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Carbon-Nanotube Ink and Laser Engraved Lignin on Fabrics for Wearable Electronics

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ABSTRACT

With technological advances occurring worldwide, wearable electronics have garnered significant attention within diverse fields, from medical to industry. Carbon Nanotube (CNT) ink has had a big impact on these applications of e-textiles. Conductive patterns can be made by printing the CNT ink directly on fabrics. However, a new process and chemical have been tested, where alternatively, a conductive pattern can be applied by laser burning of a lignin-coated layer over a piece of fabric. In this work, we evaluated the quality of patterned laminated polyester ripstop fabric with the two methods of silk screen printing of the CNT ink and the laser burning of lignin. A major focus within these two methods is their resistance values. CNT ink has succeeded with a lower four-probe resistance of about **19.69** $\Omega/\square$, making it preferable for wearable applications. However, patterning can become an issue when coating CNT ink. Laser burning has its pros and cons: while it can be much simpler to pattern, it has a much higher four-probe resistance of about **49.21** $\Omega/\square$. In this study, the laser power and rastering are evaluated and compared to the resistance values of CNT ink coating. With this success, further testing on different fabrics and patterns can lead to more inexpensive yet efficient applications and devices.

Keywords: Laser engraved lignin, CNT Ink, E-textiles, Wearable Electronics

1. INTRODUCTION

Electronics and fashion trends are evolving every day; however, the integration between the two is a new groundbreaking novel. Electronic textiles (e-textiles) mount electronic components onto fabrics by simple patterning to advance countless industries. Carbon nanotube (CNT) ink has had multiple successes with e-textiles, but the natural polymer lignin is evolving in this industry. The traditional use of CNT ink is heavily dependent on its great electrical conductivity and mechanical properties leading to wearable electronics such as non-invasive health monitoring systems [1]. In fabricating these devices, durability and flexibility are questioned for long-term sustainability. The revolution of e-textiles is to have a waterproof, flexible, and cost-efficient fabric integrated with electrical components reading low resistance.

While CNT ink-coated fabrics may follow this requirement of e-textiles, laser-engraved lignin has been introduced, being eco-friendlier and more compatible on a plethora of fabrics. Lignin's low-cost, renewable, mechanically and thermally stable properties led to the experimentation of lasering patterns onto a lignin-coated fabric. A CO_2 laser machine can transform these lignin films into porous graphene overcoming the conventional processes for creating graphene-based wearable electronics [2]. A sufficient laser power can transform lignin to possess electroconductive features to pattern a specific design or circuit using a CAD tool. This step of engraving a particular design while exposing laser irradiation to the fabric simultaneously is a quick procedure that gives design capability for various fields. Currently, studies are being done on lignin laser lithography, which can design micro-supercapacitors that provide good electrochemical properties, capacitance, volumetric energy density, and power density [3]. This laser writing onto lignin-coated electrodes has maintained flexible properties through bending deformation when fabricating supercapacitors without lowering capacitance, cyclic stability, or electrochemical performance [4]. These semi-conductive patterns produced from laser engraving lignin can obtain lower resistive pathways by hydrogen evolution assisted (HEA) electroplating [5]. We have done previous testing on this polyester ripstop fabric to grow lateral growth of copper to fabricate

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electroconductive flexible substrates using HEA electroplating [6]. This process should now be replicated for wearable sensors and electronics at a larger production with lignin coated fabrics. Laser-engraved lignin is positively progressing; however, it must be compared to previous work and other novel solutions, in this case, CNT ink.

To compare conductive patterns made of CNT ink and laser induced graphene, we have tested numerous materials that could hold lignin/CNT ink upright. In this study we present the results from flexible yellow laminated ripstop. This fabric consists of nylon and polyester, a combination of a breathable and waterproof fabric, which would be great for an everyday t-shirt. The yellow laminated ripstop was tested to isolate lignin's washability and flexibility properties on a fabric that already has these characteristics. In this analysis, CNT ink was required to be capable of withstanding on this ripstop fabric as well for comparison. The same procedure of coating and tests were performed on another fabric, 100% polyester white upholstery fabric, to display the versatility of lignin on various fabrics compared to CNT ink.

