Enhancing electrical conductivity of epoxy resin based conductive pastes through the use of NanoStrand^{TM} Silver

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Abstract

This study investigates the enhancement of electrical conductivity in epoxy resin-based conductive adhesives through the incorporation of NanoStrand™ Silver, a one-dimensional silver nanoparticle. Traditional electrically conductive adhesives (ECAs) rely on micron-sized silver flakes to achieve conductivity, often requiring high filler concentrations that affect the viscosity and processability of the adhesive. By integrating NanoStrand Silver into the composite, we significantly reduced the percolation threshold, enabling high conductivity at lower total silver concentrations. The elongated structure of NanoStrand Silver promotes more efficient conductive networks, which resulted in similar or improved electrical performance compared to composites with only silver flakes. The addition of NanoStrand Silver increased the viscosity and thixotropy index of the adhesive, which makes the product suitable for industrial applications. Surface treatment of NanoStrand Silver further enhanced conductivity by reducing capping molecules that impede electron flow. These findings demonstrate the potential of NanoStrand Silver to improve the performance of ECAs, offering a more efficient solution for conductive adhesives used in electronics manufacturing.

Key words

NanoStrand^{TM} silver, conductive adhesive, electrical conductivity, viscosity.

I. Introduction

Conductive interconnect materials are employed for bonding electronic components to circuit boards, lead frames, chip carriers, etc. providing essential electrical, thermal, and mechanical connections. Traditionally, this has been achieved using homogeneous metal solders, but electrically conductive adhesives (ECAs) have emerged as an alternative. ECAs are typically composite materials consisting of conductive filler particles held together by an adhesive polymer matrix. These adhesives offer several advantages over traditional soldering, including lower processing temperatures, printability, and improved environmental sustainability, driving their increasing demand [1-4]. Commercial ECAs are commonly composed of highly conductive metal powders like silver, copper, or nickel as fillers, combined with polymeric adhesives such as epoxy resins. Typically, the metal particles used in ECAs are micron-sized flakes, though the recent addition of nanoparticles has helped to promote low temperature joining of the metal particles, reducing contact resistance. For the composite to conduct electricity, the metal particles must make contact, which requires a minimum concentration of filler material. This concentration, known as the percolation threshold, is where the metal particles form a continuous network, allowing electrons to pass through the material. The size and shape of the metal fillers influence this percolation threshold [1, 5]. Commercial ECAs typically require a filler concentration between 60% and 80%, but this high concentration affects the product's viscosity, cost, and weight. As a result, there is growing interest in reducing filler concentrations while maintaining electrical conductivity and/or increasing conductivity at a specific metal loading.

Percolation models suggest that high-aspect-ratio particles, such as rod-like or sheet-like structures, are more effective in minimizing the filler volume fraction at percolation compared to low-aspect ratio particles, like spheroids. These elongated particles can span greater distances within the composite per unit volume, improving electrical connectivity. Therefore, one approach to reducing the filler concentration is to employ one-dimensional conductive fillers. carbon-based conductive materials, such as carbon nanotubes (CNTs) and graphene and silver nanowires, have been explored for this purpose. The CNTs and graphene sheets are capable of transferring electrons through the sp² hybridized orbitals of the carbon atoms. This structure allows π-electrons to move freely across the plane, contributing to high conductivity. However, there are no free electrons as in metals in the carbon nanotubes and graphene sheets. This lack of free electrons leads to high junction resistance, which limits their effectiveness [6, 7]. On the other hand, silver nanowires are inherently unstable and prone to degradation when exposed to chemicals, heat, or electric current, making them unstable and unsuitable for long-term use in many applications [8]. As a result, silver nanowires have not gained significant acceptance in the market. Despite ongoing research, there is still no definitive solution to reduce filler concentration while maintaining stability and conductivity of the ECA.

NanoStrand Silver is a new class of one-dimensional silver nanoparticles that can enhance the performance of electrically conductive adhesives. [9]. NanoStrand Silvers have a thickness of 25 to 50 nm and a width of 50 to 300 nm, with lengths of 1-100 microns. Their crystal structure makes them the most thermodynamically stable form of silver nanoparticles, contributing to their exceptional resistance to degradation when exposed to thermal, electrical or chemical stresses. This stability is largely due to their predominately [111] crystallographic surface texture, which allows NanoStrand Silver to resist degradation at temperatures as high as 400°C, far outperforming traditional silver nanowires that begin to degrade at room temperature and rapidly at 150°C. This makes NanoStrand Silver an ideal material for high performance applications requiring durability under extreme conditions. Despite their high stability, these particles are synthesized at room temperature through the oriented attachment of silver nanoplates, a novel method of nanoparticle fabrication [9]. This process enables the production of highly stable NanoStrand Silver, providing a reliable and scalable solution for various applications. In this research, we utilized NanoStrand Silver to enhance the conductivity of electrically conductive adhesives. To assess the performance of NanoStrand Silver in this application, we selected epoxy resin and silver flakes as the base composite materials. We then evaluated the effect of incorporating these one-dimensional silver nanoparticles into the epoxy resin-silver flake composite on both the electrical conductivity and viscosity of the final product.

