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Bio-based benzoxazine electrically conductive adhesives for sustainable and epoxy-free hybrid printed electronics

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Abstract

Electrically conductive adhesives (ECAs) are critical for the assembly of surface-mounted devices in printed and hybrid electronics; however, conventional epoxy-based systems are associated with toxicity and limited working life. In this work, we present a benzoxazine-based anisotropic conductive adhesive (ACA) derived from a bio-based diphenolic acid benzoxazine (DPA-Bz) copolymerized with 1,12-diaminododecane (DIADO), combined with environmentally preferable metallic fillers. The developed system enables reduced curing temperatures ($\sim 150^\circ\text{C}$) compared to conventional benzoxazines, improving compatibility with temperature-sensitive substrates. From an electrical standpoint, the optimized Cu-based ACA exhibits low contact resistance and clear anisotropic conductivity with electrical performance comparable to a commercial epoxy-based adhesive. Furthermore, the ACA maintains stable electrical behavior under accelerated aging (85°C / 85% RH) and thermal shock testing, indicating robust reliability under environmental stress. Finally, life cycle assessment reveals a reduced global warming potential ($5.48\text{ kg CO}_2/\text{kg}$) compared to a reference Ni-based adhesive ($6.27\text{ kg CO}_2/\text{kg}$), with further reduction potential through solvent-free formulations and increased recycled copper content. The presented benzoxazine-based ACA achieves comparable electrical and mechanical performance to commercial systems while delivering improved environmental performance and reduced toxicity, highlighting its potential as a sustainable alternative for next-generation electronic assembly and opening the path towards greener electronics.

INTRODUCTION

Conventional electrically conductive adhesives (ECA) are key materials for the assembly of surface mount devices, SMD, such as passive (e.g. resistors and capacitors) and active (e.g. μ chip, sensors) components onto hybrid printed devices where soldering is, due to material restraints (e.g. thermal stability of substrates and compatibility of Ag with existing soldering materials), not suitable. Commonly used electrically conductive adhesives are usually made of epoxide binder matrices which have quite fast curing times (~ 10 s) but also pose exposure risks during the assembly process, as they can cause an allergenic or respiratory sensitization in occupational settings.¹⁻⁴ Furthermore, they are bound to be stored in subzero temperatures since their Arrhenius-type curing mechanism can cause inadvertent curing even at room temperature. These adhesives' performance has improved through innovations in formulations, such as combinations of micro- and nano-silver that lower resistivity and enhance thermal stability; for example, resistivity values as low as $5 \times 10^{-5} \Omega \cdot \text{cm}$ and pyrolysis temperatures above 350°C have been reported in tri-modal epoxy adhesives (micro- and nano-silver blends).^{5, 6} However, major challenges persist: maintaining reliable long-term electrical and mechanical performance under thermal cycling and humid conditions remains difficult, and achieving fine-pitch component adhesion with conventional manufacturing infrastructure (vs novel advanced nano-dispensing) without compromising conductivity is a delicate balance (e.g., sintering behavior and substrate preparation are critical). From an environmental and toxicity standpoint, conventional conductive fillers such as silver or nickel fillers—while conductive—pose ecotoxicity risks, particularly to aquatic life; life-cycle assessments suggest that while isotropically conducting silver-epoxy may reduce toxicity compared to lead-based solder, they still involve substantial resource consumption and environmental burden.

Benzoxazines (BZs) are a category of thermosetting polymers that can be used as alternative binders to epoxides^{2, 3}. Benzoxazine resins are increasingly attractive as binders for electrically conductive adhesives (ECAs) because their polymerization to polybenzoxazines yields a combination of low water uptake, high glass-transition temperatures, and strong substrate adhesion—traits that help preserve percolated filler networks and contact resistance during thermo-mechanical and humidity stress. Classic and modern studies consistently document these features and show that they can be tuned by monomer design and copolymer strategies, including regiochemical control and co-curing with epoxies to balance toughness and processability. In particular, “N-activated” and other tailored benzoxazine monomers lower cure temperatures and expand processing windows without sacrificing the hallmark dimensional stability of the network—an advantage for assemblies containing temperature-sensitive components. Together, these processing/structure attributes position benzoxazines as promising drop-in binders (or co-binders) for advanced ECAs where solderless, low-temperature joining is required.

Direct demonstrations of benzoxazine matrices hosting conductive fillers support their suitability for ECA formulations. Benzoxazine/graphene (and graphene nanoplatelet (GNP)) composites show simultaneous gains in electrical/thermal conductivity and mechanical performance; aerospace-grade benzoxazine reinforced with GNPs achieves multifunctional (thermal and electrical) conductivity while retaining structural properties, and kinetic studies indicate that GNPs can beneficially influence benzoxazine curing and network development—both relevant to stable, low-resistance pathways in ECAs. Hybrid systems illustrate further versatility: polybenzoxazine filled with irregular BN@Cu hybrids reaches high thermal conductivity (useful for heat-spreading adhesives), while silver-nanowire/graphene/polybenzoxazine thin films demonstrate conductive networks embedded in a benzoxazine matrix. Chemical compatibility with metallic conductors is underscored by urushiol-based benzoxazine coatings that in situ reduce and stabilize Ag nanoparticles, and by benzoxazine-epoxy copolymer matrices that disperse graphene at low loadings for conductivity enhancement—both pointing to practical routes for metal- or carbon-filled ECA binders. Collectively, these peer-reviewed reports show that benzoxazine networks can maintain conductive architectures, offer processing flexibility, and deliver the thermo-mechanical robustness demanded by modern electronics assembly.⁷⁻¹⁰