In this review, the universal use of CNT ink has been compared to laser-engraved lignin for the future of e-textiles. While different in their production, both carbonaceous materials are known to be affected by abrasion, temperature, and washing [7]. Our work tested this by measuring resistance values before and after several destructive tests, including bending, rolling, washing, and ironing. These tests were done to reflect the abilities of the solutions and fabrics towards their possible use in wearable electronics. As an end goal, one might wear a sensor integrated into their everyday t-shirt, experimentation is required to ensure the conductive and flexible features remain after washing and ironing a dirty, wrinkly t-shirt. The future of wearable electronics is evolving, and the integration of laser-engraved lignin is essential to moving forward with batteries, biosensors, and telemedicine systems that can be durable yet electrically stable.

2. EXPERIMENTAL DETAILS

2.1 Materials and equipment

Kraft Lignin powder was purchased from Sigma Aldrich and then mixed with deionized (DI) water for the lignin solution. Multi-walled Carbon Nanotube (MWCNT), Sodium Dodecylbenzene sulfate (SDBS) was purchased from Sigma to construct the CNT solution required for the second half of the experiments. These solutions were coated onto VX25 X-PAC laminated ripstop fabric-HIVIS Yellow purchased from Rockywoods and then further tested on a Top Gun FR 765 white solids 100% polyester upholstery fabric purchased from Kovi Fabrics. A probe sonicator is required for mixing the compounds of the CNT solution. An OMTech 40W CO_2 laser engraving machine was used in this study. To perform one of the destructive tests, a Rival 11570 iron was used. A Keithley 2602A instrument was used to carry out resistance measurements using the 4-point probe method.

2.2 CNT ink synthesis and application

To synthesize CNT ink, 300 milligrams of multi-walled carbon nanotube (MWCNT), 150 milligrams of SDBS, and 30 milliliters of distilled (DI) water were added into a test tube, it was placed into a beaker full of ice and positioned under a probe sonicator. The sonicator was turned on for 30 minutes at a power of 35 milliwatts to then be used as the CNT ink solution for coating onto fabrics [8]. To apply the CNT ink onto the yellow ripstop, a 40mm x 5mm rectangle mask was made using Kapton tape to cover the bottom and top of a 40mm x 20mm piece of fabric. Once taped up, 40 µL of CNT ink was applied onto the exposed area and left in a fume hood to dry for 24 hours. This coating and drying process was repeated for three times for a total application of 120 µL, shown in Figure 1. This timely process was to ensure even coatings resulting in low resistance values. An initial measurement was taken once the sample was dry and then consecutively after multiple destructive tests to study the flexibility and durability of the coated fabric. A pluggable USB digital microscope was used to inspect the fabric weaving and whether the coatings were even before and after each test. In Figure 1a, the bare fabric of yellow ripstop is shown with (b) the even-coated CNT ink. This same procedure was then tested on a looser woven white fabric only containing polyester to ensure CNT ink was also compatible with other fabrics. This coating is displayed in microscope and camera images in Figure 1, displaying plain white polyester and 120 µL coating of CNT ink which is clear to have not coated the full fabric with empty white spaces.