II. Experimental procedure

NanoStrand Silver, with the typical length distribution (calculated via optical microscopy) are shown in Figure 1a. Scanning electron microscopy of the NanoStrand Silver, revealing the one-dimensional structure of these particles, is shown in Figure 1b. The thermogravimetry curve for NanoStrand Silver is depicted in Figure 1c.

Acetone (≥99.5%) and methanol (≥99.9%) were purchased from Sigma-Aldrich (Oakville, Ontario, Canada). Epiclon 830S epoxy resin was purchased from DIC Corporation (Parsippany, New Jersey, USA). Epodil 750 diluent was purchased from Evonik (Piscataway, New Jersey, USA), and the hardener EPO-TEK 353ND was purchased from Epoxy Technologies (Billerica, Massachusetts, USA).

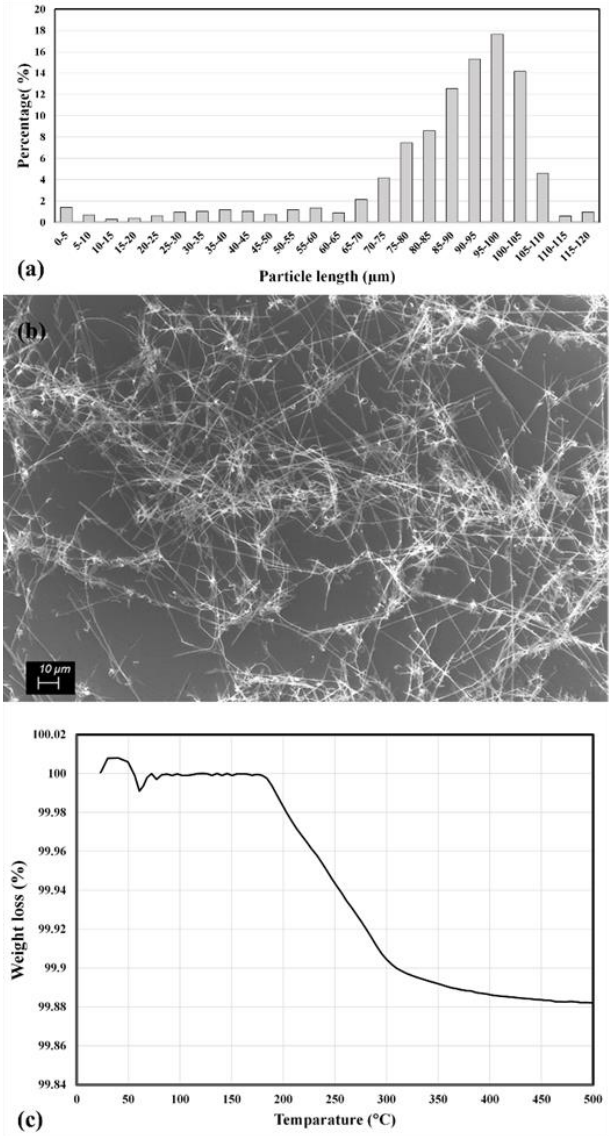

Figure 1: a) Particle size distribution of NanoStrand Silver used in this research; b) Scanning electron microscopy image showing the one-dimensional NanoStrand Silver.; c) The thermogravimetry results of the NanoStrand Silver.