Benzoxazine resins exhibit latent curing characteristics meaning that a long working life of a benzoxazine composition can be combined with rapid polymerization above a certain threshold temperature. This is in contrast to most epoxy composition typically following Arrhenius kinetics

meaning that there is a need to compromise between long working lifetime and curing rate. Accelerating the polymerization of benzoxazines is a critical area of research to enhance their processing efficiency and broaden their application range. Traditionally, benzoxazines undergo ring-opening polymerization (ROP) upon heating, but this process can be slow and require elevated temperatures. To address these challenges, various catalytic approaches have been explored. For instance, the benzoxazine curing chemistry can be controlled by the introduction of functional groups in the benzoxazine monomers, by introducing an acid catalyst or by copolymerizing them with a diamine or a phenol, while the use of thioamide catalysts has been shown to lower the ROP temperature of simple 1,3-benzoxazines synthesized from renewable compounds, facilitating a more efficient polymerization process. Similarly, the application of sodium cyanoborohydride and sodium borohydride as catalysts has been reported to enable curing of benzoxazines at lower temperatures, thereby reducing energy consumption and improving processability. These studies highlight the potential of catalytic systems to accelerate benzoxazine polymerization, making them more viable for industrial applications.^{11, 12} Furthermore, the benzoxazine monomers can be synthesized from biobased molecules such as waste phenols from the wood industry. As a result, exploring benzoxazine molecules as perspective binder systems for electrically conductive adhesives has the potential to provide more sustainable alternatives to the conventional, toxic epoxy-based systems and enhance the safety and sustainability of the assembly line for the electronic manufacturing.¹³⁻¹⁷

In this work, results regarding the use of benzoxazines as alternative binding matrix in electrically conductive adhesives is presented. We initially compared a commercial and an in-house synthesized benzoxazine for their curing temperature, and selected the one with the lowest temperature as a binder for the adhesive. We further decreased the curing temperature by introducing a diamine to the system, forming a benzoxazine – diamine copolymer. We then focused on selecting environmentally friendly conductive fillers for the adhesive, screening materials such as Zn, Cu, and Fe. The conductive fillers were mixed, at different concentrations, with the selected binder and tested for adhesiveness and electrical resistance in ACA contacts formed using a thermode. Among the tested fillers, Cu spheres demonstrated the lowest resistance in the z-axis and exhibited exclusive z-axis conductivity even at high particle loading. Parameters such as temperature, pressure, and post-annealing were optimized to ensure stable adhesion and effective conductivity between model laminates. We evaluated our developed conductive adhesive for mounting electronic components, specifically quad flat no leads (QFN) SMDs on various substrates including paper, and polyamide foil (Kapton foil). The electrical performance of our conductive adhesive was also compared to a commercial epoxy-based adhesive (Delo Monopox AC268). Furthermore, we evaluated the reliability of our adhesive by exposing the mounted components in 85°C/85%RH accelerated aging tests and thermal shock tests. Finally, we conducted life cycle assessment of the ACA in order to assess its environmental impact and compared it with a commercial ACA. Our report highlights the potential of benzoxazine-based adhesives for electronic applications and provides a foundation for future research on conductive glues.

Results and discussion

The adhesive developed in the work reported here in was based on benzoxazine binding system. More specifically two benzoxazines molecules have been tested: a commercially available Bisphenol A dibenzoxazine (Huntsman, Araldite MT 35600) (BPA-Bz) and an in-house synthesized equivalent (Diphenolic acid dibenzoxazine; DPA-BZ) (Figure 1). DPA-Bz was selected for its properties to be bio-derivable and to have a lower curing temperature in comparison to other dibenzoxazines.¹⁸⁻²⁰

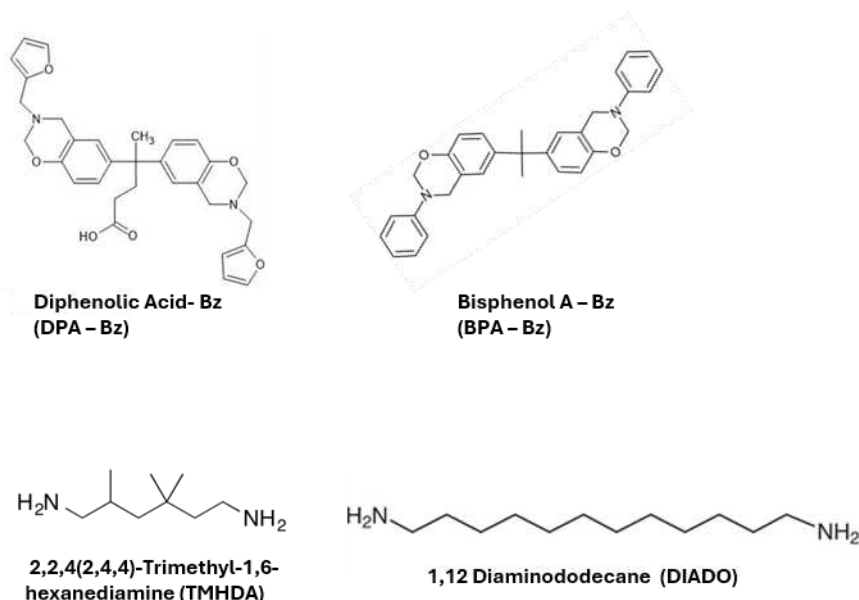


Figure 1: The dibenzoxazines and diamines used for the ECA

DPA-Bz was synthesized following a revised version of synthetic routes available in literature and based on the Mannich condensation of diphenolic acid (DPA) with furfurylamine (Figure 2).^{18, 19} The process was shown to have a yield of 96.5%. The synthesized DPA-Bz was then further evaluated for purity and structural confirmation with nuclear magnetic resonance (NMR) (Supporting Information).

