Investigations of the Water-Borne Isotropically Conductive Adhesives

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Abstract

Here we present the first study of the water-borne isotropically conductive adhesives (WBICAs) which exhibit electrical conductivity in 10^{-5} Ω·cm, which exhibit many unique characters. For example, they are one-component materials with very long shelf-life; they are convenient in processing, strong in mechanical strength, highly reliable, environmentally benign, disposable, and compatible to various substrates for mass production without the need of thermal curing process. Due to the versatile mechanical characters of the polyurethane dispersant, the WBICAs can be used as interconnects or printed as circuits on various substrates. These materials underwent a 720 hrs temperature-humidity test showed no increase of electrical resistivity. We expect these materials will find applications in the new horizons of low-cost, low-carbon, disposable, and green electronic devices immediately.

Introduction

Scientists and engineers have been long searching for low-temperature processable and printable materials to substitute the traditional printed circuit board (PCB) technique and eutectic Sn/Pb solders (melting point ~ 187 ^{o}C), so that a large pool of lower cost materials and processing method can be applied in the electronic packaging industry.[1] Recently, isotropically conductive adhesives (ICAs) have gained more attentions than before due to their environmental-benign character, much simpler and faster in mass production (e.g. screen-printing and roll-to-roll printing), and lower processing temperature to allow for more choices of the low-cost substrate materials.[1-3] As compared to the traditional eutectic Pb/Sn solders, which involves the high temperature(~230 ^{o}C) reflow process, the low-temperature character of ICAs render a larger pool of low-cost substrate materials suitable for the printed electronic applications, such as PET and paper, rather than the traditional PCBs which are based on epoxy-based composites and polyimide (PI). The ICA based technical platform also benefits the development of the organic printed transistors as well.

ICAs are a kind of composite material with micron-sized metallic conductive fillers and a polymeric nonconductive dispersant; they possess many characters such as good printing resolution and are compatible to conventional printing methods.[4] Traditional bisphenol-A type of epoxies such as Shell® EPON 828 are most studied as the resin material for the ICAs, due to their high mechanical strength, thermal stability, and excellent reliability.[5] However, the bisphenol-A derivatives and the toxic curing agents are still a concern of risks for human health.[6, 7] Moreover, a subsequent thermal curing process (usually at about 150 ^{o}C for a few minutes) after the printing process is necessary, which is aimed to improve the electrical conductivity, mechanical strength, and reliability of the objectives;[1, 3] while this thermal curing step consumes energy and adds cost. Alternatively, there are room-temperature-curable resin epoxies and the UV-curable free-radical-polymerization-based acrylic resins to supplement for those thermally curable resins; but they face the problems such as the toxicity of the amino-curing agents, the relatively short product shelf-life, and the oxidation issue due to free-radicals. To improve the performance (e.g. electricity, mechanical strength and reliability) of all kinds of ICAs, a few chemical and physical methods have been developed.[4, 8-12] For example, nano-sized silver fillers have been used to season the ICA so that the metallic fillers fuse with each other at the temperature near 200 ^{o}C, which is benefit from the melting point depression effect.[8] Chemical modifications of the silver fillers have been proved effective to improve the percolation among the silver fillers.[2, 13, 14]

Recently, our group has conducted some studies on those ICAs which are based on the aliphatic polyurethane (PU) as the dispersant material, so that we could utilize their unique characters such as the long-term reliability, excellent mechanical strength, and environmental benign character.[16] In this manuscript, we demonstrate that the water-based ICAs (WBICAs) as a room temperature curable material, is effective for mass fabricating/manufacturing flexible printed electronics. They display a few unique characters, for instance, all chemicals involved are environmentally benign, the processing steps are more energy efficient. To the second point, simply drying the resin in ambient condition is enough, rather than curing/thermally sintering the silver fillers and curing the resin for the conventional ICAs. We tentatively formulated the resin dispersant of the WBICAs, so that they possess significant mechanical strength (e.g. adhesion strength) and reliability (thermal-humidity and thermal cycling performance), which are elucidated in details in the following sections. Due to the low-temperature character, they can conveniently couple with various low-cost substrate materials such as PET, papers, woods, and textiles. In order to improve the percolation and inhibit the oxidation of silver fillers, a small dose of reducing agent such as sodium borontetrahydride ($NaBH_4$) is added. This manuscript discusses the relationship between the surface treatment

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conditions and the corresponding performances of the WBICAs, including their electrical conductivity and mechanical strength.