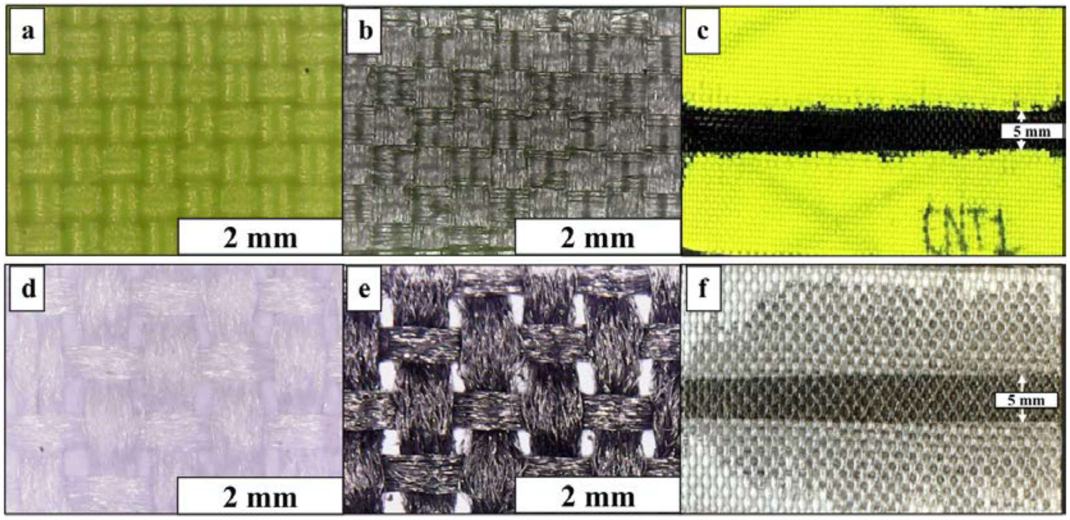

Figure 1: Microscope image of (a) plain yellow ripstop fabric, (b) yellow ripstop fabric coated with CNT ink, (c) camera image of yellow ripstop fabric coated with CNT ink, microscope image of (d) white polyester fabric, (e) white polyester fabric coated with CNT ink, (f) camera image white polyester fabric coated with CNT ink.

2.3 Lignin solution synthesis and application

Studying other alternatives that are suitable with various fabrics, lignin was experimented on using different laser powers and fabrics. Using lignin in powder form, it was challenging to find chemicals to create an appropriate gel mixture that would still possess the natural properties of lignin. Polyvinyl (PVA) gel was heavily experimented based on previous studies to create a gel layer onto fabrics however PVA consists of synthetic polymers which was not fitting for the eco-friendly lignin solution [9]. After studying various methods, simply adding water to the powder was studied. This resulted in the suitable solution of 1 gram of lignin mixed in a beaker with 5 milliliters of DI water. After stirring till a homogeneous mixture formed, 65 µL of lignin were coated on the 40mm x 5mm rectangle on the taped up 40 mm x 20 mm piece of yellow ripstop. This was left to dry in a fume hood for 24 hours and then patterned at 5% and 7% laser powers to find the best resistance values. At the time of testing, a rectangle was the most efficient pattern and the quickest way to design samples to compare to the CNT ink samples with. The 40 mm x 5 mm rectangular pattern was created in the software LaserDRW and then lasered and rastered onto the fabric. Numerous experiments were conducted focusing on various laser powers, speeds, and rastering to isolate each step of the process. The laser power of 5% and 7% were the focus for this study with a consistent laser speed of 100 milliseconds and rastering the pattern twice. Figure 2 shows a coating process of the lignin solution onto the yellow ripstop with microscopic and camera images. This figure also displays the coating of lignin onto the 100% polyester fabric which is “stamped” once lasered proving an even coating on this fabric as well.

3. RESULTS AND DISCUSSION

3.1 Resistivity (Ω/□) measurements

To assess the electroconductive coatings on the fabrics, the 4-point probe method was used on a Keithley 2602A to measure resistance. This method sends current through the two outer pins measuring voltage in the two inner pins to provide the sheet resistance, in Ω/□, of the conductive coating. These measurements were taken before any coating onto the fabrics which, as expected, had no resistance. Since the procedure for each solution differs, resistance measurements specifically for CNT ink-coated fabrics were taken only after the coating was dry and after each destructive test. Simply coating the yellow ripstop fabric with CNT ink and leaving it to dry for 24 hours showed resistance values averaging around 19.69 Ω/□ This was further tested on the white polyester to ensure the variability of CNT ink onto other fabrics but did not remain consistent. Visually from the very first coating, as seen in Figure 1c, CNT ink was bleeding through the taped-up sides which exemplified this looser fabric could not be tested on repeatedly to get consistent coatings for a close range of resistance values. This led to only testing CNT ink onto the yellow ripstop as the white polyester measured inconclusive values from the first step of coating. This proved that CNT ink has greater efficacy onto the yellow tightly woven nylon-polyester ripstop, however not onto white loosely woven polyester.

