Stretchable, Printable and Electrically Conductive Composites for Wearable RF Antennas

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***Abstract*—The rapid growth of wearable electronics has driven the demand for new material solution in electronic packaging. Highly stretchable and electrically conductive composites can be of great use as stretchable conductors in wearable devices. Recently, the reduction in package size and increase in device functionalities have posed more stringent yet challenging requirements for stretchable conductors, including the capability to provide distinctive electrical signals under strains, perform exceptional reliability, and show compatibility with printing technologies to make high resolution patterns. In this work, we have developed a novel conductive composite consisting of a modified elastomer and silver nanostructures that combines high stretchability, conductivity, and printability with fine feature sizes. The formulated composites have been applied in smart wearable bands for Internet of Things (IoT) applications.**

Keywords-Electrically conductive composites; wearable electronics; stretchable; elastomer; printing; silver fillers; RF antennas

I. INTRODUCTION

Recently, wearable electronics have been widely studied due to their potential applications in health monitoring, high frequency communications, flexible light emitting diode (LED) displays, flexible and foldable energy deices [1-10]. To realize functionality of stretchable devices, conductors need to be developed that can performance good electrical property under mechanical strains. Figure 1 shows an example of optoelectronic cells that are made on islands and wired by flexible conductors on a flexible substrate [11, 12]. Among various research, two approaches have been mostly used to fabricate stretchable conductors [12]. The first approach is based on geometric design of wavy (buckled) patterns. Inorganic materials, such as carbons or metals, are deposited on the pre-strained elastomeric substrates in the form of wavy lines. When the strain is released, the non-stretchable materials can be stretched along with the underneath substrate [13, 14]. This approach can transform non-stretchable materials into deformable patterns, but the structural design tends to be complicated and time consuming, particularly for high density designs. The second approach is to incorporate conductive fillers into stretchable polymer matrix to form composite materials [15, 16]. Conductive fillers, including carbon black, carbon nanotubes (CNTs), graphene, conjugated polymers, and different forms of silvers have been adopted [17-21]. The electrical conduction in these polymer composites is explained by percolation theory, in which conductive fillers are brought into close contact to generate electrical pathways at filler loading above percolation threshold [22]. The polymer network are designed to provide flexibility and stretchability to composites.

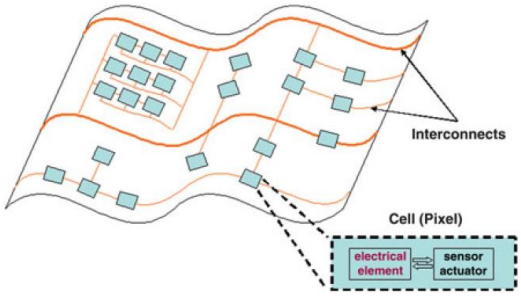

Figure 1. Schematic illustration of the surface of an elastomeric electronic architecture. [11]

Many research work has been done to prepare composites with high electrical conductivity and excellent mechanical properties. Bao's group reported a method to embed ionic liquid additives into conductive polymer matrix to make stretchable films [23]. Generally, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS) has high crystallinity to maintain good conductivity. The introduction of ionic liquid enhancers could soften PSS domains to enlarge fracture strain while ensuring high crystallinity in PEDOT regions for high conductivity via doping. Guo *et al* developed CNTs filled thermoplastic polyurethane fibers by electrospinning [24]. The as-fabricated yarns showed good cyclic stability under stretching and have been attached to human body to monitor joint motions as strain sensors. Lee *et al* fabricated a highly conductive fiber consisting of silver nanowires (AgNWs) and silver nanoparticles (AgNPs) in a styrene-butadiene-styrene (SBS) rubber [25]. The added AgNWs served as conducting bridges between AgNPs, leading to high initial conductivity and conductivity under strains. Someya and coworkers described the fabrication process of a printable and stretchable conductor by *in-situ* formation of AgNPs through mixing with microscale silver flakes, fluorine rubber, fluorine surfactant, and methylisobutylketone

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(MIBK) [26]. Fully printable silver inks were applied for wearable robotics applications, in which pressure or temperature sensors were placed on a polyurethane substrate and wired using stretchable conductors.