Experimental

1. Materials

Silver microflakes are obtained from Chengdu Banknote printing complex and activated according to the method previously reported.[13] The average size of the silver microflakes was 5.6 micron. $NaBH_4$ (95%, Aldrich) aqueous solution is added to the paste sample in various concentrations; then the paste is mixed in a THINKY AR250 mixer at 800 rpm for 2 minutes. Additional water can be added to modulate the viscosity in necessary. The pastes can be stored at room temperature for over six months.

2. Preparation of the water-borne PU

The 40 wt.% PU miniemulsion was prepared by the following procedures: 20 g (0.01 mol) poly(tetrahydrofuran)-2000 (PTHF-2000, Aldrich) and 2.68 g (0.02 mol) dihydroxylmethylpropionic acid (DHPA, Aldrich) were mixed with 13.34 g isophoron diisocyanate (IPDI, Aldrich) at 70 ^oC with the nitrogen protection. Dibutyltin dilaurate (DBTDL, Aldrich) 0.05 mL was added into the system for catalysis. After 2 hours, the temperature was lowered to 50 ^oC. Then 1.35 g (0.015) 1, 4-butandiol was added into the system dropwise in half an hour. Following with adding 2.78 mL (0.02 mol) triethylamine (TEA) into the system for neutralization for half an hour and adding 68 mL water drop-by-drop into the system in 2 hours. The system was distilled under vacuum at 35 ^oC to remove the acetone for 2hrs. The transluscent miniemulsion with 40 wt % of the PU solid was acquired. The M_n of the polymer was 21×10^3 g/mol. Polydispersity was 1.32.

3. Characterizations

^1H NMR spectra was obtained on a DMX 400 MHz spectrometer with tetramethylsilane (TMS) as the internal standard and $CDCl_3$ as the solvent. Gel permeation chromatography (GPC) was performed on a Waters HPLC system with a G1310A pump and a G1362A refractive index detector, using tetrahydrofuran (THF) as eluent at 35 ^oC with an elution rate of 1.0 mL/min. Two Styragel columns (HR 3 THF and HR4E THF, Waters) were calibrated by polystyrene standards (Polymer Source). The WBICA thin films were printed onto a piece of DuPont Melinex PET film (~30 μm in thickness) using a DEK-260 screen printer at a printing speed of 250 mm/sec. The as-printed thin film is cured in a Memmert oven at 50 ^oC for 15 minutes for acceleration of cure. The thickness of the printed ICA samples is confirmed using a caliper and a Surface Profile System, Model Alpha-Step 200 (Tencor) to ensure the range is about 30 ± 5 μm.

FT-IR absorption of the pure solid PU thin film was carried out on a BioRad FTS 6000 ATR-FT-IR system, based on the transmittance mode (scanning range: 400 ~ 4000 cm^{-1},). 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^oC/85% relative humidity) for 720 hours for the temperature-humidity testing (THT). The printed resistor samples with different filler content were aged for different time periods and their respective electrical resistivity was measured and compared with the result before the aging tests. Cross sections of the bulk ICA samples were prepared on a Leica Ultracut microtome machine at liquid nitrogen temperature for the transmission electron microscopy (SEM) analysis on a JEOL 2010 (Japan).

Tensile test was carried out on an Advanced Rheometric Expansion System (ARES) (TA instruments, USA). After the samples were cured on a smooth low density polyethylene (LDPE) substrate, the free-standing WBICA thin films were obtained by peeling them carefully from the LDPE substrate and then cut into small strips with the dimension near 40 x 3 x 0.1 mm^3 (each was accurately confirmed by a caliper), and mounted onto the thin film tensile test fixture for the testing. The measurement was conducted at 25 ^oC with a 2000 g·cm transducer. The extension speed was 0.2 mm/s in a strain-controlled mode. In each condition, 12 specimens were measured for data analysis.