To make the conductive adhesive, the required amount of NanoStrand Silver was weighed into a 20 mL glass vial. A sufficient amount of thinner (acetone or methanol) was added, and the solid was mixed using an X120 Handheld Homogenizer (CAT Scientific Laboratory, Cincinnati, OH) for at least 1 minute. Afterwards, the vial was placed in a Kurabo

Mazerustar planetary mixer (Osaka, Japan). Subsequently, the highest possible amount of thinner was removed via vacuum filtration (the remaining amount of thinner must be equal to or below the initial weight of the sample). Thereafter, the resin and diluent were added, mixed for at least 1 minute with the X120 Handheld Homogenizer stirred in the Kurabo Mazerustar planetary mixer, homogenized again with the X120, and then dispersed a second time in the planetary mixer. Next, the desired amount of silver flakes was added, and the composite was mixed in the planetary mixer. After that, the quality of the ink was visually inspected, manually stirred, and blended again in the Planetary Mixer. Finally, the required amount of hardener was added and mixed in the Mazerustar Mixer. If the final concentration of NanoStrand Silver is equal to or below 5%, adding thinner is unnecessary, and the resin and diluent can be added directly to the strands.

Vinyl stencil templates were cut using a Cricut Maker® (South Jordan, Utah, USA) in a rectangular shape with an opening of 0.5 x 5.0 cm. The vinyl stencil was affixed to regular glass slides (2.6 x 7.5 cm), and a sufficient amount of the composite was deposited on one end of the slide. Then, with constant speed and force, the applicator was drawn from one side of the glass slide to the opposite end. Afterward, the vinyl stencil was removed, and the samples were cured in an oven at 170 °C for 1 hour. Once this time had elapsed, the glass slides were removed from the oven and allowed to cool to room temperature. Subsequently, the four-probe resistance of the samples was measured using a Keithley 2450 SourceMeter® (Keithley Instruments, LLC, Ohio, USA). Measurements were taken in three different spots. Afterward, the thickness of the samples was recorded in the same spot where resistance was measured, using a Mitutoyo Digital Micrometer (Kawasaki, Kanagawa, Japan). The volume resistivity (VR) was calculated as follows:

$$VR=4.53*CF*R*t$$

Where CF (0.5194) is a correction factor depending on the sample geometry, R is the resistance conveyed by the Keithley 2450 SourceMeter and t is the thickness. Four samples were prepared for all the conditions studied.

For viscosity measurement, immediately after paste preparation, 0.5 g were deposited at the center of the DVNext Cone/Plate Rheometer (Brookfield Engineering, Middleboro, Massachusetts, USA). The samples were allowed to equilibrate for at least 3 minutes. Afterward, the viscometer was run for the first 20 seconds at 5 rpm to equilibrate the sample, and then the viscosity was recorded every 5 seconds for 2 minutes at 0.5 rpm and under the same conditions at 5 rpm. The first 5 data points at each speed were discarded, and the viscosity was taken as the highest repeated value in each condition. The thixotropy index (TI) was calculated by dividing the viscosity at 0.5 rpm by that at 5 rpm.

III. Results and Discussion

The benefits of using one-dimensional silver particles in ECA were assessed by comparing the electrical conductivity percolation limits of the composite containing solely the NnaoStrand Silver as filler against one prepared only with silver flakes The percolation threshold for electrical conductivity in conductive composites occurs when a sufficient amount of conductive filler is added to create a continuous pathway for electrons to flow. As a result, the electrical resistivity of the composite drops from a very high resistance value, and the composite becomes electrically conductive. Figure 2 shows the volume resistivity of the composites versus the concentration of silver flakes or NanoStrand Silver in the range where the electrical resistivity dropped. As shown in Figure 2, the percolation threshold is achieved at a significantly lower concentration for NanoStrand Silver compared to silver flakes. This is due to the high aspect ratio of the one-dimensional NanoStrand Silver, which allows these elongated particles to form conductive networks more efficiently than the silver flakes. The one-dimensional structure of NanoStrand Silver particles spans greater distances within the composite, facilitating electrical connectivity at lower filler concentrations. In contrast, silver flakes require higher concentration to achieve similar levels of conductivity. This difference highlights the advantage of using NanoStrand Silver as a one-dimensional conductive nanoparticle in reducing the amount of filler required while maintaining or enhancing electrical conductivity.

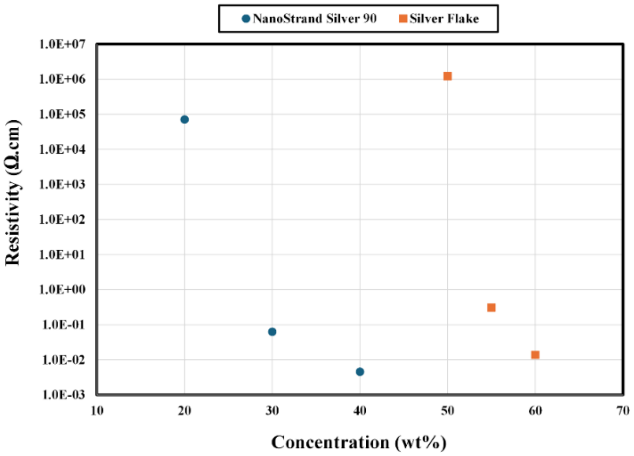

Figure 2: Resistivity of the composite versus concentration of the silver flake or NanoStrand Silver showing the percolation threshold when we add only strands and only flakes.

