

# Washable PEDOT:PSS Coated Polyester with Submicron Sized Fibers for Wearable Technologies

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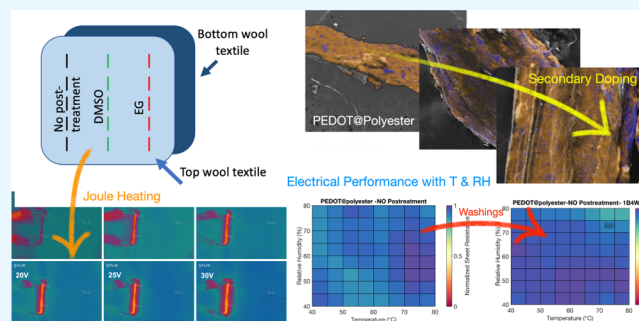


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Supporting Information

**ABSTRACT:** The use of non-metallic conductive yarns in wearable technologies like smart textiles requires compliant washable fibers that can withstand domestic washing without losing their conductive properties. A one-pot coating with PEDOT:PSS conductive polymers was applied to polyester submicron fibers, increasing the water resistance and washability under various domestic washing conditions. Plasma treatment of the untreated samples improved the anchoring of the coating to the fibers, producing smooth and homogeneous coatings. The primary doping of PEDOT:PSS with ethylene glycol (EG), dimethyl sulfoxide (DMSO), and a non-ionic surfactant as well as the secondary doping of the composite fibers improved the sheet resistance at room temperature. The as-obtained composite materials showed similar mechanical properties as the parent fibers, indicating that the coating and post-treatment do not affect the overall mechanical property of the composite. The performance of the composites under different temperature and humidity conditions and washability using the standardized ISO 6330:2012 procedure for domestic washing and drying showed that the obtained composites are good candidates for reliable washable wearable technologies, such as all-organic washable Joule heaters in functional textiles.



The use of smart textiles in everyday life is now becoming a reality. Clothing is no longer only a protective barrier against the environment but also a tool to improve connectivity and facilitate human modern life.<sup>1</sup> Among smart textiles, also called e-textiles, functional textiles are a subgroup of materials in which new functionalities are added by changing the material composition or processing.<sup>2,3</sup> These functionalities could be new materials or modifications of pre-existent ones, aiming to seamlessly integrate electronics or sensors of interest into wearable technology. To achieve this goal, the modification of textiles from the fiber is highly desirable. Cherenack et al.<sup>4</sup> defined “fibertronics” as the higher order electronic functions introduced at the fiber level and the means to electrically connect the electronics within the textile through embroidery, weaving, knitting, etc. Initially, metal-based conductive yarns were used to perform the electrical connections, but soon the interest shifted toward inherently conducting polymers, as they have better processability and tunability than their metallic counterparts.

Among the most interesting conductive polymers is the poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) or PEDOT:PSS due to its biocompatibility,<sup>5</sup> high electrical conductivity,<sup>6–8</sup> and the ability to be processed in films,<sup>9,10</sup> fibers,<sup>11,12</sup> coatings,<sup>13,14</sup> and tunability through composite formulations with carbon nanotubes or graphene nanoparticles,<sup>15–17</sup> nanosized ceramics,<sup>18</sup> ionic liquids,<sup>19</sup> cellulose,<sup>10</sup>

etc., or via secondary doping with acids,<sup>20,21</sup> solvents,<sup>22–26</sup> surfactants,<sup>27–29</sup> salts,<sup>30</sup> etc.

Nowadays, PEDOT:PSS is commercially available in different formulations according to the applications such as solar cells,<sup>31</sup> thermoelectric devices,<sup>10,32</sup> sensors,<sup>33,34</sup> and textile-based devices.<sup>35–37</sup> Smart textiles usually have the disadvantage of being poorly recyclable, using non-sustainable materials like metallic coatings or toxic materials present in batteries or in nanomaterial-based composites.<sup>38</sup> To increase sustainability of functional textiles using PEDOT:PSS, we can employ strategies such as using recycled raw materials as carrier fibers and lengthening the lifetime of these devices by increasing water resistance and durability during washing. Regarding this challenge, washability is one of the key points and has been of great interest among the scientific community.