Results and Discussion

Recently, our group have conducted the investigations of the end-group blocked polyurethanes (PUs) as a resin dispersant for the ICAs.[16] PUs have been widely applied in coating and sealant industry,[17-19] which display a few characters such as the adjustable mechanical properties, shape-memory property, and excellent stability. Moreover, many PU-based resins are biocompatible and can be obtained from renewable resources such as natural oils.[20, 21] Concerning all these advantages, we investigate the feasibility of applying the water-based PU resin as the dispersant material for the ICAs. Here we work on the cycloaliphatic PU which is prepared in the emulsion based reaction. As shown in **Scheme 1**, the water-borne PU dispersant is prepared mainly in four steps: 1. polyether polyol (here is polytetrahydrofuran 2000), dihydroxylmethylpropionic acid (DHPA), and isophorone diisocyanate (IPDI) are mixed together for preparing the prepolymer; 2. chain extender (butylene diol) is added until the chain propagation is terminated; 3. TEA is added to neutralize the system; 4. water is added dropwise so that the PU is transferred into aqueous solution. Finally, the organic solvent and the unreacted chemicals are removed by vacuum. The resulting PU emulsion is translucent bluish with long shelf-life and stable rheological property. The structure of the PU resin was confirmed by using ^1H-NMR and FT-IR spectra. As shown in **Figure 1**, the FT-IR spectrum of the dried film of the as-prepared water-borne PU is investigated. The peaks at 2933 cm^{-1} and 2854 cm^{-1} confirm the existence of the $-CH_2-$ group, the 1698 cm^{-1} the carbonyl group, and 1239 cm^{-1} and 1108 cm^{-1} confirm the C-O vibrations. The as-prepared PU has excellent thermal stability, which was confirmed by using thermalgravimetric analysis (TGA). The temperature of the sample was ramped from room temperature to 600 ^oC with the speed of 20 ^oC/min in the air (**Figure 2**). The sample lost less than 10% weight before it reached 250 ^oC. Further raising the temperature resulted in the total decomposition, until the temperature reached 430 ^oC. This result suggests that the PU

dispersant is suitable for the general solder reflow process as well when it is applied in the traditional packaging process.

The WBICAs were prepared by mixing the PU resin and a certain portion of the modified silver microflakes together by using a THINKY ARE250 mixer.[22] By adjusting the ratio between the two components we are able to achieve an optimum between the mechanical strength and electrical conductivity. $NaBH_4$ has been concerned as a very powerful reducing agent for protecting many metals from oxidations. For example, addition of small amount of $NaBH_4$ has been demonstrated effective for improving the percolation among the copper and nickel powders via an in-situ reducing process for ink-jet printing conductive lines.[23] Here we tentatively added in 0.5% (by weight) and 1% (by weight) of $NaBH_4$ (*vs.* Ag) into the WBICAs, as an agent for preventing the oxidation issue during the processing steps. The cross section images of the samples were studied on both transmission electron microscopy (TEM) and scanning electron microscopy (SEM). As shown in **Figure 4**, the electrical resistivity of the printed resistor which is based on different silver content and $NaBH_4$ treatment condition are listed in Table x. From **Figure 4**, we can observe that the addition of $NaBH_4$ can effectively reduce the electrical resistivity of the printed resistors which were prepared by using the WBICAs. The improvement of the resistivity is about one order of magnitude.