Figure 3 illustrates the change in resistivity of the conductive adhesive as different amounts of NanoStrand Silver were added to the system. We evaluated the conductivity of four systems: (1) only silver flakes with concentrations ranging from 50% to 70% by weight; (2) 50% silver flakes with varying amounts of NanoStrand Silver (1%, 2.5%, 5%, 7.5%, and 10%); (3) 55% silver flakes with 2.5% and 5% NanoStrand Silver; and (4) 60% silver flakes with NanoStrand Silver in concentrations from 1% to 10% (1%, 2.5%, 5%, 7.5%, and 10%). The results revealed that by incorporating NanoStrand Silver, we can achieve similar levels of conductivity at lower total silver concentrations. As mentioned previously, this is due to the high-aspect-ratio of NanoStrand Silver, which enhances the conductive network within the composite at a lower overall filler content. Consequently, the use of NanoStrand Silver allows for reduced filler amounts without compromising the composite's electrical performance, making it a more efficient and cost-effective solution for conductive adhesives.

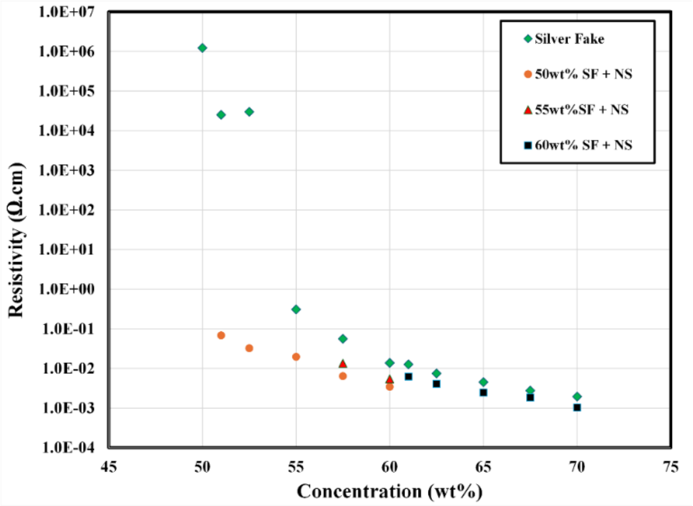

Figure 3 Resistivity of the composite versus total concentration of silver showing the effect of replacing silver with NanoStrand Silver (SF: Silver Flake, NS).

According to the graph presented in Figure 3, at low total silver concentrations (50% to 60% total silver content), adding NanoStrand Silver can significantly increase the conductivity of ECAs. However, the conductivity of the two systems tends toward convergence at higher concentrations, suggesting the system becomes saturated with conductive metal. One possible explanation for this phenomenon is that the resistance at the contact points between the silver flakes and NanoStrand Silver may become the primary limiting factor for the overall conductivity of the adhesive. It is well known that the surface of silver flakes is usually coated with surfactant molecules during production to make them compatible with specific resin systems. Similarly, the thermogravimetric results reported for NanoStrand Silver (Figure 1c) indicate the presence of capping molecules on the surface of the NanoStrand Silver used in this research. To test this hypothesis, the NanoStrand Silver was heat treated at 250°C for 30 minutes under an Ar-5% H atmosphere to clean the surface of the NanoStrand Silver. This heat-treated NanoStrand Silver was then used to make a composite to evaluate the effect of surface chemistry on the conductivity of the final product. Figure 4 shows the resistivity of three systems: one with 60% silver flakes, another where 5% of the silver flakes were replaced with NanoStrand Silver, and a composite containing 55% silver flakes and 5% heat-treated NanoStrand Silver. By heating the NanoStrand Silver, which removes some of the capping molecules from the surface, the resistivity of the composite drops by 86%, while the untreated NanoStrand Silver was able to reduce resistivity by 60%. The results presented in Figure 4 support our hypothesis that the presence of capping molecules on the surface of silver flakes and NanoStrand Silver is the dominant factor in controlling the resistivity of the composite at high concentrations.