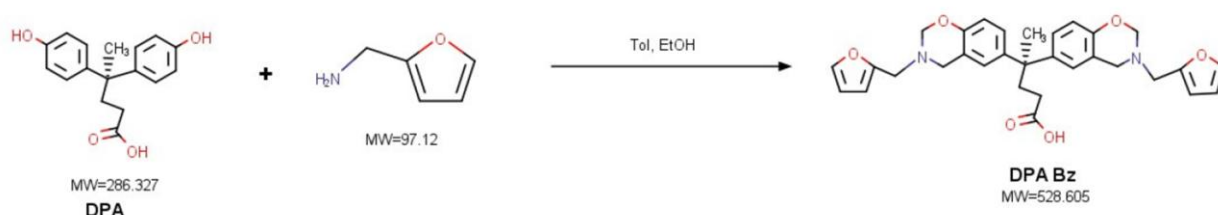


Figure 2: The Mannich condensation of the DPA and furfurylamine into DPA-Bz

To experimentally evaluate the curing properties of the two benzoxazines differential scanning calorimetry (DSC) experiments were performed. DSC experiments were performed using a TA Instruments Discovery DSC250 setup: in these measurements ~10mg of the resin were heated using a scanning speed of 20°C/min from 40°C up to 300°C. As seen in Figure 3 the BPA-Bz (black line) exhibits a curing onset temperature of ~220°C and a peak exotherm temperature of ~250°C, which both are relatively high for adhesives aiming for application in printed electronics where temperature sensitive materials (e.g. PET) are often used. The curing temperature of the DPA-Bz was then evaluated (Figure 3) and as expected the onset temperature (~175°C) and the peak temperature (~200°C) for the curing were lower than those recorded for the BPA-Bz.

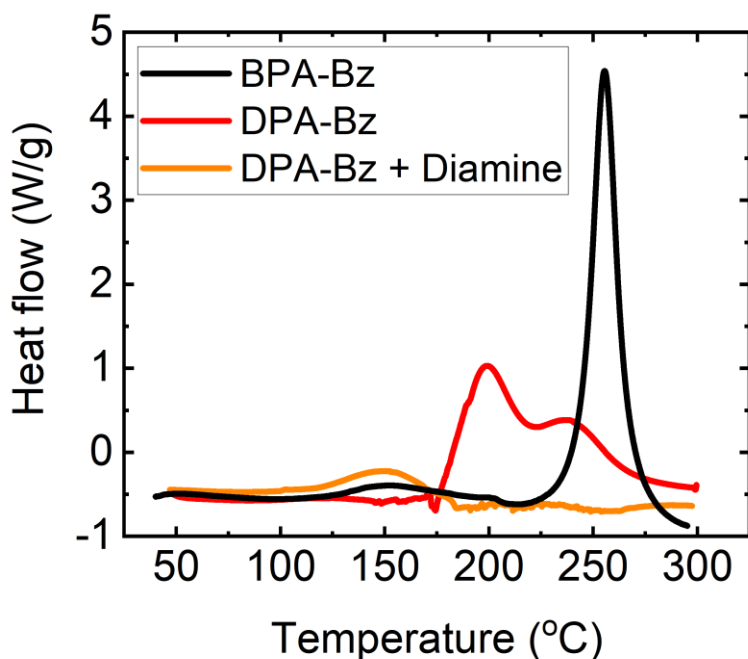


Figure 3 : The DSC results for the various binders systems under investigation

The curing temperature of benzoxazines can be decreased by chemically modifying them (e.g. introducing carboxylic acids in the structure) or by polymerizing them in the presence of a catalyst (diamines or other phenols forming copolymers). In the work reported herein reduction of the polymerization temperature was obtained by adding diamines in the reaction mixture. Two diamines were selected for this scope: 2,2,4(2,4,4)-Trimethyl-1,6-hexanediamine (TMHDA) and 1,12 diaminododecane (DIADO) (Figure 2). Ideally diamines with high boiling point to avoid evaporation during the curing process would be required. However, TMHDA has a low boiling point and that resulted in the formation of bubbles in the matrix during the polymerization process, that would act as failure points in the adhesive. This was not observed when DIADO was used as it has a relatively high boiling point ($\sim 340^{\circ}\text{C}$). Subsequently DIADO was selected for further implementation. In order to evaluate the impact of the diamine on the benzoxazine curing DSC experiments of the DPA-Bz/DIADO (1:1 molar ratio) were also conducted. As can be seen from Figure 3 (orange curve) the onset ($\sim 125^{\circ}\text{C}$) and peak temperatures ($\sim 150^{\circ}\text{C}$) were indeed decreased. As a result, we choose the DPA-Bz/DIADO binder composition as the binder to proceed for an ECA.

Conventional electrically conductive adhesives utilize metal particles such as Ni or Ag as conductive fillers^{4, 21}; these are neither environmentally safe nor user-friendly materials as they are hazardous and toxic. For that reason, more environmentally friendly metallic fillers have been screened. These included: Zn flakes ($<10\mu\text{m}$), Fe flakes (APS 6- $10\mu\text{m}$), Cu flakes (APS 3.25- $4.75\mu\text{m}$ size) and Cu spheres (diameter $\sim 10\mu\text{m}$). The different fillers were mixed at constant concentration (w/w %) in a binder matrix comprised of DPA-Bz/DIADO (1:1 molar ratio) and Benzyl Acetone as a solvent, enabling a stencil printable paste (see supporting Information for images). The paste was then used to bond two copper sheets: bonding was performed for 15 min. on a hot plate at 150°C , and under the weight of 20g. The copper sheets used were of 10mm width and 50mm length, with the bonding overlap of 10x10mm. A schematic representation is presented in Supporting Information. A multimeter was then used to assess the resistance of the sheet/bond/sheet system for the various metal-based ECAs. In Table 1 are presented the results of this screening activity. As seen in Table 1, the Cu sphere based ECAs presented the lowest resistance among the fillers for

the Cu sheet/bond/sheet samples. This result is in accordance with the favorable behavior of spherical structure in ACA.

