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ELECTRICAL AND MECHANICAL BEHAVIOR OF SILVER-COATED POLYMERIC FIBERS

by
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14. ABSTRACT The fundamental behavior of electrically-conductive, silver-coated nylon fibers was studied to understand the relationship between the fiber composition and morphology, tensile behavior, and electrical resistance in the strained state, as well as the post-strained or post-damaged state. Environmental effects on electrical resistance were also studied including immersion in aqueous solutions of various pH levels, as well as exposure to elevated temperatures and thermal cycling. Samples of continuous filament yarns (100 denier base nylon fiber, 34 filaments) were obtained from Saquoit Industries, Scranton, Pennsylvania. The work on the silver/nylon fiber reported here is part of an overall research program that addresses the fundamental electrical and mechanical properties of conductive textile materials.																					
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Preface

This report documents testing carried out on continuous filament, electrically conductive silver-coated nylon fibers (100 denier base nylon fiber, 34 filaments) obtained from Saquoit Industries, Scranton, Pennsylvania during the period November 2005 – November 2006. The results contained in this report were produced by the Macromolecular Science Team, Supporting Sciences and Technology Directorate (SS&TD) in support of In-House Laboratory Independent Research program, "Modeling of Electrical & Mechanical Properties of E-Textiles." The work was funded under Program Element number 611101.91A00, Project number A91A.

ELECTRICAL AND MECHANICAL BEHAVIOR OF SILVER-COATED POLYMERIC FIBERS

1. Introduction

Electro-textiles are under development for use in military uniforms to incorporate signal and power transmission between electronic devices. A significant problem is the interconnection of these devices through traditional cables, which pose snag hazards and reduce the agility and mobility of the soldier. Consequently, electrically-conductive fibrous materials are of considerable interest.

A key objective in e-textiles is the development of conducting textiles which are flexible, comfortable, durable, and function reliably as part of a rugged clothing system. In this study, the fundamental behavior of silver-coated conductive fibers is studied to understand the electro-mechanical response of the material including how manufacturing and end-use conditions may affect the electrical behavior of the yarn/signal conductor.

2. Background

Much of the work in e-textiles has been focused on prototyping and demonstration, rather than studying the underlying mechanics of electrically conducting textile materials; however, fundamental material behavior is essential to developing a science base for e-textiles.

The electromechanical response of conducting textile materials dictates their applicability and feasibility within the area of e-textiles. The resistance/strain behavior of solid metals and metallic alloys is well established¹ where the resistance of a uniform conductor increases with increasing strain. Strain sensitivity is defined as the resistance change per unit of initial resistance divided by the applied longitudinal strain and is given to first order approximation by Equation 1.

$$S = \frac{dR/R}{\varepsilon} = \frac{d\rho/\rho}{\varepsilon} + (1 + 2\nu) \quad (1)$$

Here, ε is the longitudinal strain, ν is Poisson's ratio, and ρ is the specific resistance. Resistance change is due to both dimensional change, as reflected in the $(1 + 2\nu)$ term, and change in specific resistance. The strain sensitivity ranges from -12 to 6 pure metals and from 2 to 4 for metallic alloys. Considering the composite characteristics of the fiber and structure of the coating, we anticipate much different results in the strain sensitivity.

As with any electronic device, exposure to environmental conditions is an important consideration. This is particularly true of e-textiles, where materials will be exposed to a variety of harsh conditions. For functional clothing these conditions include laundering, storage at high temperatures, and climatic conditions.

This work supports efforts to incorporate electro-textiles within Army combat clothing and a range of systems by providing greater understanding of material behavior.

3. Experimental Approach

A technique to measure the electrical resistance of single fibers was developed. Mechanical deformation of the fiber and changes in the fiber structure could pose reliability issues; therefore, the type and degree of damage that develops and the attendant effect on conductivity was investigated. The response to environmental conditions including exposure to aqueous environments and thermal exposure was also studied.

3.1. Structure and Morphology

The conductive fibers are composed of a nylon 6.6 base fiber coated with a thin layer of silver by electroless deposition. The coating morphology was observed by imaging using scanning electron microscopy (SEM).

3.2. Mechanical Properties

Tensile testing of the coated fiber and substrate nylon fiber was performed to obtain strength and elongation-to-break data. Tests were performed on an Instron 5500 Universal testing machine following ASTM standard D3822 for Single Textile Fibers.

3.3. Electrical Properties

Conductivity of single fibers and multifilament yarns were measured on a custom built apparatus using a two-point probe method. Samples were tested by applying a known current through the fiber by means of contact with copper wire leads and measuring the voltage drop per length with a digital multi-meter (see Figure 1).