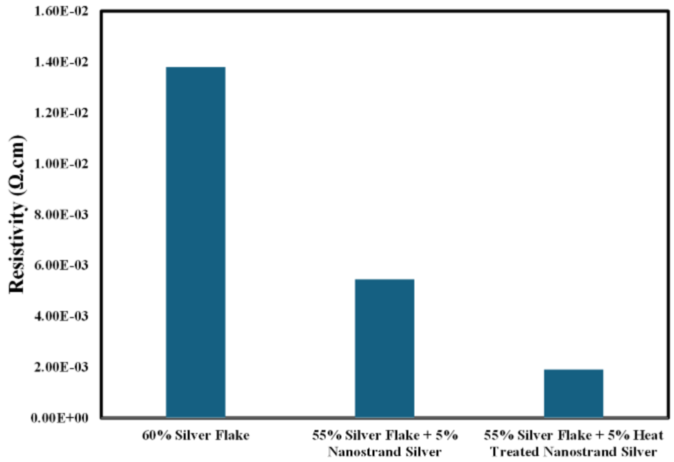

Figure 4: Resistivity of the composite with 60% Silver flake, 55% silver flake plus 5% Nanostrand Silver, and 55% silver flake plus 5% heat treated Nanostrand Silver.

It is well known that the rheology of conductive adhesives is a key property of this material. Conductive adhesives can become ineffective if their viscosity is too low or too high or if they exhibit improper shear thinning or thickening behavior, as this prevents proper dispensing. The adhesive's viscosity was measured to assess the rheological properties when one-dimensional NanoStrand Silver is added. Table 1 reports the viscosity data of the silver flake and combined silver flake and NanoStrand Silver composites. Based on the data presented in this table, replacing silver flakes with NanoStrand Silver increases both the viscosity and the thixotropy index of the product. For example, replacing just 1% of the flakes in a system with 51% total silver by NanoStrand Silver increases the viscosity at 0.5 rpm by approximately four times, while the 5 rpm measurement shows only a 2.8-fold increase in viscosity, leading to an increase in the thixotropy index from 3.5 to 4.8, which is the acceptable range for industrial applications. However, samples with a high load of the NanoStrand Silver show a very high viscosity and thixotropy index, which may be undesirable for practical use.

Table 1: Viscosity and thixotropy index of the silver flake and silver flake plus NanoStrand Silver composites

Silver content	**Viscosity (Cp), 0.5 rpm**	**Viscosity (Cp), 5.0 rpm**	**TI**
Silver flake			
50 %	10770	3065	3.5
51 %	12430	3314	3.8
52.5 %	14810	3911	3.8
55 %	24030	5468	4.4
57.5 %	27340	6379	4.3
60 %	56340	10850	5.2
61 %	57990	11350	5.1
Silver Flake (F) + NanoStrand Silver (N)			
50% F + 1% N	42250	8865	4.8
50% F +2.5% N	91960	19800	4.6
50% F +5% N	160700	31730	5.1
50% F + 7.5% N	281700	42000	6.7
50% F +10% N	243600	28750	8.5
55% F + 2.5% N	79530	17070	4.7
55% F + 5% N	73740	12920	5.7
60% F + 1% N	96930	20050	4.8

III. Conclusion

In this study, we explored the use of NanoStrand Silver as a one-dimensional conductive filler to enhance the electrical conductivity and rheological properties of epoxy resin based conductive adhesives. Our results demonstrated that Incorporating NanoStrand Silver significantly reduces the percolation threshold compared to traditional silver flakes, allowing for similar conductivity at lower total silver concentrations. This is due to the high aspect ratio of NanoStrand Silver, which promotes more efficient formation of conductive networks within the composite. Furthermore, while NanoStrand Silver enhances conductivity, it also increases the viscosity and thixotropy index of the adhesive. Moderate additions of NanoStrand Silver resulted in acceptable viscosity and thixotropy levels suitable for industrial applications, though excessive amounts led to impractically high viscosity. Additionally, surface treatment of NanoStrand Silver reduced the presence of capping molecules, further improving conductivity by minimizing interfacial resistance between the silver fillers. Overall, the findings suggest that NanoStrand Silver offers a promising route for improving the performance of conductive adhesives, balancing high electrical conductivity with manageable viscosity for practical use in electronics manufacturing.

As future work, the compatibility between the surface chemistry of silver flakes and NanoStrand Silver to improve the functionality of the one-dimensional NanoStrand Silver, particularly in enhancing adhesive conductivity at higher silver loadings will be investigated. In addition, the role of the NanoStrand Silver as a thermal conductivity enhancer across varying concentrations and temperatures in this and similar systems will be studied.

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