Table 1: The selection of the conductive filler. The resistance in the z-axis is presented as the average and standard deviation value between at least three samples

Conductive filler	Metal filler concentration (w/w)	Resistance in z axis (Ohm)	Resistance in xy plane (Ohm)
Zn flakes	35%	1.1±0.3	Not conducting
Fe flakes	35%	500±10	Not conducting
Cu spheres	35%	0.23±0.01	Not conducting
Cu flakes	35%	2.2±0.1	Not conducting

Following demonstration of the ability of the developed adhesive to electrically connect two metal foil, its anisotropy was investigated. An ECA can be either anisotropically (only along one direction; usually z-axis) or isotropically (along the three directions; xy plane and z axis) conductive. To perform this investigation a specific setup was engineered (In Supporting Information are presented a schematic and images of the designed setup). By bonding two overlapping copper sheets the z-axis conductivity of the different adhesives were measured (Table 1). In order to investigate whether there is electrical conduction along the xy plane, a parallel configuration was established; this was achieved by bonding a three-part system where two copper sheets were placed a distance of 1mm and bond using the developed adhesives to a Kapton foil which provided a mechanical support. Adhesives were deposited onto the Kapton foil in such a way to ensure a continuity under and between the Cu foils. Following curing xy-plane conductivity was assessed by measuring the resistance between the copper sheets. Table 1 highlights the result of this investigation and it is observed that none of the ECA exhibits electrical conduction along the xy plane confirming the anisotropic nature of the developed adhesive system.

Having verified the ACA nature of the developed adhesive, the possibility to implement it in a process resembling those adopted for mounting components in the field of hybrid or conventional electronics was investigated. More specifically the use of a thermode, a widely used tool for assembling surface mounted devices (SMD) components during prototyping of printed or conventionally electronics, was investigated. This allows to apply controlled force and Temperature for a well-defined time and using a pre-defined profile on the component to be mounted it on the circuit. To investigate the use of the thermode two copper strips with bonding overlap of 10x10mm (as from DIN EN 1465:2009-07 standard for adhesion tests) were bonded using ~50µl of the ACA. In this optimization work three different thermode temperatures (25, 150 and 200°C) were explored: these were applied to the sample for 30sec under a pressure of 30N; furthermore, the use of a post annealing oven treatment (150°C, 1h). A 'PASS' / 'FAIL' score was defined and based on the conductivity and adhesive strength of the samples. In the Supporting Information the results of this optimization are summarized. In summary it was observed that a thermode temperature of at least 150 °C and a post annealing of 150 °C/ 1h are needed to pass. Furthermore, it was observed that when 150 °C were used for the thermode a pressure (in the form of a weight of 500g) was needed during the annealing step to achieve a good adhesion and conductivity; this was not necessary when 200 °C were used. Furthermore, a pretreatment at 70°C for 10min prior to the thermode bonding further improved the adhesion between the laminates probably due to solvent evaporation.

Following demonstration of the adhesive concept and identification of a scalable bonding process the next step of the study was to optimize the adhesive in terms of the concentration of the copper sphere filler. This is important since the concentration of the conductive filler can affect the electromechanical performance of the adhesive (e.g. conductivity, anisotropy and adhesion), its cost and its environmental impact. Consequently, ACAs with a varied concentration from 5 up to

60% w/w, of the Cu spheres were formulated and tested electromechanically. All samples were not only characterized electrically but also mechanically via shear stress testing using a Tensile Tester Z3 (Thumler GmbH) following the DIN EN 1465:2009-07 standard. In the Supporting Information the recorded stress -displacement plots for the different DPA-Bz:DIADO based adhesives are presented. It is noteworthy that all the systems showcase a similar mechanical performance, which potentially indicates that the mechanical properties of the adhesive are dominated by the binder matrix. The results of the mechanical testing are presented in the Supporting Information. In order to acquire a more clear understanding on the mechanical performance of the adhesives, we further extracted a “Stress at Break” from the stress/strain curves (namely the stress after which the bond between the laminates is broken). In parallel, the electrical resistances of the different samples were measured with a multimeter with a 2-probe setup. The “Stress at Break” and the electrical resistance of the samples are presented as the statistical average between at least three samples, along with the standard deviation in Figure 4. The Stress at Break increased with the sphere weight percent, from ~60kPa, 5%w/w up to 75kPa, 60% w/w, while the deviations between the samples of the same Cu sphere w/w% decreases as their concentration increased, which might translate to potential inhomogeneities in the coating due to the lower Cu sphere concentration. Meanwhile the electrical resistance appears to decrease with the conductive filler concentration, reaching a plateau at ~35% w/w; this result is possibly related to the Cu spheres having saturated the area of the bonding overlap. Based on these results, the 35% w/w Cu spheres as the optimized concentration in the conductive filler for the DPA-Bz/DIADO ACA was selected.

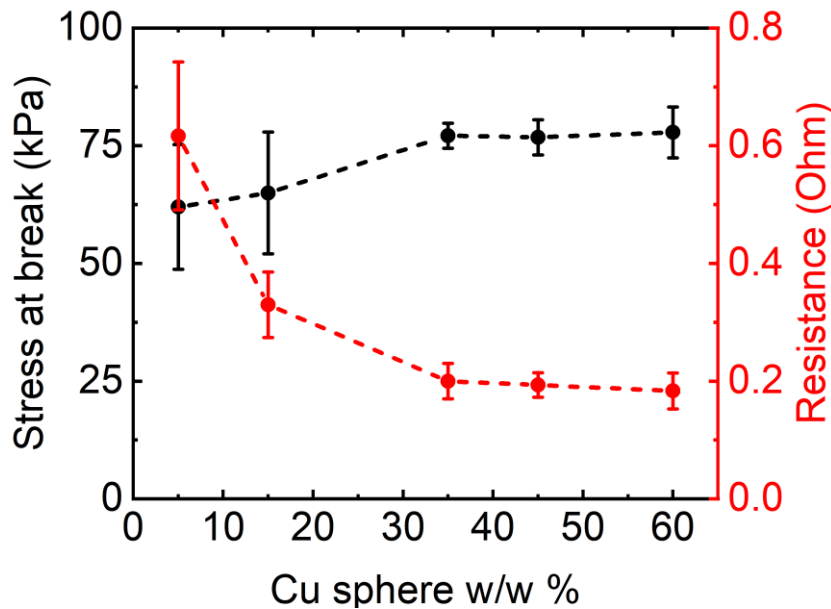


Figure 4: The Stress at Break (black) and the electrical resistance (red) vs the conductive filler concentration in the ACA ink

Following the optimization work described above, the optimal ACA was explored for the mounting of SMD components; more specifically this was used to assemble, as a test model system, daisy-chain QFN chips with 500 μ m pitch, onto Ag landing pads printed on paper and Kapton foil.