The measurement of the variation of electrical resistivity of all printed resistor samples were conducted in a TERCHY MHU-150L humidity chamber (85^{o}C/85% relative humidity) for 720 hours for the temperature-humidity testing (THT) (**Figure 5**). As shown in **Figure 4**, we can observe a trend of decrease of the electrical resistivity over the period of time. The reasons for the decrement of the electrical resistivity of all the samples are related to the following points: 1) the water-borne PU dispersant is intrinsically an emulsion which contains both the hydrophilic part and the hydrophobic part; water molecules trapped in the interstitial sites are eliminated during the aging process or thermal curing process which renders shrinkage of the total size; 2) since the glass transition temperature (T_g) of the water-borne PU dispersant is much lower than room temperature (~-20 ^{o}C), the creeping of the hydrophobic polymer chain enhances the phase separation of the hydrophobic/hydrophilic regions, which results in a stronger interaction among the polymer chains by hydrophobic interaction and hydrogen bond as well. These two factors take effect both in the thermal curing process (if there is any) and the aging process as well. Thus we observed kind of variation of the electrical resistivity. After all, we did not observe any increase of the electrical resistivity of all samples after the aging test, which suggests sufficient reliability for real applications. For example, by simply printing a straight line of the WBICAs on a piece of stretchable latex rubbery film (**Figure 6**), this WBICA based circuit can support a few LED chips as a demonstration of LED arrays. Since many rubbery substrates are very sensitive to the high temperature (due to their extremely low T_g), they can be used as the stretchable circuit boards and fabricated at room temperature by using the WBICAs as the circuits and interconnects.

The relation between the silver content and the tensile property of the WBICA thin film samples were investigated on an Advanced Rheometric Expansion System (ARES) (TA instruments, USA). The specimens were prepared on a piece of smooth low density polyethylene (LDPE) substrate, so that they could form an even and flat thin film. When they were naturally dried, they were peeled off carefully from the substrate and then cut into small strips with the dimension near 40 x 3 x 0.1 mm^3 (each was accurately confirmed by a caliper), and mounted onto ARES by a thin film tensile test fixture. The measurement was conducted at 25 ^{o}C with a 2000 g·cm transducer. The extension speed was 0.2 mm/s in a strain-controlled mode. As shown in **Table 1**, we can observe that the Young's modulus of all the three samples does not change significantly along with the different silver content level. This suggests that the addition of $NaBH_4$ does not have significant influence to the mechanical strength of the WBICA samples.

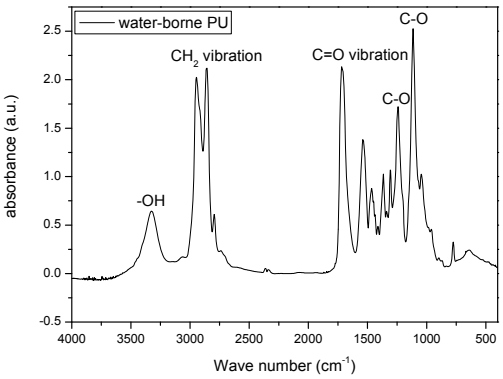


Figure 1. FT-IR spectrum of the dried film of the water-borne PU.

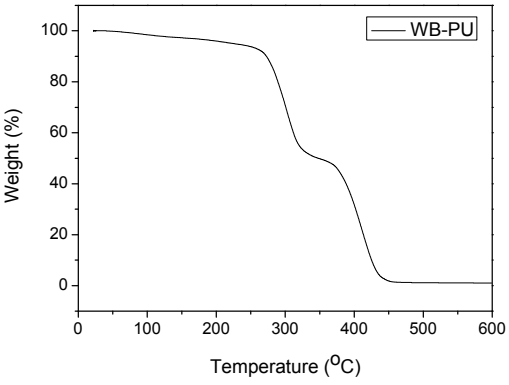
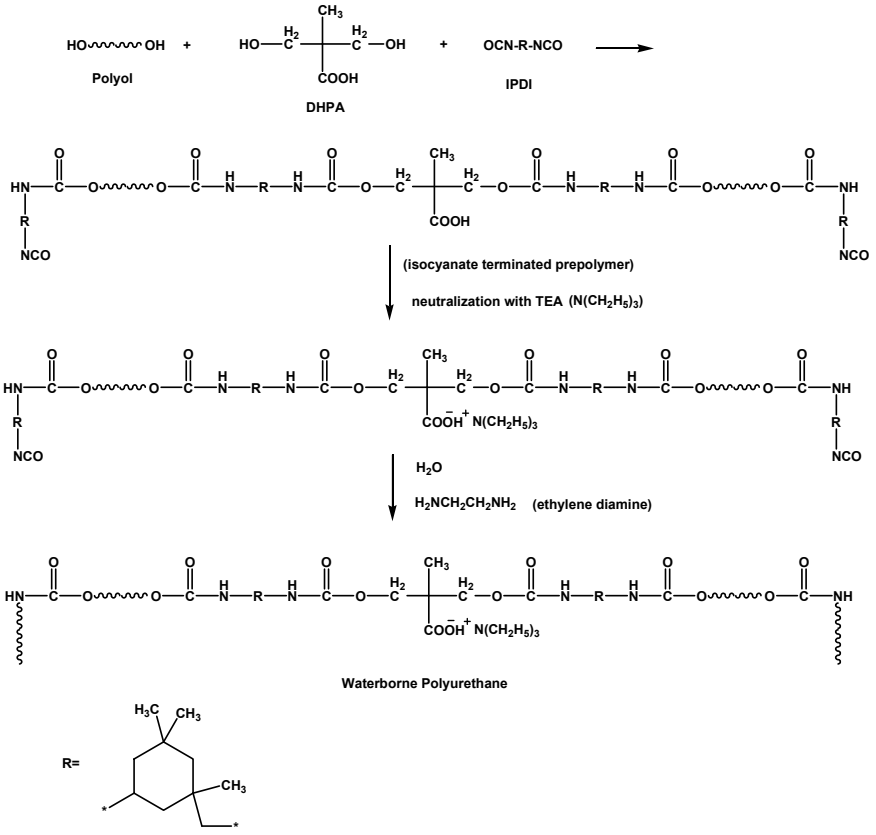