Despite rapid advancement in stretchable and conductive composites, there are still technical limitations such as limited current carrying capability and inability to maintain good conductivity in all directions under stretching. To promote further improvement, it is important to control the shape, length scale, surface roughness of fillers that can result in higher electrical properties under strains. Percolation theory of conductive polymer composites can be described by the following equation [27],

$$\sigma \propto \sigma_0 (V_f - V_c)^s \quad (1)$$

where σ is the conductivity of the composite, σ_0 is the intrinsic conductivity of the fillers, s is the critical exponent, V_f and V_c is the filler loading and percolation threshold in volume fraction respectively. Different s values have been reported for different filler shapes: 1.3 for 3D fillers, 2 for 2D fillers, a wide range of values from 1-10 for 1D fillers [22]. Results showed that percolation threshold is dependent on the tunneling current. The percolation threshold for polymer composite filled with various filler shapes have been evaluated based on models [28].

The conductive polymer composites loaded with conductive fillers usually experience large resistance change under mechanical stress. The resistance of a conducting composite usually consists of two main components, the resistance from conductive fillers and the contact resistance between two neighboring particles [29]. For contact resistance, tunneling is the main mechanism for conduction. According to the tunneling model by Simmons [30], contact resistance is given by

$$R_c = \frac{8\pi hs}{3\alpha^2 \gamma e^2} exp(\gamma s), \quad \gamma = \frac{4\pi}{h}\sqrt{2m\varphi} \quad (2)$$

where m is the mass of an electron, e is the charge of an electron, h is Planck's constant, φ is the height of the potential barrier, s is the tunneling distance, α^2 is the effective cross-section area when tunneling occurs, v is Poisson's ratio, and ε is applied strain. Among the three tunable parameters listed above, tunneling distance s is the dominating factor, as the relative resistance change varies exponentially with s. The objective of shape engineering of the fillers is to decrease the tunneling distance during stretching. Generally, silver loading is much higher than the percolation threshold for the composites, so s is already small at the initial state. However, during stretching, the inter-particle distance changes due to the displacement of the fillers. This change is strongly dependent on the shape of fillers.

Figure 2 illustrates the possible distributions of fillers with different shapes both at static state and under stretching. For 0-D spherical fillers, the contact area is only one point. Thus, it is easiest to lose contact for spherical fillers. In the case of randomly dispersed 1-D fillers, e.g. silver nanowires, though they begin with a random network, they will become aligned under the applied stress during stretching. The contacts will be maintained in the stretching direction but the loss of a number of the conduction paths will occur in the other two directions. For 2-D sheets/flakes, the dependence of tunneling distance on the applied strain is mitigated, because the shortest interparticle distance will not change if the local displacement of fillers is in the same plane with flakes. The tunneling distance will only increase when separating the flakes in the direction perpendicular to the flakes themselves. Therefore, we see a lessened dependence on applied strain with the increasing "dimensionality" of the filler particles.

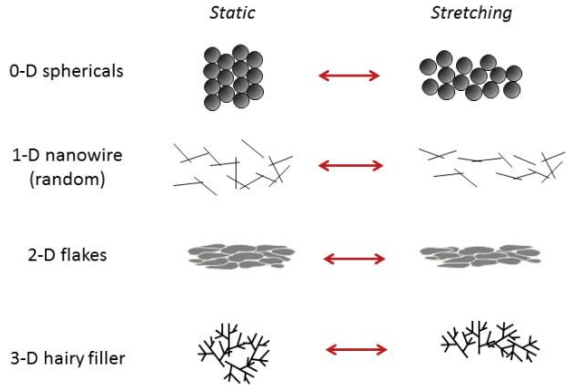

Figure 2. Schematic illustration of silver fillers with various shapes under lateral extension.