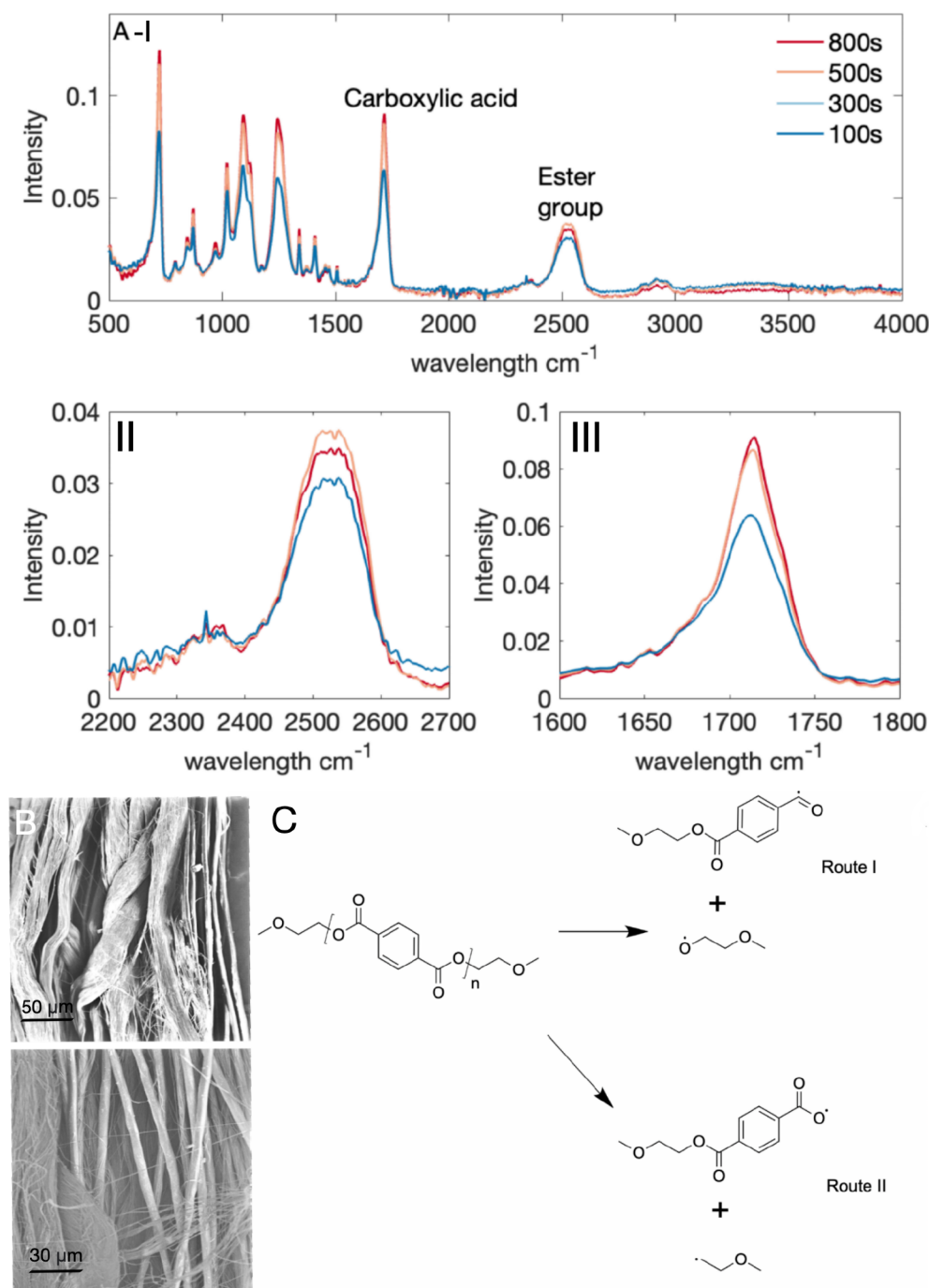
The solubility of PEDOT:PSS in water and the loss of conductivity of the textiles are the main disadvantages of these composites. Several studies have shown the washability of the PEDOT:PSS-treated textiles,<sup>39–42</sup> but no standardized wash-

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**Figure 1.** (A) (I) FTIR measurements of atmospheric plasma-treated polyester fibers for 100, 300, 500, and 800 s. (II and III) FTIR signals corresponding to ester and carboxylic groups, respectively. (B) SEM micrography of polyester fibers: plasma-treated fibers at 800 s (top) and non-treated fibers (bottom). (C) Chemical surface modification of polyester due to plasma treatment and the possible free radical production routes.