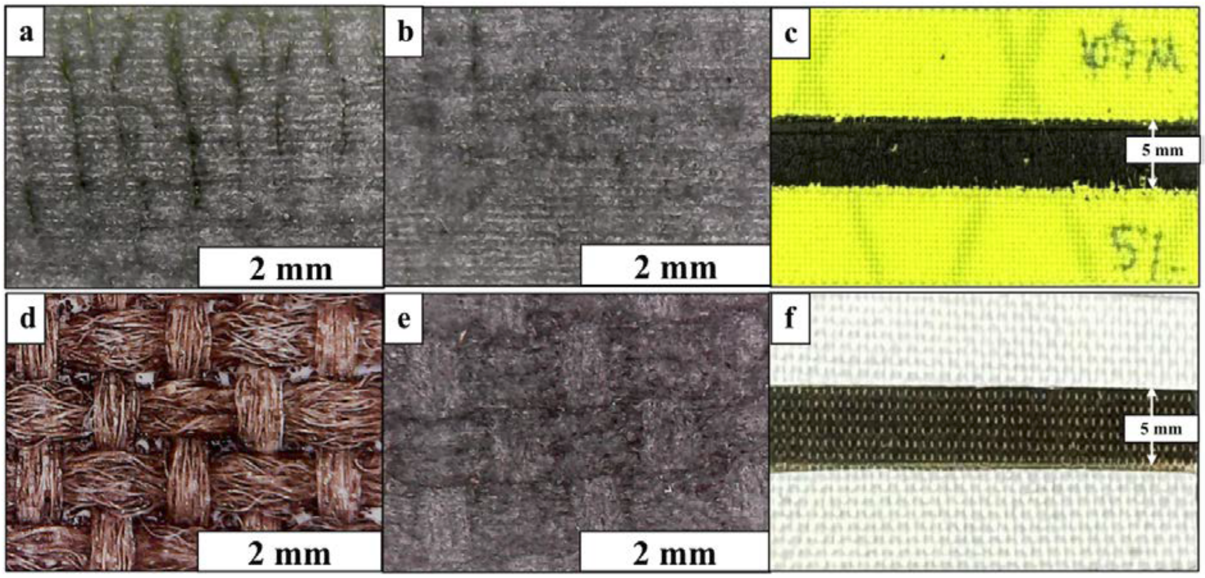

Figure 2: Microscope image of (a) yellow ripstop fabric coated with the lignin solution, (b) patterned by 5% laser power, (c) camera image of lasered lignin on yellow ripstop fabric, microscope image of (d) white polyester fabric coated with lignin, (e) patterned by 5% laser power, (f) camera image of white polyester fabric laser engraved lignin.

Measurements for lignin-coated fabrics were done once lasered and after each destructive test. After the coating process, unlike the CNT ink samples, the lignin coating needs to be lasered to reflect any resistivity. This explains why measurements were never taken before the lasering process, as it was of no significant value. After the 5% lasering process on lignin samples, however, was able to measure resistance an average of 51.18 $\Omega/\square$. Alternatively, a 7% laser power on the samples increased the resistance measuring much higher to an average of about 137.8 $\Omega/\square$**,** which indicated the laser power to be too high, causing degradation of lignin. These samples were still tested to examine the lignin properties and check for further decline after destructive tests. Repeating the process with the white polyester, the resistance values were higher, ranging from 393.7 $\Omega/\square$; however, it was still consistent in the coating and patterning process. This proves laser engraved lignin to be compatible with fabric while the usual conductive CNT ink is not. The applications of this novel lasered lignin are significant with its variability because the resistance can always reduce by using processes like electroplating, while the patterning and coating process is repeatable [5].

3.2 Destructive Tests

To ensure that e-textiles are truly efficient, several experiments must be done to test durability, flexibility, and washability. This led to several tests performed, including rolling, bending, washing, and ironing, to reflect the basic behaviors one can perform while wearing a t-shirt. The first set of tests was to test flexibility, including rolling and bending. Considering if these solutions were used in wearable electronics applications, the fabric needs to be bent and maneuvered onto like an actual worn t-shirt. A Scanning Electron Microscope (SEM) was used before any of these tests were performed to inspect the coating and layer displayed in Figure 3a. The SEM image shows that even with the yellow ripstop CNT ink still bled through a bit outside the taped region seen to the right of the image. SEM imaging was done for the laser engraved lignin as well shown in Figure 3b which confirms an even and denser layer over the lasered section on the left versus the plain yellow ripstop on the right.