In this work, we have developed a scalable and low cost method to synthesize 3D silver structures as conductive fillers. The 3D structures have high aspect ratio branches in every direction, thus a low tunneling distance is maintained regardless of the deformation direction. The secondary or tertiary structures with low temperature sintering capability can reduce the percolation threshold, and increase the roughness of the fillers to mitigate the interparticle separation in the stretching state for improved electrical conductivity. The 3D fillers have been embedded into elastomeric polymer matrix to realize high conductivity under stains. The designed materials have also been applied to make wearable RF antennas.

II. EXPERIMENTAL

A. Materials

The pre-polymer containing isocyanate functional groups were provided by Covestro. The hydroxyl groups based reactant and other reducing agents were purchased from Sigma Aldrich. Silver precursors were purchased from Fisher Scientific and silver flakes were provided by commercial suppliers.

B. *Synthesis and Formulation*

3D silver fillers were synthesized by a simple vibration method. The PU polymer matrix were prepared based on stoichiometric ratio of functional groups. Silver fillers were mixed with the polymer matrix at different loadings and thermally cured.

C. *Characterizations*

Morphology of the silver fillers was characterized by scanning transmission electron microscopy (STEM) with a 200kV cold field emission source. Thermal mechanical analysis (TMA) was used to investigate dimension change of PU resin as a function of temperature during curing. The sample was measured on a TMA Instrument (TA, Q400) with extension mode at a heating rate of 5ºC/min. Lap shear test was conducted on an Instron Microtester according to an ASTM standard. Metal substrate was polished and cleaned before use. The area and height of the bonding area were fixed for all samples. The bonded parts were placed in room temperature for 24 h after the thermal cure before testing.

To measure the resistivity/conductivity, the conductive pastes were coated uniformly on glass slides. The resistance (R) of the cured conductive films was measured by a Keithley 2000 multimeter. The bulk resistivity (ρ) was determined by

$$\rho = R\frac{wt}{l} \tag{3}$$

where w, t, and l are the width, thickness and length of the film. The conductivity (σ) was calculated from reciprocal of the resistivity value. Resistance change under stretching was tested by placing specimens in a tensile test set up and electrical probes were connected to the sides of samples.

III. RESULTS AND DISCUSSION

The material design involves (1) decoration of stretchable polymer chains and (2) incorporation of 3D silver structures as conductive fillers to formulate printable composites. To design polymer network, chain length, curing profiles, modulus, and viscosity of the polymer chains were adjusted to be compatible with the printing process. The low Tg of the elastomer allows easy rearrangement and diffusion of polymer chains to restore the initial strength and modulus. For shape engineering of silver fillers, a simple one-step solution processable method can achieve easy control of silver structures. The morphology of synthesized fillers is shown in Figure 3. Silver fillers with branched structures have larger surface area than silver flakes and nanowires, so wetting in polymer matrix can become an issue. Therefore, surface treatment is necessary to reduce the viscosity of the composite for smooth printing process.

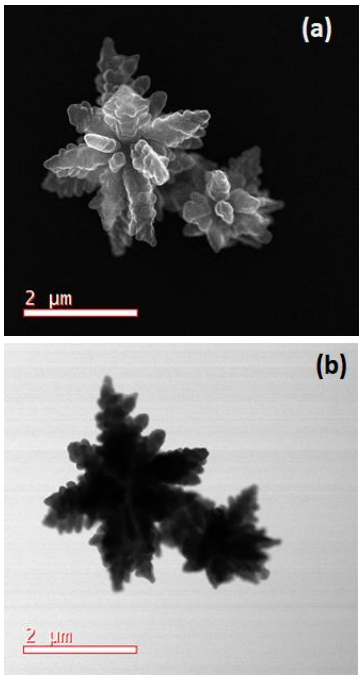

Figure 3. STEM images of 3D silver in (a) SE and (b) TEM mode.

The dimension change of PU resin during curing was monitored by TMA. As shown in Figure 4, the dimension reduction ocurred below 65ºC, and specimen became slowly expanded until 160ºC. It was reported that epoxy and PU resin can experience large shrinkage during curing, and this compressing force contributes greatly to the conductivity enhancement by bringing fillers closer together [31]. In this case, the reduction of sample dimension was not observed at elevated temperature, which can be explained that thermal expansion predominates over the effect of curing shrinkage.

