Effect of water immersion, laundering, and abrasion on the conductivity of reduced graphene oxide coatings on aramid fabrics

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Abstract. Opportunities for developing end-of-life sensors for fire resistant fabrics are explored using reduced graphene oxide coatings on textiles. Fire resistant fabrics are known to experience significant losses in performance over time. Large reductions in mechanical properties have also been recorded when these fabrics were subjected to accelerated aging conditions simulating the use in service. In addition, the fabric loss in performance may exceed the safety requirement threshold before any sign of damage is visible to the naked eye. Electrically conductive coatings and tracks were prepared on an m-aramid woven fabric using graphene oxide that was further reduced. The preparation technique allowed wrapping the individual aramid fibers with rGO sheets. No significant change in sheet resistance was recorded after up to 120h of immersion of the rGO-coated fabric specimens in water. An increase in resistance after 10 accelerated washing cycles was measured on the rGO-coated specimens prepared with 5 coating cycles while no significant effect was detected for specimens prepared with 10 and 15 coating cycles. Under abrasion exposure, the electrical resistance of rGO tracks increased gradually until 150 cycles, after which the conductivity dropped abruptly. These results show the potential of reduced graphene oxide applied as a coating on m-aramid fabrics to prepare end-of-life sensors for fire resistant fabrics.

1. Introduction
Graphene is well-suited to flexible electronic applications. The oxygen-containing functional groups of graphene oxide have allowed good bonding to be achieved for coatings prepared on fabric materials of natural (cotton, wool) and synthetic origin (nylon, polyester, para-aramid) [1]. After reduction of the graphene oxide, a reasonable electrical conductivity can be obtained. The main application of these coatings is strain gauges and heaters.

Opportunities for developing end-of-life sensors for fire resistant fabrics are explored using reduced graphene oxide coatings on textiles. Fire resistant fabrics, which are made with high performance fibers such as para- and meta-aramids, polybenzimidazole, and polybenzoxazole [2], are known to experience significant losses in performance over time, for example when used in firefighter protective garments [3]. Large reductions in mechanical properties have also been recorded when these fabrics were
subjected to accelerated aging conditions simulating the use in service, for instance thermal [4], UV [5], moisture [5], and exposure to a combination of abrasion and laundering cycles [6]. In addition, the fabric loss in performance may exceed the safety requirement threshold before any sign of damage is visible to the naked eye [7].

This study investigates the production of conductive coating and tracks on aramid fabrics using graphene oxide and their stability upon exposure to water immersion, laundering and abrasion.

2. Material and Methods
Reduced graphene oxide (rGO) coatings were prepared on a meta-aramid woven fabric (2/1 twill, 222 g/m²) using a technique described in [8]. Fabric specimens were first dipped in a graphene oxide solution (4 wt%) for 15 min and dried at 65°C for 30 min. Then, the graphene oxide coating was reduced by immersion in L-ascorbic acid at 90°C for 4 hours, rinsed in DI water and 2-propanol, and dried at 80°C for 30 min. This dip-dry-reduce process was repeated for a number of times (up to 15 times). Between each coating cycle, the rGO flakes not firmly attached to the fabric substrate were removed with adhesive tape.

Rectangular rGO tracks were also prepared on the fabric surface by covering the backside of the fabric with a wax film (figure 1). The specimen was then sandwiched between two acrylic molds, a solid one located on the specimen face covered with the wax film and the other one with cutout tracks. The GO solution was deposited on the patterned specimen areas using a pipette. The rest of the process was the same as when coating the entire fabric.