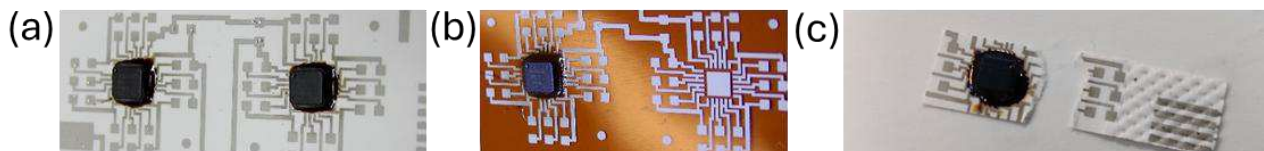


Figure 5: Photographic depictions of the SMD components on (a) XD200 paper, (b) polyimide foil using the ACA developed in WP2. (c) a photographic depiction of a paper based sample after the shear stress tests

Upon mounting the components and probably due to the better heat and pressure distribution it was noticed that a stable bonding was achievable also without the use of the annealing treatment in the

oven. In order to have a reliable electrical characterization, structures allowing for 4 point probing measurements over the mounted QFN chip were designed and manufactured (Figure 6). The 4-probes measurement structures not only allow to identify potential failed bonds between the various printed pads and decouple contact contributions from intrinsic adhesive conductivity but they also make possible to calculate an average value for the electrical resistance over all contacts. As a first step QFN chips were mounted on structure printed on paper using the ACA with different concentration of Cu spheres; as seen in the Supporting Information, the trend obtained with the 4-probe measurements was consistent with those summarized in Figure 5, reassuring the choice of the 35% in Cu spheres as the best performing ACA. As a means of comparison components were also mounted using a commercial Epoxy/Ni based ACA (Delo Monopox AC268).

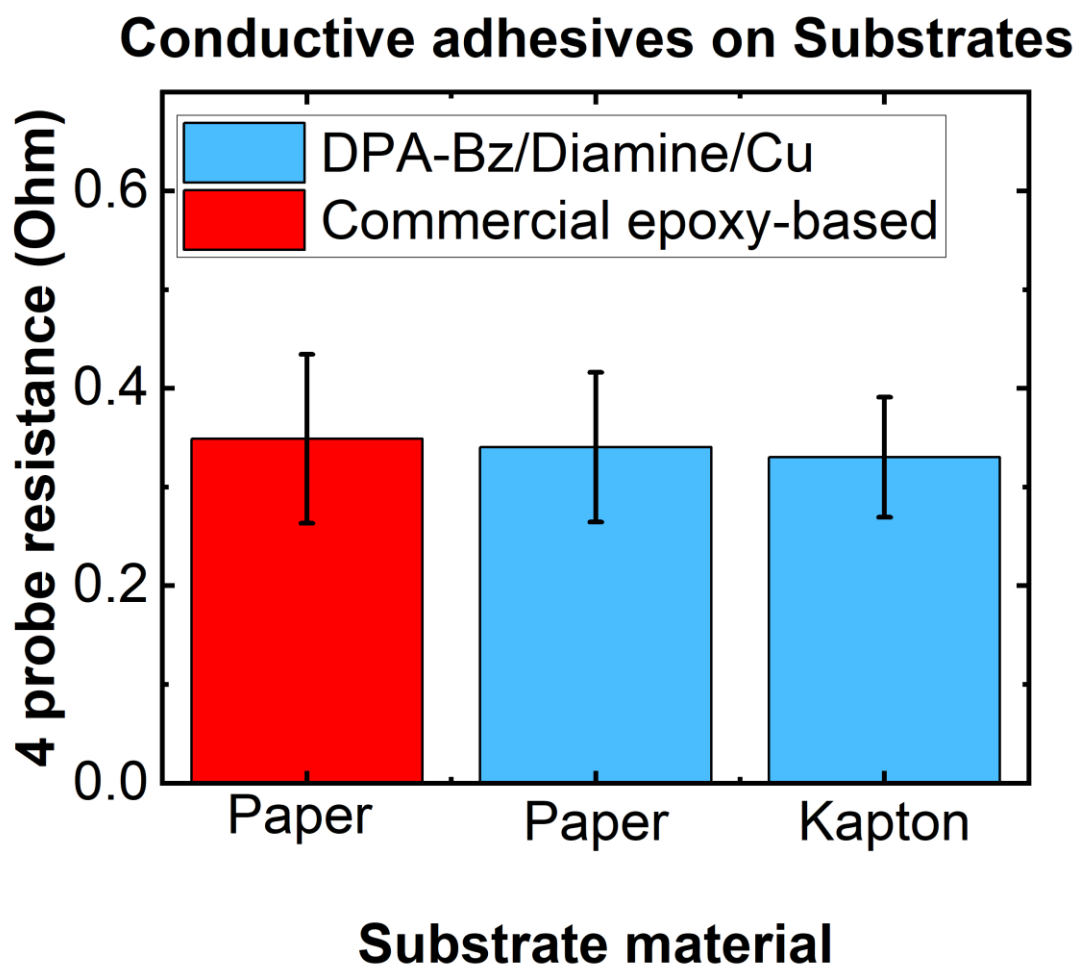


Figure 6: The 4-probe resistance of the ACA on the various substrates and the respective value of the Commercial ACA on XD200 Paper

In Figure 6 the 4-probe electrical resistance for QFN SMD components mounted with the reported ACA on paper and Kapton foil, and the 4-probe resistance of the commercial ACA on paper are compared; clearly the Bz-based ACA proposed herein had comparable electrical performance to the commercial epoxy-based adhesives highlighting its suitability as a less toxic (at least from a filler prospective) alternative. Following the electrical characterization the assessment of the mechanical strength of the bonding was assessed as described above. For these shear stress tests, a homemade adapter was used so that the SMD/substrate samples can be characterized, adapted from the DIN EN 1465:2009-07 measurement standard. For the components mounted on the Kapton foil, we extracted a Stress at break of 2 MPa (See Supporting Information). However, we observed that the bond was stronger than the mechanical stability of the paper substrate, which underlines the promising behavior of the developed materials as an adhesive for electrical components. In order to gain further understanding of the bonding and conducting mechanism of our adhesive high-resolution optical microscope image of assembled components were acquired (Figure 7). In Figure 7 a particle gradient can be observed, with a higher concentration of particles near the component;

this accumulation of particles near the component area could be expected, if excessive amounts of adhesive are used, to lead to shorts.