Figure 2. TGA analysis of the PU dried film. The sample was ramped from 25 ^{o}C to 600 ^{o}C in the air.



Scheme 1: the preparation route of the water-borne PU dispersant for the ICAs.

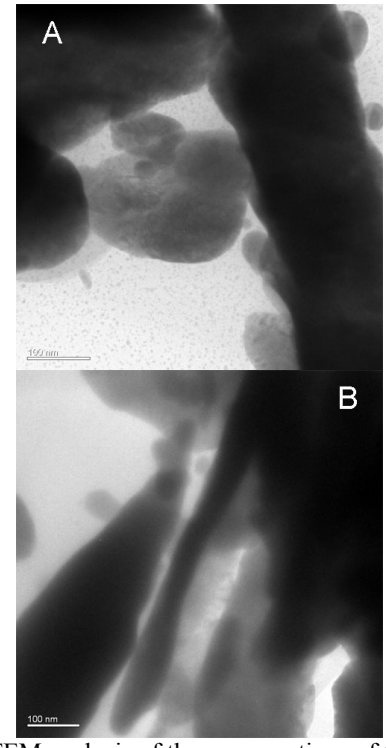


Figure 3. TEM analysis of the cross sections of the WBICAs. (A) untreated WBICA sample (70% Ag); (B) 1% $NaBH_4$ treated WBICA sample (70% Ag).

Compared to the other traditional dispersants for the ICAs, such as epoxy, polyester, and polyacrylates etc., water-borne PU as the resin dispersant displays a few advantages: 1. the resin is dispersed in water, thus the manipulation process does not involves toxic volatile materials and the residues can be conveniently removed by using water; 2. the PU materials can be prepared from a large variety of sources such as from plants, thus PU has better environmental benign character and adjustable mechanical strength; 3. the urethane bond is relatively strong, thus the materials have a high reliability for general electronic packaging applications; 4. the curing step for the ICAs can take place at even room temperature (of course a higher temperature may help accelerate the process) thus it saves energy; 5. the WBICAs have adjustable rheological property thus they are suitable for many types of printing process such as screen printing, gravure printing, and roll-to-roll printing etc.