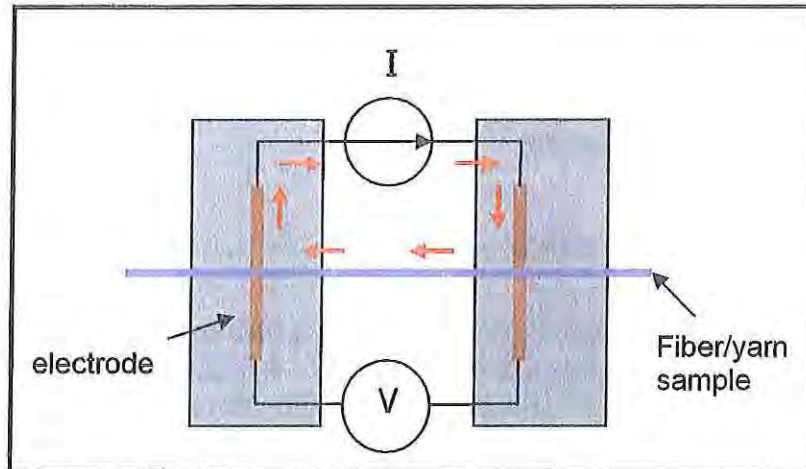


Figure 1. Test fixture for electrical conductivity measurements.

The electrodes on the test fixture are positioned on separate platforms: one fixed and the other free to translate in the axial direction of the specimen such that electrical measurements can be made during application of static strain. Calibration weights were placed at specimen-electrode crossover points to insure good electrical contact and prevent fiber slippage under strain. Fibers were preloaded with calibration weights to eliminate crimp.

3.4. Mechanical Strain-Single Loading

The conductivity of single fibers was measured as a function of strain in order to quantify piezoresistive behavior. Fibers of one inch gauge length were loaded and unloaded for prescribed durations to reveal hysteresis effects which could alter the electrical response. Three sets of tests were performed where samples were strained to 5, 10, and 15 percent. A low current level of 0.1 milliamps was chosen to prevent heating of the fiber, and was used throughout the test. Electrical resistance was recorded in the unstrained state. Using the translating stage, fibers were strained to the specified level, held for one minute, and then returned to gauge length. Resistance measurements were made at each stage. Following the release of mechanical strain, resistance measurements were made after one and two minute durations, allowing elastic recovery of the fiber.

3.5. Mechanical Strain-Cyclic Loading

Electrical measurements were made before and after strain cycling at a variety of strain amplitudes to compare the performance of single and multifilament yarns, and to identify damage thresholds. Using the Instron® universal testing machine, cyclic loading at large strain amplitude (10 percent elongation) was performed on both single fibers and multifilament yarns for 10

cycles. The work was extended to determine the threshold for strain amplitude in the multifilament yarns. Low to moderate strain levels were tested, while the number of cycles was kept constant at 10 cycles (sample size 30 for each test series).

3.6. Durability with pH Exposure

The durability of the multifilament yarns was further evaluated by immersing them in aqueous solutions of pH levels 2.6, 4.6, 6.0, 8.8, and 10.1 for durations of 1, 2, 4, and 6 hours. Solutions were prepared by diluting sodium hydroxide and hydrochloric acid (Aldrich) with deionized water. The solutions were adjusted with an acetic acid buffer to attain the desired pH. The pH of the solutions was measured using a digital pH meter. After treatment, samples were rinsed with deionized water and dried for 24 hours under ambient conditions, and electrical resistance measured. A sample size of 10 was used for each combination of factors.

3.7. Effect of Thermal Exposure and Thermal Cycling

The effect of prolonged exposure to elevated temperature and thermal cycling was examined for the multifilament yarns. Coated yarns were heated in a Lab-Line vacuum oven (model no #3608-5) just beyond their glass transition temperature (T_g) for a 6 hour period and allowed to cool to room temperature.

The effect of thermal cycling was investigated by heating yarns to their T_g for 10 cycles, holding for 20 minutes, and cooling for 10 minutes. A sample size of 30 was used in each experiment.

Differential scanning calorimetry (DSC) was performed on the coated fiber to determine the degree of crystallinity of the base fiber and to determine the T_g to be used for thermal cycling experiments. DSC was also performed on the base nylon fiber to observe any differences due to the presence of the coating.

4. Results

4.1. Structure and Morphology

Images of the silver cladding obtained through SEM suggest a porous, fine particle structure rather than a continuous solid film (see Figure 2).