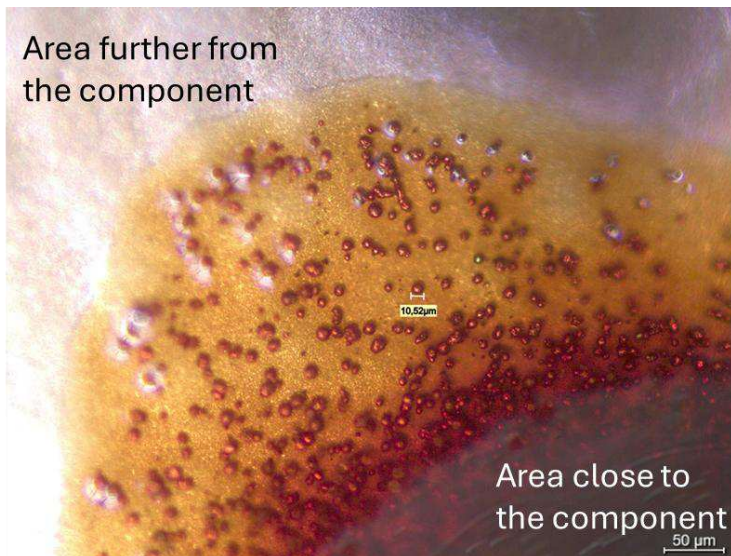


Figure 7: A photographic depiction of the ACA around a mounted component with Optical Microscopy

In continuation preliminary accelerated aging and thermal chock tests were performed. Aging tests were conducted by placing SMD components assembled on Kapton substrates at 85% RH, 85°C for a certain amount of time. For the conventional tests, an exposure time of ~1.5 months is needed, however, as a first step, we conducted only a 15 days exposure.

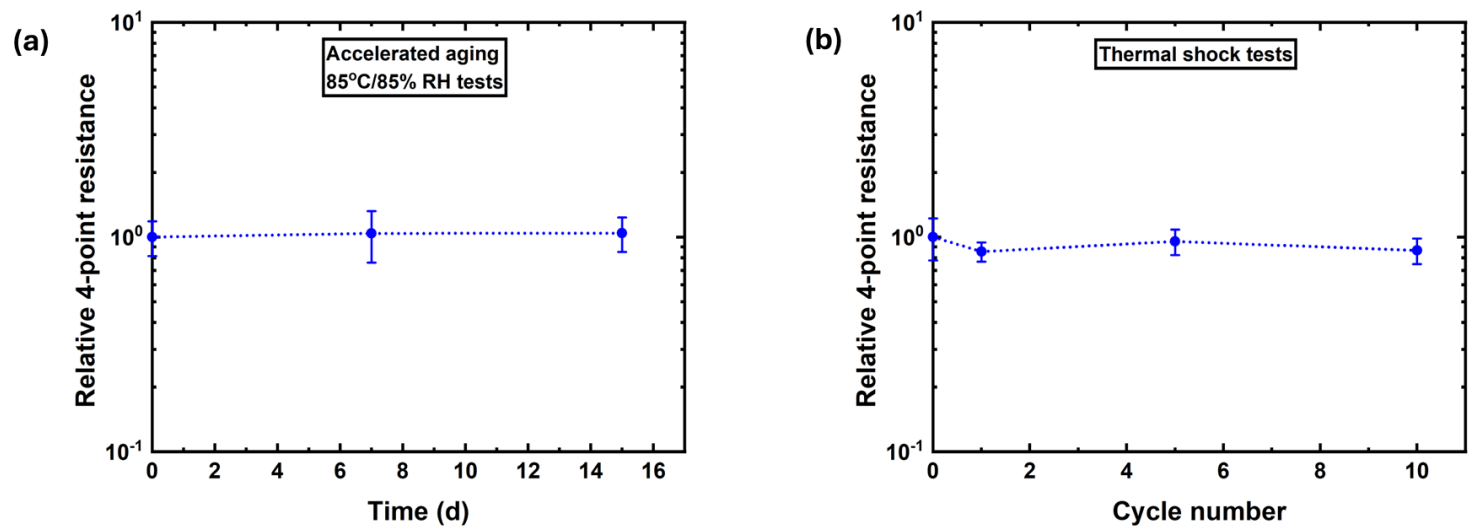


Figure 8 : (a) The 85%RH / 85°C tests for the ACA on Kapton foil and (b) the respective results for the thermal shock tests

The results are presented in Figure 8a where the relative 4-point resistance (resistance at time n divided by resistance at time 0) is plotted against time. It should be noted that for each point different samples were measured, so to prevent any thermal or humidity 'shock' effects on the measurement. As seen in Figure 8a the relative 4-probe resistance of the mounted components was unaffected by the accelerated aging tests, proving the resilience of the developed adhesive. Following the Hallberg-Peck model^{22, 23} for the accelerated aging tests of electronic devices, we can thus estimate that the 15 days of operation at 85%RH, 85°C, translates roughly into 29 years of usage at 50% RH and 25°C; of course more prolonged and detailed accelerated aging tests (e.g. longer duration, higher humidity, temperatures) can further validate this statement, but this is not part of this work. In order

to further evaluate the reliability of the ACA, thermal shock tests, adapted from the IPC-TM-650 2.6.7.1 standard, were performed. The protocol is described in the Materials and Methods section. The results are presented in Figure 8b. In this case the relative 4-point resistance is defined as the ratio between the 4-point resistance at a given cycle number divided by the 4-point resistance at cycle 0 (thus at the beginning of the shock tests). As can be seen from Figure 8b, the ACA was unaffected from the thermal shock tests, further proving the robustness of the adhesive in relation to environmental variations.