A 0.5-inch diameter cylinder was 3D printed for the rolling test to detect if any small particles of lignin or CNT ink would follow onto the rolling cylinder. This cylinder-shaped pin was rolled onto the fabric 10 times back and forth. After this test was done, the yellow ripstop coated with CNT ink had no visual change or any significant change to resistance values from one sample reading 27.95 Ω/□ once coated and then following the rolling test measured 28.94 Ω/□. The bending test was done following the rolling test which consisted of bending the coated fabric over a 3D-printed semicircle with a diameter of 1.5 inches. This in fact resulted in measurements lower than before changing to 28.35 Ω/□. Considering the bending maneuvered more movement than the rolling test, it was significantly evident that CNT ink coated onto yellow polyester fabric was flexible. After performing the rolling test on the 5% laser engraved lignin yellow ripstop sample however, there was a few particles left on the rolling pin and was reflected in measurements changing slightly from 51.77 Ω/□ once lasered to 60.24 Ω/□ after the test. After these slight changes, the bending test was performed to increase the resistance to 64.37 Ω/□. The slight difference in values after the rolling and bending test ensured flexibility to a certain extent. These tests were then repeated with 7% laser engraved lignin on yellow ripstop however did not result in the same low values. Once lasered the sample read 143.31 Ω/□ and subsequently after the rolling test measured 172.24 Ω/□ and then 173.03 Ω/□ after the bending test was performed. Both samples, despite the laser power, can demonstrate that the bending and rolling tests can impact the lignin-lasered sample slightly yet remain within range.

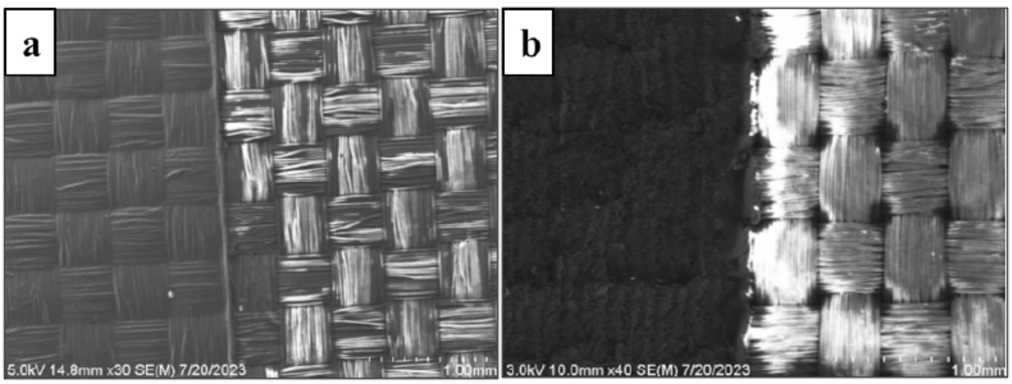

Figure 3: Scanning Electron Microscopic (SEM) image of (a) CNT ink coated versus noncoated yellow ripstop and (b) laser engraved lignin coated versus noncoated yellow ripstop.

While the rolling and bending tests were to test flexibility and not too harsh to the samples, the samples were washed after these tests as any worn t-shirt would be put in the washer. This was demonstrated through dipping the sample into a beaker filled with 200 mL of DI water for 5 minutes. Once left to dry for 24 hours, the sample was measured. Even though it was expected to have a huge change onto the sample, the yellow ripstop coated with CNT ink had very little change from 28.34 Ω/□, measured after the bending test, to 29.92 Ω/□ once dry. When taking the sample out of the water, it was visually seen there was not any CNT ink dripping out into the water or even off the sample to assume there would be much change. This "permanent" trace proved by resistance measurements that the CNT ink coated fabrics to be waterproof. For the laser engraved lignin yellow ripstop, the same washing procedure was done to reflect little change as well, increasing the resistance for 5% lasered lignin from 64.37 Ω/□ to 64.49 Ω/□. For 7% laser engraved lignin, the resistance increased in the same pattern of only a few ohms: 173.03 Ω/□ to 174.8 Ω/□ once dry. This was quite surprising as it did not increase significantly higher based on the hypothesis it might wash away the lignin once put under water for quite a while. While there was a small layer of residue on the uncoated part of the sample once taken out of the water, the small change in resistance shows it is insignificant. Considering this test was executed successfully with the white polyester fabric proved further for the success of waterproof laser engraved lignin for e-textiles. Figure 4 shows the resistance changes over the various destructive tests.

