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Research paper

Highly stretchable and conductive conductors based on Ag flakes and polyester composites

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ABSTRACT

In stretchable electronics, the development of conductors that have high stretchability and low electrical resistance is a crucial technical issue. In this study, we developed a highly stretchable Ag conductor composed of Ag flakes and a polyester binder. We focused on the IR-curing technique to develop the stretchable Ag conductor, which was printed on the polyurethane elastomer substrate. The effects of the temperature and duration of curing on the electrical resistance and electromechanical properties of the Ag conductor were investigated. The electromechanical properties of the stretchable Ag conductor were evaluated in stretching, bending, and cyclic endurance tests. We achieved stretchable conductors with a low sheet resistance of 46 mΩ/sq., a superior stretchability of 150%, and a bending radius of 1 mm. The Ag conductor also exhibited outstanding mechanical durability in the cyclic stretching and bending endurance tests. In this study, the optimized IR-curing duration and temperature were 5 min and 130 °C, respectively. However, in future research, the curing duration could be further reduced by the optimization of the IR parameters. The results of the pencil hardness test and the peel-off adhesion test (i.e., the cross-cut test) indicated that the stretchable Ag conductor had excellent hardness and strength of adhesion between the conductor and the substrate.

1. Introduction

Stretchable electronics have the potential to enable the development of novel devices, such as electronic skins, stretchable circuits, foldable and stretchable displays, stretchable sensors, and wearable devices made of smart textiles [1, 2]. However, achieving the stretchability of component devices and their interconnections is challenging because of the high performance and mechanical stability required. The development of stretchable conductors that interconnect several active devices, such as sensors, silicon chips, and integrated circuits, is a key technical issue. Stretchable interconnections must withstand high mechanical deformation while maintaining high electrical conductivity. Wearable devices must accommodate a large number of repeated deformations associated with body motion without degrading their performance. Several novel approaches have been suggested to improve the stretchability of these interconnections. A common method used to increase stretchability is to develop a relief structure that can compensate mechanical deformations, such as serpentine [3], mogul [4], and helical coil-shaped interconnections [5]. The wavy structure of metal film was developed by prestretching the elastomeric substrate to form buckled metal film [6]. Although these approaches are very useful for absorbing the stress caused by mechanical properties, mismatches of the stretchable elastomeric substrate and the stretchability of the interconnection remain a limitation. Another approach to achieving high stretchability is to develop a conductive nanocomposites filler mixed with the elastomer matrix. Conductive nanomaterials, such as carbon nanotubes (CNTs) [7], Ag nanowires (NWs) [8], and graphene [9] have been used for the conductive filler. High aspect-ratio carbon nanotubes that are uniformly dispersed in a rubber matrix as a conductive filler have also been used [10]. A stretchable conductor with AgNWs embedded in polydimethylsiloxane (PDMS) has been suggested [11]. However, carbon-based nanocomposite materials, such as CNT and graphene, exhibited low electrical conductivity. Recently, metal-based nanocomposites that used metal nanoparticles (NPs) have attracted attention because of their excellent electrical performance. A hybrid composite material of Ag NW and Ag NP in an elastomer matrix was demonstrated to have a highly stretchable interconnection [12, 13]. However, the conductivity of these materials at large strains is still too low to satisfy the requirements of the practical applications of stretchable interconnections. It is considered very difficult to develop a stretchable conductor that satisfies high conductivity and high mechanical stretchability simultaneously because of the trade-off between

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mechanical and electrical characteristics. In an alternative approach, silver (Ag) flakes were used as a conductive filler because of their larger contact area compared with spherical nanoparticles [14–16]. Matsuhisa et al. [17] demonstrated a printable and stretchable conductor that had a conductivity of 182 S/cm and stretchability at a strain of 215% using a nanocomposite material composed of Ag flakes and fluorine rubber. In general, these nanocomposite materials or inks were composed of a conductive filler, a binder (polymer matrix), and a solvent. The synthesis of these nanocomposites with an appropriate mix of fillers in the polymer matrix is crucial for performance and stretchability. Furthermore, these nanocomposite inks typically require that the thermal curing process removes the solvent and organic components from the printed layer in order to form a continuous and conductive metal structure. Because conventional curing methods using a thermal oven or hot plate require long curing times and high temperatures, these methods are not compatible with the process used to manufacture stretchable devices. Several novel techniques were suggested for developing a fast, simple, and cost-effective curing solution, including electrical [18], plasma [19], laser [20], intense pulsed light (IPL) [21], and microwave [22] techniques. However, these approaches have limitations in mass production because of their low throughput, high complexity, and high system cost. Among these techniques, infrared (IR) is considered the most suitable because of its low cost, simple system, easy scalability, and compatibility with the R2R process [23]. Recently, the ultrafast IR drying techniques were presented by several researches. Sowada et al. [24] demonstrated IR drying and sintering of Ag nanoparticles within 1 s. Park et al. [25] also reported the fast sintering of Ag flake within 1.08 s in R2R gravure printing.

In this study, we developed a highly stretchable Ag conductor composed of Ag flakes and a polyester binder. The stretchable Ag conductor was screen-printed on polyurethane (PU) substrate. Infrared radiation was explored as a curing method. The effects of the curing temperature and duration were investigated. The electromechanical properties of the stretchable Ag conductor were evaluated in stretching, bending, and cyclic endurance tests. The hardness and the adhesion of the Ag conductor were also evaluated.

