 2, a similar relationship between adhesion strength and silver filler content was observed. The decrease of the adhesion force suggests that the effective contact area between the PU dispersant and the PET substrate is a major factor determining the interfacial adhesion strength. Comparing the trends of the two series of samples, we observe that series 1 exhibits a sharper drop of adhesion strength than series 2. This difference is closely related to the nature of the resin material. We know that series 1 is composed of the IPDI-based prepolymer (BL 4265) and polypropylene oxide-based polyol (1380 BT) (eq. –OH 11.7 wt.%), while series 2 is composed of the HDI-based prepolymer (BL 3175 SN) and ethylene glycol (eq. –OH 54.8 wt.%). Due to the lower hydroxyl group content of the polyol (1380 BT) in series 1, more of it is added in the formulation of series 1 compared with ethylene glycol in series 2. Since polyol is a hydrophilic linear compound, during the aging test, more moisture penetration may take place. In this case a sharper drop of the mechanical property is shown in Fig. 6a.

To further evaluate the performance of the flexible PU-based ICAs in real applications, we conducted measurements of the read range of RFID tags using these ICAs as the tag antenna. Since the silver filler

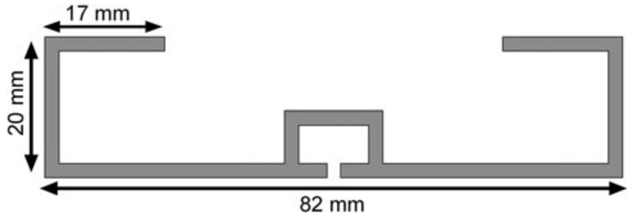

Fig. 7. Designed geometry of RFID tag antenna based on the ICA paste with 30 wt.% silver content.

is both the electric current carrier and the major materials cost driver, decreasing the silver filler content can reduce the materials cost of RFID tags, but the corresponding increase in electrical resistivity may limit signal transmission performance due to the greater loss. Usually, the RFID antenna is designed based on a dipole antenna about half a wavelength in length, as illustrated in Fig. 7. We selected Alien Technology's Gen2 RFID chip, which has an impedance value of 30–110j Ω, so we designed the tag antenna with an impedance of 30 + 110j Ω to conjugate-match with the chip. Based on simulations, we considered both the resistivity of the materials, surface roughness, and the configuration of the antenna. The antenna is an 82-mm-long dipole with a short line connecting two parts, as shown in Fig. 7.[21] By adjusting the dimensions of the antenna, the simulated impedance of the ICA antennas at 915 MHz matches the Alien Technology RFID strap (30–110j Ω). The calculated return loss value is −24 dB, which means that over 99% of the power is transmitted to the RFID chip. We found that the −10 dB power transmission bandwidth of the antenna is 60 MHz, which covers the operation frequency of North American, China, and Hong Kong standards.[22] The minimum turn-on power of the reader was used as an index of RFID tag antenna performance. The reader was located 1 m away from the RFID tag (a piece of EPCglobal Class1 Gen2 RFID chip adhered to the center of the antenna). From Fig. 8 we can observe that the minimum turn-on power of the reader is consistent with the electrical resistivity of the ICA samples; i.e., with increasing resistivity of the antenna, the reader needs a higher minimum turn-on power 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 read range requirements. In real RFID technology applications, the power output of the reader is often fixed to a certain value. Controlling the resistivity of the ICA may be a convenient way to cater for different read range requirements. The performance of PU-based ICAs with ≥62.5 wt.% silver filler content showed similar minimum turn-on power to copper foil-based antennas using the same chip.

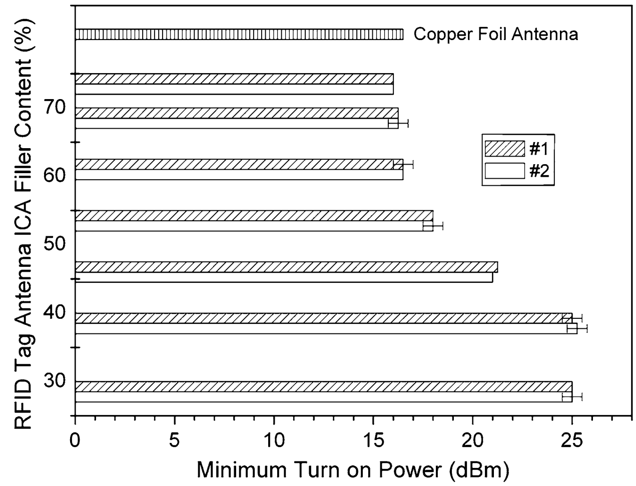

Fig. 8. Minimum turn-on power of the reader to detect the RFID tags with the antenna printed using the ICAs, compared with the read range performance of control metal foil-based RFID tag samples.

CONCLUSIONS

In this study, we present our study on a new kind of flexible polyurethane-based ICA material. ICA samples with different silver contents were prepared and printed into predesigned geometries, and their performances such as electrical resistivity, adhesion strength to a PET film, and antenna read range were studied. From the experimental results, by adjusting the silver content, the electrical and mechanical properties of the ICAs can be modulated. For example, ICAs with a silver content as low as 47.5% maintained acceptable conductivity (6.56×10^{-4} Ω cm and 5.96×10^{-4} Ω cm for series 1 and 2, respectively), which is efficient for high-frequency microelectronic applications, such as for UHF RFID antennas. On the other hand, we observed that, for ICA samples with different silver contents ranging from 30 wt.% to 75 wt.%, there was no significant variation of electrical resistivity after either 720-h 85°C/85% RH aging or 720-h thermal cycling. Regarding mechanical properties, lap shear testing was carried out to measure the adhesion strength of these ICA materials to PET films. With increasing silver content, there was a decrease in adhesion strength to the PET film. Aging the samples for 168 h resulted in a ∼20% decrease in adhesion strength. The signal transmission performance of UHF RFID tags based on these ICAs was evaluated. The results suggested that ICAs with a silver content above 62.5 wt.% exhibit similar read range performance to copper foil-based antennas. These results suggest that MEKO blocked aliphatic PU-based dispersants are feasible for preparing environmentally friendly, low-cost, flexible ICAs for high-frequency applications. We believe that these new materials would have vast applications in, e.g., printing ultralow-cost electronic tags for consumer commodities such as garments and food packaging.

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