The last test for the future application of wearable electronics would experiment with heat levels for ironing. This was a vital test due to theoretically washing the fabric and follow with ironing out the wrinkly shirt. This was done by ironing the back of the sample for 20 seconds back and forth using multiple temperature settings starting from low, medium, and high settings. Considering that both fabrics are synthetics, the iron manual states that all synthetics should be ironed at the low setting so there is no damage to the fabric. With this, testing the fabrics past the recommended setting would see how what the fabric could withstand before melting or ruining the sample. To ensure the temperature was consistent each test, an infrared thermometer measured the low setting to be 75°C, medium setting as 125°C, and the high setting having a temperature of 160°C. The CNT ink coated yellow ripstop fabric was tested at the low, medium, and high temperatures yet only increased minimally as any other test to increase from 29.92 Ω/□ to 30.31 Ω/□ (low setting), 30.51 Ω/□ (medium setting), 30.1 Ω/□ (high setting). This consistent minor resistance change was consistent through the flexibility and washability tests however after all these temperatures, exceptionally passed the durability test by remaining stable after high temperature ironing. When testing the 5% and 7% lignin engraved fabrics for the ironing test the minimal change between temperatures remained. The 5% laser engraved lignin yellow ripstop increased from 69.49 Ω/□ to 70.28 Ω/□ on low temperature, 70.28 Ω/□ to 78.74 Ω/□ on medium temperature, and 78.74 Ω/□ to 89.96 Ω/□ on high temperature. The 7% laser engraved lignin yellow ripstop also slightly increased as expected from 174.8 Ω/□ to 174.21 Ω/□ (low), 177.76 Ω/□ (medium), and 192.32 Ω/□ (high). This minimal change, shown in Figure 5, was repeated with white polyester as well. The little change shown from ironing at the highest setting, not recommended to synthetic fabrics, reflects how lasered lignin should be tested with future use of silks, wools, cottons, and linens which is very capable for these high temperatures. These fabrics can possibly maintain higher resistance values since they are preferred to be ironed at such high settings. Throughout all the destructive tests performed on lignin coated fabrics had insignificant change within resistance values confirming the innovation of laser engraved lignin towards wearable electronics. The graph below, Figure 5, shows the resistance changes over the various temperature settings.

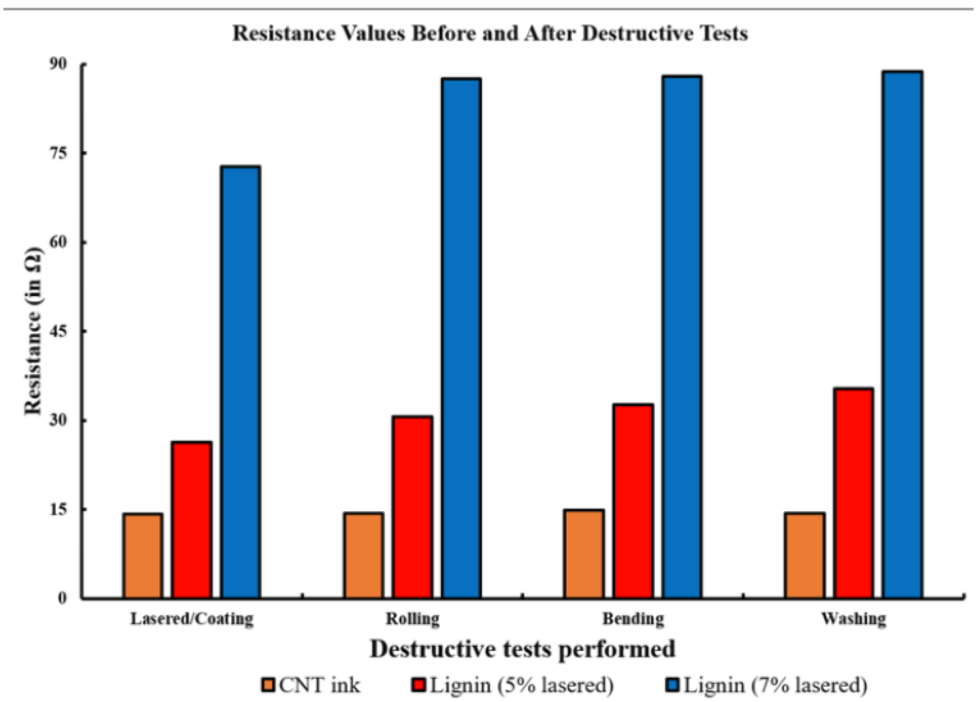

Figure 4: Resistance values (Ω/□) before and after rolling, bending, and washing tests.