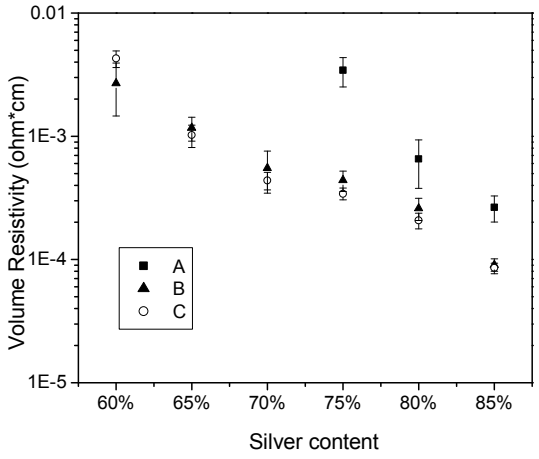


Figure 4. Volume resistivity of the WBICAs (80 wt% of silver) versus different addition amount of $NaBH_4$. (A) no $NaBH_4$ addition; (B) 0.5% of $NaBH_4$; (C) 1% of $NaBH_4$.

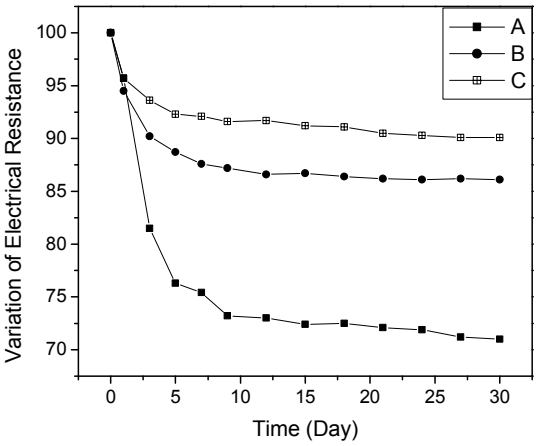


Figure 5. Thermal-humidity reliability of the WBICAs versus aging time. (A) no $NaBH_4$ addition; (B) 0.5% of $NaBH_4$; (C) 1% of $NaBH_4$.

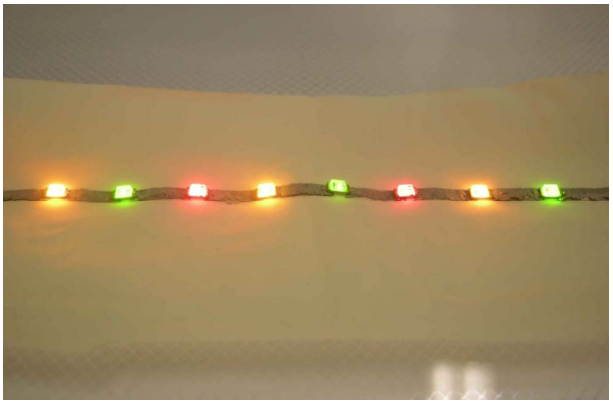


Figure 6. A photographic image of a piece of WBICA printed circuit line (2 mm x 150 mm) which supports 8 LED chips in different color. (Ag: 80 wt%, $NaBH_4$: 0.5%).

Table 1. A table showing the Young's modulus of the WBICA thin film samples including the untreated, 0.5% of $NaBH_4$ treated, and 1% of $NaBH_4$ treated ones.

Young's modulus (MPa)	60% silver	70% silver	80% silver	85% silver
no treatment	0.291	0.322	0.311	0.309
0.5% $NaBH_4$	0.289	0.338	0.364	0.358
1% $NaBH_4$	0.297	0.319	0.347	0.339

Conclusion

In summary, we have prepared a water-borne PU resin as the dispersant for the ICAs and evaluated these WBICAs' electrical property, reliability, and mechanical property. From the experimental results, we observed that sensitizing a small amount of $NaBH_4$ can effectively improve the electrical conductivity of the WBICAs of about one order of magnitude and reduce the percolation threshold of the silver filler. The lowest electrical resistivity ever measured in this material was in the order of 10^{-5} ohm·cm. The mechanical strength of the thin films of the free-standing WBICAs improves along with the PU dispersant amount. These WBICAs can be applied in the general printing process for general applications as ordinary ICAs can do, while they display many unique properties, such as amenity for processing, environmentally benign, excellent shelf-life and reliability in long-term storage and applications, water-proof, and the mechanical property can be adjusted by choosing different prepolymers. Since they have all these advantages, we believe they have vast applications in the blooming flexible and green electronics.

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