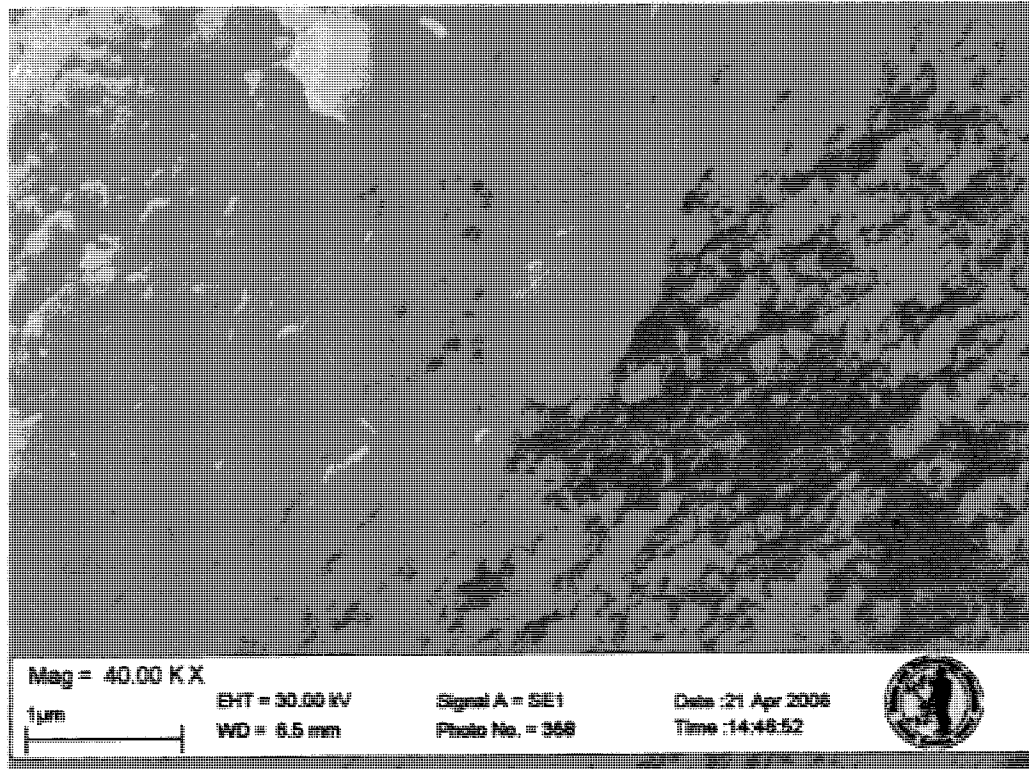


Figure 2. Surface morphology of nylon base fibers, coated with silver by electroless deposition.

In the electroless deposition process, metal ions are directly reduced into metals by the introduction of a reducing agent.

The fiber diameter is approximately 17 microns with a very thin silver coating. From manufacturer's data of fiber denier, the ratio of thickness to fiber radius is $\sim 2:100$.

4.2. Mechanical Properties

Tensile strength and elongation to break for the coated fiber are slightly lower relative to the base fiber (coated fiber: 15 gf, 37%; base fiber: 16 gf, 41%). The fiber coating process consists of knitting the base fibers, applying the coating, then un-knitting; therefore, minor differences in tensile properties may be attributed to damage incurred during processing.

4.3. Electrical Properties

We were interested in measuring the resistance of single fibers and whether, in fact, the fibers demonstrate Ohmic behavior, where voltage and current are proportional.

Conductivity of single and multifilament yarns was linear over a wide range of applied currents. There was some variability in the measurements between individual fibers, possibly due to damage incurred during processing, and non-uniformity in the conductive coating along the fiber length; however, tests were repeatable such that all demonstrated Ohmic behavior. The average resistance per length of fibers and yarns was 205.3 ± 17.0 ohms/in and 5.8 ± 0.36 ohms/in respectively, in agreement with manufacturer's specifications of $R < 260$ ohms/in for multifilament yarns.

4.4. Mechanical Strain-Single Loading

We expected that the fiber's electrical response to strain would be quite different than that of a typical metal or alloy since the coated fiber is a type of composite structure-where each component will contribute to its behavior. Specifically, the base fiber dictates the mechanical response, an important aspect of which is viscoelasticity and the conductive coating governs the electrical response, where the particulate configuration will rearrange with movement of the base fiber. Resistance change of fibers under applied static strain was measured and results are shown in Figure 3.