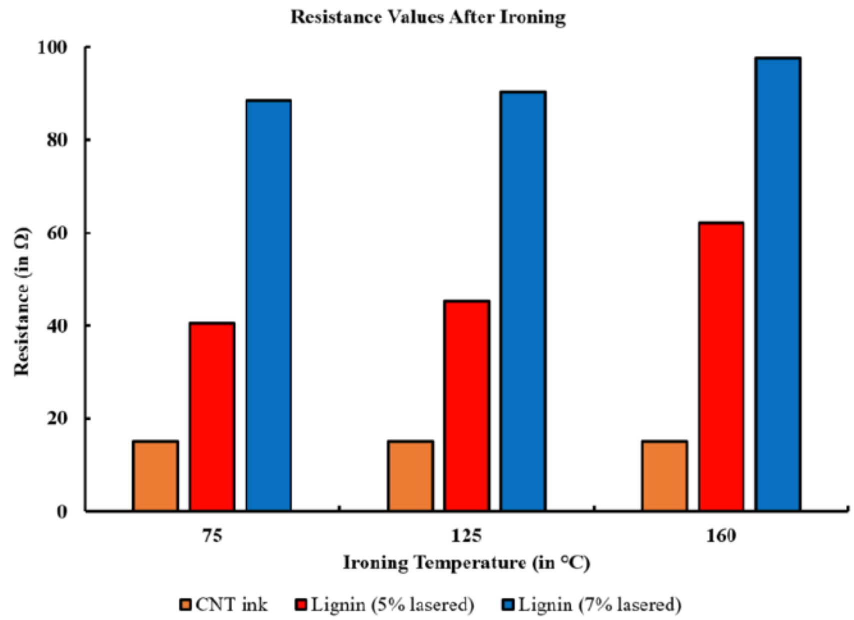

Figure 5: Resistance values (Ω/□) after ironing

4. CONCLUSION

Experimenting with laser engraved lignin on various fabrics has led to innovative methods of patterning conductors remaining low cost and easy to work with. The simple coating of 65 µL of the lignin solution followed with lasering at 5% and rastering twice has resulted in low resistance values that remain consistent throughout its trial run mimicking an everyday worn t-shirt. This was tested on yellow ripstop and white polyester using different flexibility and durability tests to validate the novelty of this process to succeed in e-textiles. In comparison to lignin coated fabrics, CNT ink was tested on the same fabrics. With three daily 40 µL coatings, CNT ink was only able to withstand on polyester ripstop but was superior in its low change in resistance despite the destructive test. Even with CNT ink's resistive properties, laser patterning lignin has the potential to be studied further for the fabrication onto wearable electronics.

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REFRENCES

[1] T. Dinh, H.-P. Phan, T.-K. Nguyen *et al.*, "Environment-friendly carbon nanotube based flexible electronics for noninvasive and wearable healthcare," Journal of Materials Chemistry C*,* 4(42), 10061-10068 (2016).

[2] M. Wang, Y. Yang, and W. Gao, "Laser-engraved graphene for flexible and wearable electronics," Trends in Chemistry*,* 3(11), 969-981 (2021).

[3] W. Zhang, Y. Lei, F. Ming *et al.*, "Lignin Laser Lithography: A Direct-Write Method for Fabricating 3D Graphene Electrodes for Microsupercapacitors," Advanced Energy Materials*,* 8(27), 1801840 (2018).

[4] F. Mahmood, H. Zhang, J. Lin *et al.*, "Laser-induced graphene derived from kraft lignin for flexible supercapacitors," ACS omega*,* 5(24), 14611-14618 (2020).

[5] S. M. Rosa-Ortiz, K.-K. Phan, N. Khattak *et al.*, “Hydrogen evolution assisted cyclic electroplating for lateral copper growth in wearable electronics,” Journal of Electroanalytical Chemistry, 902, 115796 (2021).

[6] S. M. Rosa-Ortiz, and A. Takshi, "Copper Electrodeposition by Hydrogen Evolution Assisted Electroplating (HEA) for Wearable Electronics." 1-5.

[7] S. Tan, S. Afroj, D. Li *et al.*, “Highly sensitive and extremely durable wearable e-textiles of graphene/carbon nanotube hybrid for cardiorespiratory monitoring,” iScience, 26(4), 106403 (2023).

[8] F. Rahimi, and A. Takshi, "Energy storage capability of the dye sensitized solar cells via utilization of highly porous carbon electrodes." 9937, 146-152.

[9] P. Posoknistakul, C. Tangkrakul, P. Chaosuanphae *et al.*, “Fabrication and Characterization of Lignin Particles and Their Ultraviolet Protection Ability in PVA Composite Film,” ACS Omega, 5(33), 20976-20982 (2020).