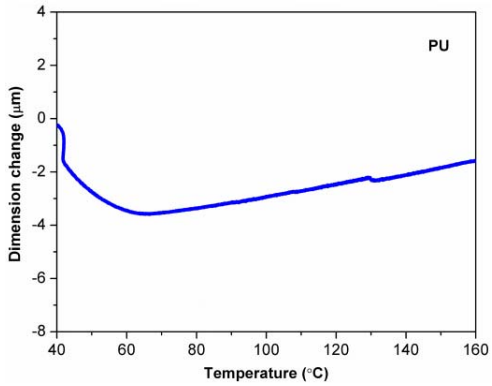

Figure 4. TMA dimension change of PU resin during cure.

Lap shear tests were performed to evaluate the adhesion strength of the conductive composite to metal substrate as interconnect conductor materials. The schematic illustration of lap shear set up was shown in Figure 5a. From Figure 5b, it can be seen that pure polymer showed adhesion load of 122 N, while PU filled with 50 wt% 3D silver showed much higher adhesion load up to 242 N. The improved adhesion

strength may correspond to the stronger interfacial bonding to the metal substrate at the presence of 3D silver. The PU adhesive with the same loading level of silver flake only exhibited a slightly higher load than pure resin, suggesting that highly branched 3D fillers may enable better filling/bonding on substrate surface through atomic diffusion.

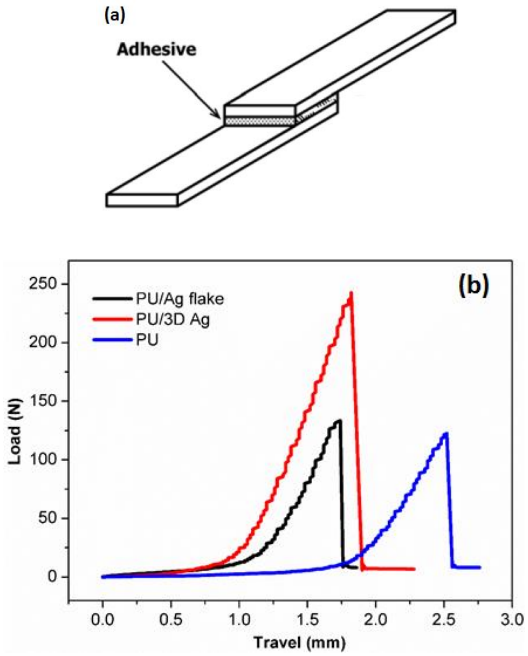

Figure 5. (a) Schematic illustration of lap shear test set up; (b) adhesion strength of PU and composites with load vs travel distance.

Generally, the incorporation of nano-sized fillers can reduce the percolation threshold and introduce more contact points, thus inducing larger contact resistance compared with micron-sized fillers. However, it was found that nano-sized fillers can show sintering behavior at elevated temperature while the polymer resin is cured. When the nanoscale fillers sinter together to form metallic connection, the number of contacts points between fillers will be reduced [29, 32]. Therefore, a lower bulk resistance of the composite can be achieved. For the 3D silver structures, nanoscale branches also showed sintering behavior during thermal cure. Typically, sintering processes are accelerated at higher temperature due to faster atomic diffusion. The effect of temperature on sintering behavior of the fillers and overall conductivity of the formulated composites were studied. As shown in Figure 6, composite cured at 150ºC exhibited the lowest conductivity as a consequence of high contact resistance. Increasing the temperature to 160ºC led to conductivity enhancement with an order of magnitude. The maximum conductivity approaching 10^4 S/cm was obtained at 180ºC. Further increase in curing temperature might cause degradation of the polymer resin, which are not acceptable for real applications.

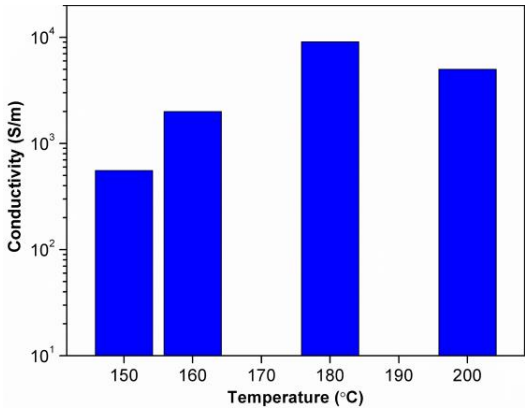

Figure 6. Conductivity of the composites cured at different temperatures.