As a final step a cradle-to-gate lifecycle assessment (LCA) of the optimized ACA composition (35% Cu spheres) was performed; furthermore, LCA of the developed ACA was compared with those calculated for a commercial reference Ni-based ACA adhesive (AC268; Delomonopox). In the analysis the mounting of one QFN SMD with 20 μ L of adhesive was chosen as the functional unit. Furthermore, due to many unknown parameters in the process (e.g. source of metal etc), the assessment was limited to climate change (Global Warming Potential; GWP), for which a larger literature exists. In the analysis (Figure 9) the supply of raw materials, the formulation of the ACA, its storage and application were included; the LCA inventories used in this work are presented in the Supporting Information. The manufacturing of particles from metal was neglected because of the high uncertainty in the manufacturing route. In this work it was assumed that the same manufacturing route was used for both Cu and Ni; under these (simplified) assumptions, the particle manufacturing would shift the impacts of the same amount in all cases. In reality, the contribution of the particle manufacturing can vary greatly and overwhelm the impact of the material itself, and this should be considered in a more accurate comparison.²⁴ The source of the metal (e.g. virgin metal or recycled metal) is unknown for both metals; Eurostat reports recycled input rates in Europe of 16 % and 55 % respectively for nickel and copper.²⁵ Considering the raising awareness for sustainability and for supply chain vulnerabilities (both Cu and Ni are strategic raw materials according to the CRM list 2023), the push for implementation of recycled materials also for high-end applications such as electronics is expected to rise (WEEE Forum)).²⁶ In this work three different metal inputs were envisaged: (i) only primary raw material (worst rate), (ii) European recycling input rate (ERI rate; 55% for Cu and 16 % for Ni), (iii) only secondary raw material (best rate). To represent the large variety of manufacturing routes (in particular for recycled metal) and regions, a generic impact factor was used to represent metal extraction and processing.²⁷ Polymers and other chemicals are always modelled as primary raw materials from fossil sources. The pinning/curing energy (thermode-based assembly) is measured to be 1.33 Wh (as measured with an energy meter from Voltcraft (SEM6000)), the cold storage demands 0.1 Wh for 6 months (estimated based on common lab freezers, 6 months at -15 °C). The emission factor for the European energy mix is taken from European Environment Agency.²⁸ A GWP of 5.48 kgCO₂/kg was calculated for the Cu-ACA, and 6.27 kgCO₂/kg for the commercial Ni-ACA. It must be noticed that the calculated GWP for the commercial adhesive is significantly lower than the carbon footprint provided by the manufacturer (22.48 kgCO₂/kg). This could be explained by the larger scope of their analysis (which includes packaging, infrastructure, and transport and storage at facilities), better data quality and/or different

emission factors. Not knowing the details of the analysis from supplier, the carbon footprint calculated herein will be used in the discussion.

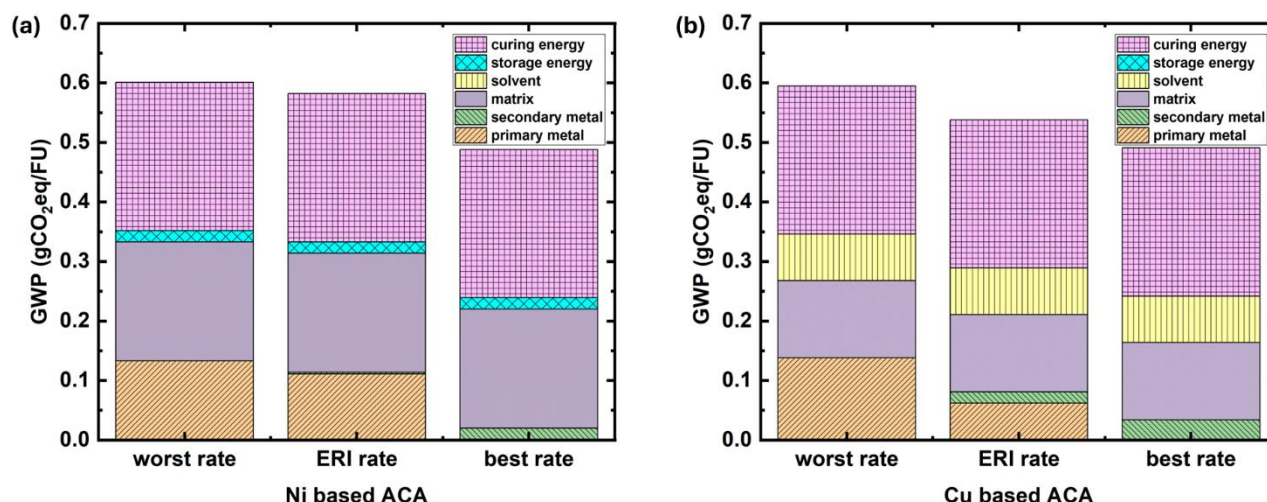


Figure 9: The Global Warming Potential of the ACAs for mounting one QFN device

In terms of the chosen functional unit, the GWP of both adhesives (worst case) is about 0.6 gCO₂eq/FU, but the single contributions differ in the two cases. In particular, the Bz-DIADO resin is better than the epoxy resin. Nevertheless, the use of solvent in the formulation proposed herein counterbalances the benefit from the resin; a solvent-free formulation could save about 13 % of the emissions. Primary Cu and Ni are extracted with similar processes, often as co-products, and have thus similar emission factors, but the market for recycled copper is better established than that for recycled Ni and is expected to grow further even in the most conservative scenarios.²⁷ High recycled content in Cu-ACA is thus realistic already in the near future.