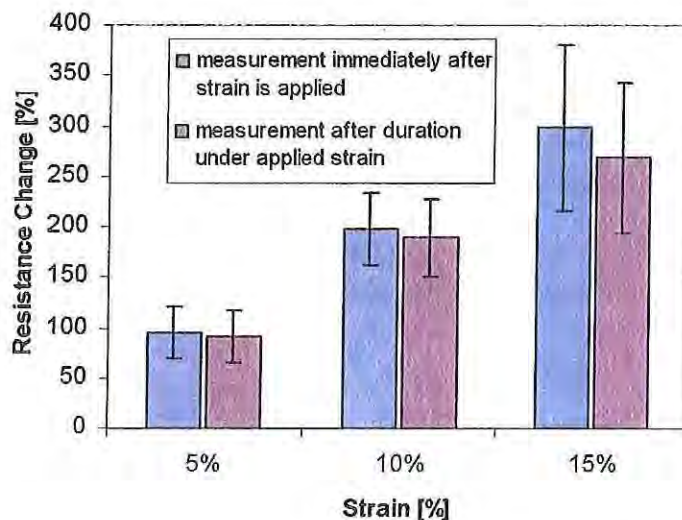


Figure 3. Percent change in resistance of single fibers from reference state (average of 10 samples).

The first measurement was made immediately after application of the strain to the fiber, and demonstrates the sensitivity of the fiber to dimensional change. The resistance should increase proportionally with length and modestly with decreasing cross-sectional area due to the Poisson effect; however, the changes observed were greater than what can be attributed to geometry alone. We presume that the elongation of the base fiber causes the particle

configuration of the conductive surface to change, altering the specific resistance of the fiber.

For the second measurement the fiber was held at constant extension for one minute, and a drop in resistance was observed with time. The change was shown to be statistically significant by repeated measures analysis of variance. The viscoelastic deformation response of the nylon substrate may be the cause, where the time dependent, increasing Poisson's ratio causes further thinning of the fiber. We suspect that as the fiber relaxes and becomes thinner, particles move closer together circumferentially, causing the specific resistance of the fiber to decrease.

Using the first set of measurements, the dimensionless resistance change versus strain was plotted (see Figure 4).

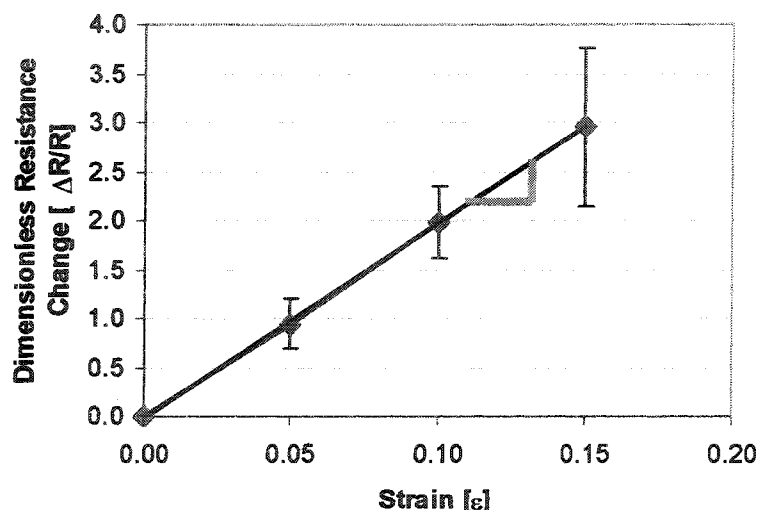


Figure 4. Dimensionless resistance change from reference state.

From the slope of the curve, the strain sensitivity was found to be approximately 20. In discontinuous silver films strain sensitivity values of 10-300 have been reported². Similarities between the silver coated fiber and island films may be seen in the strain sensitivity, where the particulate microstructure dictates the electrical behavior.

After the previously described resistance measurements at 5, 10 and 15 percent strain, the fibers were returned to gauge length (i.e., zero extension) and electrical resistance measurements were made immediately, and after elapsed times of one and two minutes (see Figure 5).