Conductivity variation of the stretchable composite under tensile strains is shown in Figure 7. At high filler loading, the initial conductivity can reach 2×10^3 S/cm. The conductivity only had a small dropp after stretching. A high conductivity over 10^3 S/cm can be maintained over 30% of strain. The highly branched 3D silver structure with sintering capability upon curing can ensure sufficient electrical contacts and reduce the tunneling distance between fillers under stretching conditions.

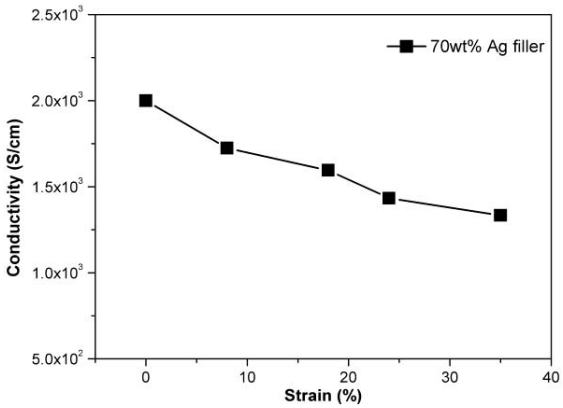

Figure 7. Conductivity of the composite under mechanical strains.

A 1.9 GHz compact planar inverted F-antenna (PIFA) for LTE applications was designed for 2 mm thick polymer substrate. This antenna offers a moderately omnidirectional radiation pattern in a very compact package, and is often used in modern cell phone designs, and remains ideal in wearable, stretchable and flexible designs. The antenna was fed with a coplanar waveguide on a 56 x 52 mm ground plane. The composite was deposited with printing techniques at a thickness of 150 um. Simulations were done in CST STUDIO SUITE. Based on the simulations, a stencil was fabricated using a Form2 3D printer. The stencil was fabricated out of Formlabs Clear material, with a 150 um height printed at 25 um layers. The max directivity was 3.763 dBi (2.01 realized gain) with an efficiency of 66.80%.

Simulated reflection coefficient vs frequency for the 1.9 GHz PIFA antenna on elastomeric substrate is shown in Figure 8.

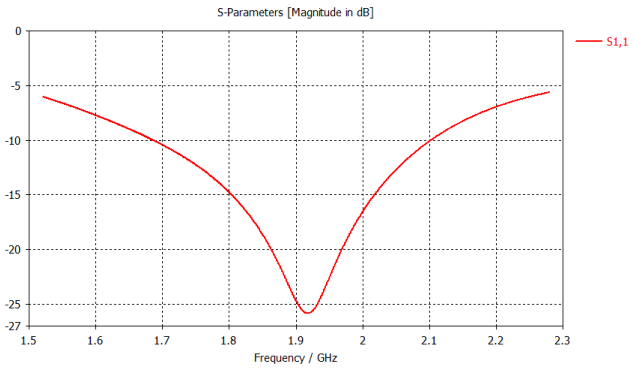

Figure 8. Reflection coefficient vs frequency for the designed antennas with formulated conductive composite on substrate.

IV. Conclusion

In summary, we have formulated a stretchable and conductive composite material by delicate design of elastomeric polymer matrix and shape engineering of conductive fillers. The synthesized 3D silver fillers showed high surface area structures with nanoscale branches. Lap shear test revealed that the filled adhesives exhibited improved adhesion strength to metal substrate, which are a prerequisite when used as interconnect conductors. The sintering characteristics were studied at different temperature. The stretchable composite also demonstrated a high conductivity under mechanical strains due structural and design benefits. Moreover, the composite can serve as stretchable conductors for high frequency antennas. Further modifications on material and structural designs have the potential to realize fully printable and wearable antennas in more complicated electronic packages.

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