Conclusion

In this work the use of biobased benzoxazines, DPA-Bz, and composition of it (e.g. with diamines) was investigated as perspective binder systems for electrically conductive adhesives and more specifically Anisotropic ones (ACAs). After a screening of various conductive fillers, Cu spheres were selected as the key conductive filler material. Following the w/w% filler concentration was optimized. Following electrical and mechanical analysis 36% w/w of filler was shown to provide the best electromechanical performances. The electrical performance of the proposed ACA was shown to be comparable with those of commercially available epoxy-based system (AC268; Delo Monopox) and to be independent from the used substrate. Engineering of assembly process was also in focus of this work with the aim to verify if the developed ACA could be successfully implemented in “conventional” hybrid printed electronics assembling protocols; subsequently, an assembling process based on the use of thermode was demonstrated. Additionally, the developed ACA was shown to endure an accelerated aging test (2 weeks at RH 85% and T 85 C) and a 10 cycles of thermal shocks. Even if further tests, as for example longer aging tests and recycling evaluation (e.g. when used in paper electronics), are needed these findings pave the way to the development of more green alternatives to conductive adhesives for application in hybrid printing electronics manufacturing.

Materials and methods

Chemicals

Benzyl acetone, DIADO, Zn flakes (<10µm), Fe flakes (APS 6-10µm), Cu flakes (APS 3.25-4.75 µm size), Cu spheres (diameter ~ 10µm) were purchased from Thermofisher. Ag ink (CXT XXX) was purchased by Sun Chemicals . BPA-Bz was purchased by Huntsman. Epoxy based adhesive AC268 was purchased by Delomonopox. Copper sheets were kindly provided by ICAPE-MMAB. The SMD components were purchased by Infineon.

Benzoxazine Synthesis

The synthesis of the dibenzoxazine of diphenolic acid (DPA-Bz) was an upscaled version of the synthesis reported by Qian et al²⁰ by carrying out the synthesis in a 1 liter jacketed reactor. Paraformaldehyde, 36 g, and furfurylamine, 58,2 g were charged into the reactor. The mixture was stirred at ambient temperature (19 C of the circulating heating / cooling medium). After 15 minutes, the temperature increased to 39 C in the reactor and the mixture transformed into a thick but agitable suspension. After another 15 minutes, DPA, 85,9 g, was added followed by dioxane, 240 ml, The temperature of the heating medium was set to 90 C. The reaction mixture gradually transformed into a clear homogeneous solution. After keeping the reaction mixture was kept at 90 C for five hours, it could an orange color of the reaction mixture was observed and reaction mixture was cooled until reaching 20 C in the reactor. The reaction mixture was left overnight before adding 2-butanone, 240 ml, and water, 250 ml to the orange solution under agitation. Agitation continued for 25 minutes. After agitation, the mixture separated and the product was found to reside in the brown heavy phase. The upper almost colorless aqueous phase was extracted with 2-butanone and combined with the heavy phase. The heavy phase was extracted with two 200 mL portions of 10% NaCl and concentrated to produce a highly viscous fluid. After drying at 50 C under vacuum, a solid was formed that was crushed and grinded to produce 153 g of the crude product. ¹H NMR spectral peaks were consistent with those reported by Feng et al.²⁹

Benzoxazine characterization

DSC was conducted with a TA Instruments Discovery DSC250 setup , while NMR spectra were recorded on a 500 MHz Bruker AV1 spectrometer.

Ink manufacturing

A speedmixer Hauschild DAC 600.2 VAC-P was used to mix the various components. Benzyl acetone was mixed in a molar ratio of 3.3:1, solvent:resin, with the various benzoxazines (DPA-Bz or BPA-Bz) at 100C for 30min in order to dissolve the resin. Then, the mixture was brought in room temperature and the diamines were added in 1:1 molar ratio with the resin. Finally the conductive fillers were added in the mix and the mixture was introduced in the speed mixer for mixing at 1200rpm for 8min.

Electromechanical testing

A Keithley Semiconductor Parameter Analyzer 4200 was used for the electrical characterizations, while a Tensile Tester Z3 by Thumler GmbH was used for the mechanical testing.

Component assembly

A thermode (MIYACHI) was used to mount the QFN, SMD components (0 Ohm resistance AMKOR MLF 4mm DC Sn) with pitch of 500µm, 250µm line and 250µm space. The process begins with depositing 10 µl, onto the printed pads. Next, the printed pads and paste are bonded to a QFN component using the thermode, applying a temperature of 200 °C for 30 seconds under a force of 30 N. After bonding, the assembled samples undergo environmental conditioning in accordance with the ISO 291 standard, at 23 °C and 50% RH for 88 hours. Once conditioning is complete, the samples are subjected to mechanical and electrical testing to assess their performance and reliability.

Visual inspection

For the visual inspection of the ACA, optical microscopes Leica DM6 (top-down view images) and Leica M205C (oblique view images) was used.

Reliability tests

A humidity chamber Vötsch LabEvent C/64/40/3 was used to expose the devices on the accelerated aging tests. The Chamber was set at 85% RH and 85°C and the samples were placed inside for 7 days and 15 days respectively. After each timeslot, the samples were removed from the chamber and the electrical resistance was measured with a Keithley 4200 Semiconductor Parameter Analyzer.

Thermal shock conditions

For the thermal shock tests, a TERMAKS ventilated oven was used and a Siemens freezer. The electrical resistance was measured with a Keithley 4200 Semiconductor Parameter Analyzer. The procedure is as follows: Initially (cycle number 0), the electrical resistance of the samples is measured. The samples are then placed at -20 °C for 15 minutes, returned to 25 °C for 2 minutes, exposed to 125 °C for another 15 minutes, and again returned to 25 °C for 2 minutes. After completing this sequence, if the cycle number corresponds to 1, 5, or 10 cycle, the resistance of the samples is measured again. If not, the process repeats starting from the low-temperature exposure step. This loop continues until 10 cycle numbers are reached, with resistance measurements taken at those defined intervals.

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