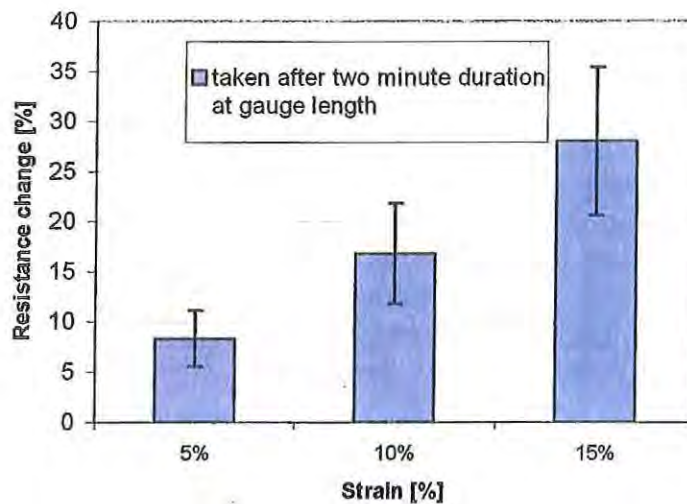


Figure 5. Percent change in resistance of single fibers from reference state following two minute relaxation.

Electrical resistance decreased significantly after the strain was removed from the fiber, and continued to decrease over time. The magnitude of the resistance change and its time dependence was consistent with the viscoelastic recovery behavior of the fiber.

4.5. Mechanical Strain-Cyclic Loading

The change in resistance following cyclic loading at large strain amplitudes (10 percent elongation, 10 cycles) was statistically significant for both single and multifilament yarns. Resistance increase was higher for the single filament samples, which can be attributed to loss of connectivity due to damage of the coating surface. In the case of multifilament samples, the impact of surface damage is less dramatic since percolation can still occur by alteration of the current path along any of the fibers.

The damage threshold for the multifilament yarns was investigated by cycling at a range of strain amplitudes and measuring the resistance. At 1% strain, resistance change was not significant while at 5% conductivity decreased. The threshold was found to be in the 3 to 3.5% strain range. This result is consistent with stress-strain diagrams which show a slope change in this range, indicating the onset of plastic deformation and physical disconnection of surface particles.

4.6. Durability with pH Exposure

Over the range of acidic and basic conditions tested, repeated measure analysis of variance indicated that neither the effect of pH nor time were statistically significant.

This result is significant because exposure to environmental conditions and laundering are important issues for electrot textiles.

4.7. Effect of Thermal Exposure and Thermal Cycling

Differential scanning calorimetry (DSC) was performed to determine the degree of crystallinity of the base fiber. Thermal expansion occurs with swelling of amorphous regions in the base fiber, which could cause cracking or separation of the coating. The exothermic peak for glass transition was not prominent; indicating that the fiber is highly crystalline and swelling will be minimal. There was no discernable difference between the results for coated and uncoated fibers. A reference value of 120 °C was used for the thermal exposure and cycling tests.

Prolonged temperature exposure and thermal cycling tests had no adverse effect on conductivity. In fact, single factor statistical analysis of the data revealed that resistivity increased in each case. Any adsorbed water or oxide present on the surface would hinder electrical contact, which may have been removed during heating.

5. Conclusions

We have shown in this study that the piezoresistant behavior of the silver-coated fibers is dependent on the mechanical behavior of the base fiber as well as the surface microstructure, where resistance changes can be attributed to both dimensional change and surface particle separation. Fibers used in apparel fabrics are not normally subjected to large induced strain. The weave or knit of the fabric, composition of yarn, and yarn crimp allow give in the garment; therefore, the strain in the individual filaments is low relative to the fabric strain. Nevertheless, any imposed strain in the fibers and subsequent changes in the electrical resistance will pose reliability issues. Following removal of the applied strain, fibers recovered and electrical conductivity was almost completely restored; however, the response time is much too great for the fibers to be used in any practical applications. A plausible solution may lie in the design of novel yarns or fabric structures, where the configuration eliminates most or all of the induced strain. Simple solutions may be reached by exploiting the flexibility of the fibers, e.g., fabricating highly crimped or coiled yarns encased in a protective polymer coating. Recommendations for further work may include design of creative yarn structures and evaluation of their strain sensitivity.

Fibers demonstrate no adverse effects, and actually exhibit improved electrical performance following thermal exposure. Consequently, cleaning the fiber surface of adsorbed impurities and applying a protective coating to the yarn may be beneficial in obtaining optimal performance.

6. References

¹ Dally, James W., and Riley, William F., *Experimental Stress Analysis*, 2nd Edition, McGraw-Hill, Inc., New York, NY, 1978

² Pattabi, Manjunatha, and Rao, K Mohan, The Effect of Overlayers on the Stability of Discontinuous Silver Films Deposited on Softened Poly(2-vinylpyridine) Substrates, *J.Phys. D: Appl. Phys.*, **31**, pp. 2412-2415, 1998.