2. Experimental procedure

Stretchable conductor pastes were fabricated by uniformly dispersing microsized silver flakes (HP0202END, Heesung Metal, Korea) in polymer binder. Ag flakes have an average diameter of 2 μm and thickness of 200–300 nm. Fig. 1 shows an SEM image of the Ag flake powder used in this study. Unsaturated polyester resin was used as the polymer binder, which disperses well with Ag flakes. Ethoxyethylacetate (ECA) was used as the solvent. Additives, including a dispersant (BYK-180, 0.7 wt%) and a thermal initiator (benzoyl peroxide, 0.6 wt%), were also used. As a coupling agent, 3-aminopropyltriethoxysilane was used to improve the adhesion of the silver paste. To make the binder, the unsaturated polyester resin and ECA solvent were added at a ratio of 50:50 wt% and stirred at 65 °C for 24 h. After removing the foreign residue and the unmelted resin, the mixture was filtered using a 300-mesh screen. The binder solution then was mixed with silver powder using a high-speed mixer (PDM-300, Daewha Tech, Korea) at 1350 rpm for 30 min until uniform dispersion was achieved. The additives were then added to the binder, which was degassed at 1200 rpm for 5 min. In the final step, the Ag paste was prepared by dispersing the mixture using a three-roll mill (Gyeongyong Machinery Co., Korea) at 25 rpm. The stretchable Ag paste contained 83 wt% of Ag flakes.

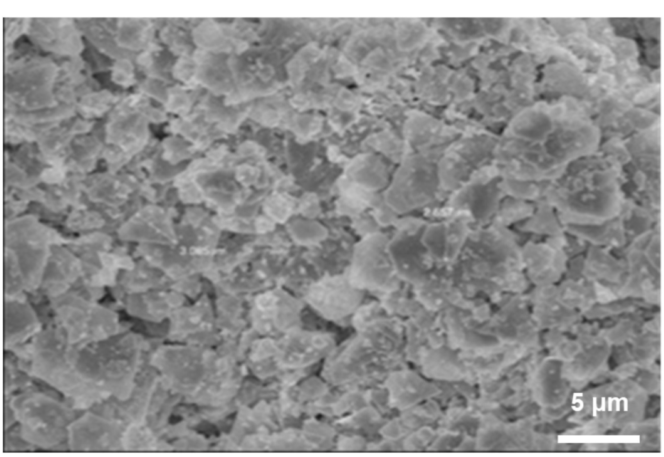

Fig. 1. The SEM image of the silver powders used in this study.

The stretchable conductive paste was screen-printed on polyurethane (PU) elastomer substrate (ESMAR-URS, Nihon matai) at a thickness of 200 μm using a semi-automatic screen printing machine (MT-550TV, Micro-Tec, Japan). PU was chosen as the substrate because of its high stretchability and its high adhesion to the Ag conductor material without the need for additional surface treatment. The thickness of the printed Ag paste film was around 8 μm. A hard squeegee was used to spread and press the paste into the mesh. The squeegee speed and angle were 50 mm/s and 70°, respectively. After printing, the printed Ag paste films were cured using IR irradiation to remove the excess solvent using an IR-curing system (SDKD-IR 400, SDK, Korea). Strip light bulbs (Ceramicx HQE) of 1000 W were used. The IR output wavelength was 6–10 μm, and the distance between the IR lamp and the sample was 120 mm. The temperature of the sample was monitored in real time using a k-type thermocouple sensor inside the IR-curing system. A conventional oven (J-300S, JISICO, Korea) was used as a thermal curing method. It was also used to cure the samples. The curing performances were compared. The IR-curing was conducted at 70, 100, and 130 °C. The thermal curing was conducted at 130 °C. To investigate the effects of the duration of IR-curing, the Ag paste was cured for 1, 3, 5, 7, and 10 min, respectively. The thermal curing was also conducted at 10, 20, and 30 min, respectively. In the IR-curing system, the total length of the curing zone was 2 m; therefore, the moving velocities of the sample in the IR-curing system were 2, 0.66, 0.4, 0.28, and 0.2 m/min, respectively. The sheet resistance of the Ag conductors was measured using a four-point probe analyzer. A field emission scanning electron microscope (FE-SEM, Nova 200) was used to analyze the surface morphology and surface cracks on the Ag paste conductors. The thicknesses of the Ag conductors were measured using an alpha-step surface profiler (Tencor P-11, Surface Profiler) and were confirmed by cross-sectional SEM images.

The electromechanical properties of the stretchable Ag conductor deposited on the PU substrate were evaluated in stretching, bending, and cyclic endurance tests conducted using testers made in the laboratory. Fig. 2 shows schematic drawings of the stretching and bending testers. The long-term cyclic endurance behavior of the stretchable conductors was evaluated by the cyclic stretching and bending endurance tests. The cyclic stretching endurance tests were performed by applying 10,000 stretch/release cycles from 0% to 40% in tensile strains. The possible external effects caused by stretching speed were avoided by performing the test at a low speed of 0.1 mm/s. The cyclic bending endurance tests were carried out at a frequency of 1 Hz for 10,000 cycles. In the cyclic bending tests, the sample was bent from plane (∞) to a specific bending radius in the customized cycles setting. During the tests, changes in electrical resistance were continuously measured by the two-terminal method using a multimeter (34401A; Agilent). The existence of cracks in the films was also continuously monitored with an optical microscope (OM) mounted on the tester. The sample size of the electromechanical tests was $25 \times 10\ mm^2$. Four samples were used in each test.

The hardness of the Ag paste conductor was estimated qualitatively by a pencil test. The pencil test was performed using Mitsubishi pencils according to ASTM standard D 3363 [26]. The pencil was placed on the