![Figure 1. Preparation of rectangular rGO tracks on fabric samples a) wax layer deposition, b) patterning and reduction process [8].](image)

The durability of the rGO coating on the m-aramid fabric was assessed by immersing specimens in DI water at room temperature for 5 successive 24h periods, for a total of 120h. Between each immersion, the specimens were dried at 65°C for 30 min and their sheet resistance measured with a 4-point probe. The washing fastness was assessed using a Launder-Ometer according to the ISO 105-C06 test method (test procedure A1M). After being subjected to a defined number of accelerated washing cycles (up to 10), the specimens were rinsed with DI water and dried at 65°C for 15 min before their sheet resistance was measured. For the determination of the abrasion resistance, fabric specimens with three 1.5cm wide
rGO tracks were abraded for a defined number of cycles with a Martindale Abrasion Tester using the standard wool abradant fabric at 47.5 rpm according to ASTM D4966. The residual electrical resistance of the conductive tracks was monitored. All measurements were performed in triplicate. Complementary imaging was carried out by field emission scanning electron microscopy (FE-SEM) and helium ion microscopy (HIM).

3. Results and discussion

3.1. Initial condition
In an unaged condition, the rGO coating on the m-aramid fabric exhibited a sheet resistance of about 860 kΩ/□ after 5 dip-dry-reduce cycles with an add-on ratio of 6.8% [8]. After 10 cycles, the sheet resistance decreased to 310 kΩ/□ and the add-on value increased to 8% (figure 2). They reached about 225 kΩ/□ and 9.2% after 15 cycles. Figure 3 illustrates that each individual aramid fiber is wrapped by rGO sheets. This is attributed to the removal of the loose rGO flakes between each dip-dry-reduce cycle. It is essential to ensure that the bending of the fabric during normal use does not lead to a premature decrease in the electrical conductivity of the coating.

Figure 2. rGO add-on (left axis) and sheet resistance (right axis) as a function of the number of coating cycles.

Figure 3. HIM image of an rGO-coated m-aramid fiber [8].
3.2. Effect of water immersion
The effect of water immersion was studied with specimens prepared with 15 coating cycles. No statistically significant difference in sheet resistance (p-value of 0.73) was obtained between the 5 successive 24h periods of water immersion. This could be attributed to the scaly nature of the rGO coating around each fiber, with free spaces being able to accommodate the potential slight increase in the aramid fiber volume due to moisture absorption. In addition, the individual graphene sheets may have some ability to slide relative to each other.

3.3. Resistance to laundering
When exposed to 10 successive washing cycles (corresponding to 50 domestic launderings), rGO-coated fabric specimens prepared with 5 coating cycles showed an increase of 50% in the sheet resistance (figure 4). This was attributed to damages suffered by the rGO coating as a result of the washing cycles; FE-SEM inspection of the surface revealed cracks in the rGO coating and partially delamination of the rGO sheets. On the other hand, no statistically significant change in the sheet resistance with the number of washing cycles was obtained when the specimens were prepared with 10 (p-value of 0.16) and 15 (p-value of 0.29) coating cycles. The coatings did not show any signs of cracking or delamination either.

3.4. Effect of abrasion
The rGO coating behavior under abrasion is illustrated in figure 5. The three series of data correspond to the three tracks formed on each fabric specimen (prepared with 15 coating cycles). The electrical resistance of the tracks increased gradually with the number of abrasion cycles. Above 50 abrasion cycles, the track situated in the center of the specimen experienced a larger decrease in conductivity, which was attributed to an imperfectly distributed stress applied across the specimen width by the foam padding inserted between the fabric specimen and the sample holder. Figure 5 also shows a dramatic increase in resistance for all three tracks above 150 abrasion cycles. At that point, the ability of the rGO conductive tracks to conduct electricity was completely lost.
4. Conclusion

Electrically conductive coatings and tracks were prepared on an m-aramid woven fabric using graphene oxide that was further reduced. The preparation technique allowed wrapping the individual aramid fibers with rGO sheets. No significant change in sheet resistance was recorded after up to 120h of immersion of the rGO-coated fabric specimens in water. An increase in resistance after 10 accelerated washing cycles was measured on the rGO-coated specimens prepared with 5 coating cycles while no significant effect was detected for specimens prepared with 10 and 15 coating cycles. Under abrasion exposure, the electrical resistance of rGO tracks increased gradually until 150 cycles, after which the conductivity dropped abruptly. These results show the potential of reduced graphene oxide applied as a coating on m-aramid fabrics to prepare end-of-life sensors for fire resistant fabrics.

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