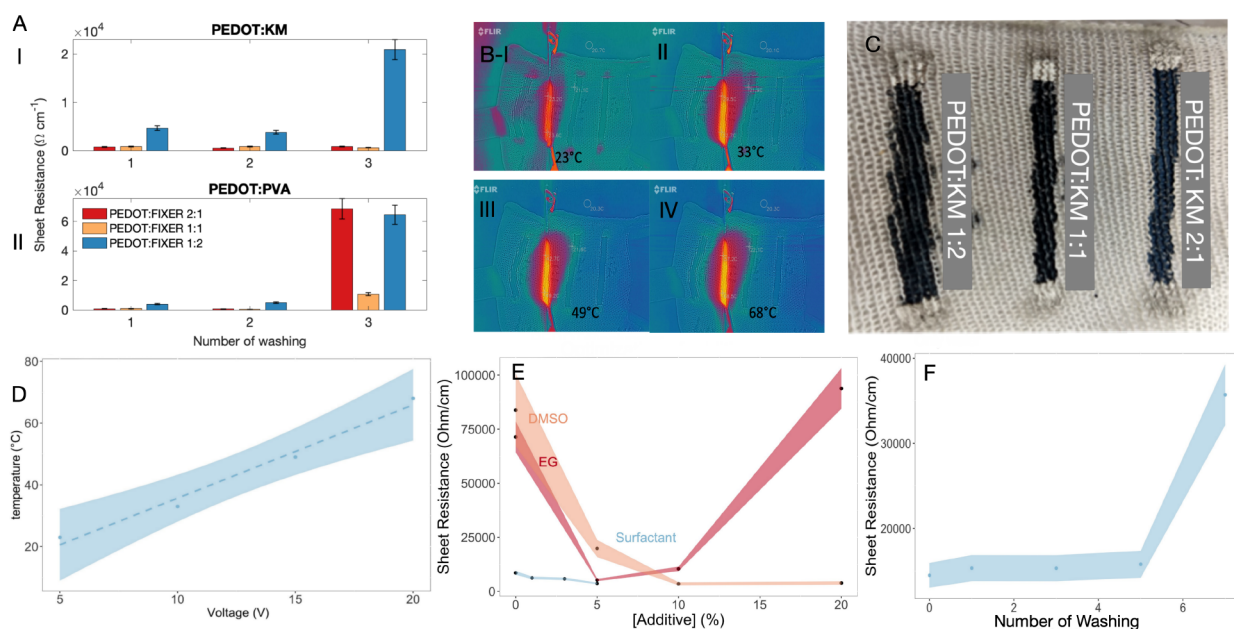
ing conditions according to ISO normative<sup>43</sup> were applied. Therefore, the influence of the washing conditions can be difficult to reproduce.

Further, using polyester-based fibers may increase the sustainability of the smart textiles, as they can be obtained from reused PET bottles,<sup>44–47</sup> therefore reducing the impact, compared to virgin fiber, on the environment. In this work, we present a one-step secondary doping process for conductive and washable polyester submicron fibers using a PEDOT:PSS coating. The resulting composites are processed using standard

washing procedures, and their potential applications in wearable technologies are discussed.

## RESULTS AND DISCUSSION

**Plasma Treatment Increases Coating Adhesion to Polyester Fibers.** The use of polyester submicron sized fibers allows for an increase in the surface area available for performing the coating with the conductive polymer, without affecting the mechanical properties of the fibers. To improve the physicochemical anchoring of PEDOT:PSS to the polyester fiber surface, we aimed to increase the wettability



**Figure 2.** (A) Sheet resistance of polyester fibers coated with PEDOT:PSS with different fixers and number of washings. (B) Thermo-camera images of the Joule heating on PEDOT:KM 1:1 coating at different applied voltages (5, 10, 15, and 20 V) onto a polyester knitted sample. (C) Polyester knitted samples with PEDOT:PSS:KM coatings at different proportions. (D) Temperature achieved using different applied voltages at the PEDOT:KM 1:1 coating on PEDOT:KM 1:1. (E) Sheet resistance of the PEDOT:polyester coatings with secondary doping. (F) Effect of water-washings to the sheet resistance measured on the PEDOT:polyester fiber obtained under optimized conditions. Shaded areas correspond to 95% confidence intervals.

and roughness of the polyester fibers using plasma treatment. The atmospheric plasma treatment allows the degradation of a very thin layer of the polymer surface into free radicals with high reactivity, without creating wastewater or other environmentally hazardous byproducts. This breakdown increases the interactions with PEDOT macromolecules during the coating step.<sup>13,48,49</sup> FTIR showing the possible breakdown paths and SEM micrographs of the fibers are shown in Figure 1A.

FTIR measurements (Figure 1A) showed an increase in the signals of carboxylic acids with increased treatment time, especially at  $1714\text{ cm}^{-1}$  (O=C=O carboxylic acid) and  $1093\text{ cm}^{-1}$  (—O—H out of plane of terminal carboxylic acids), and a decrease in the signal of ester groups with time at  $2530\text{ cm}^{-1}$  (C—H stretching). FTIR measurements allowed the optimization of the proper conditions for polyester surface modification and assessment of the effectiveness of the treatment. After the plasma treatment, all of the samples were stored in an airtight container and used within 3 h. In Figure 1B, SEM micrographs showed differences in the roughness of the samples' surfaces. Plasma-treated samples were more uneven and rough than non-treated samples. According to Leroux and co-workers,<sup>49</sup> plasma treatment produces two oxidation routes (I and II in Figure 1C) increasing the number of hydroxyl and carboxylic groups in the surface and thus increasing the wettability and adhesion of coatings to the polyester fiber.

**PEDOT:PSS Coating. Fixer Type and Proportion.** The direct usage of PEDOT:PSS suspensions is limited, as they have high solubility in water, making their use in washable conductive fibers difficult. Previously in our group, PEDOT:PSS:PVA self-standing fibers were developed,<sup>50</sup> showing an average conductivity value of  $20\text{ S cm}^{-1}$ . However, these fibers were designed for different purposes and no washing tests were performed. Here, the importance of the washability

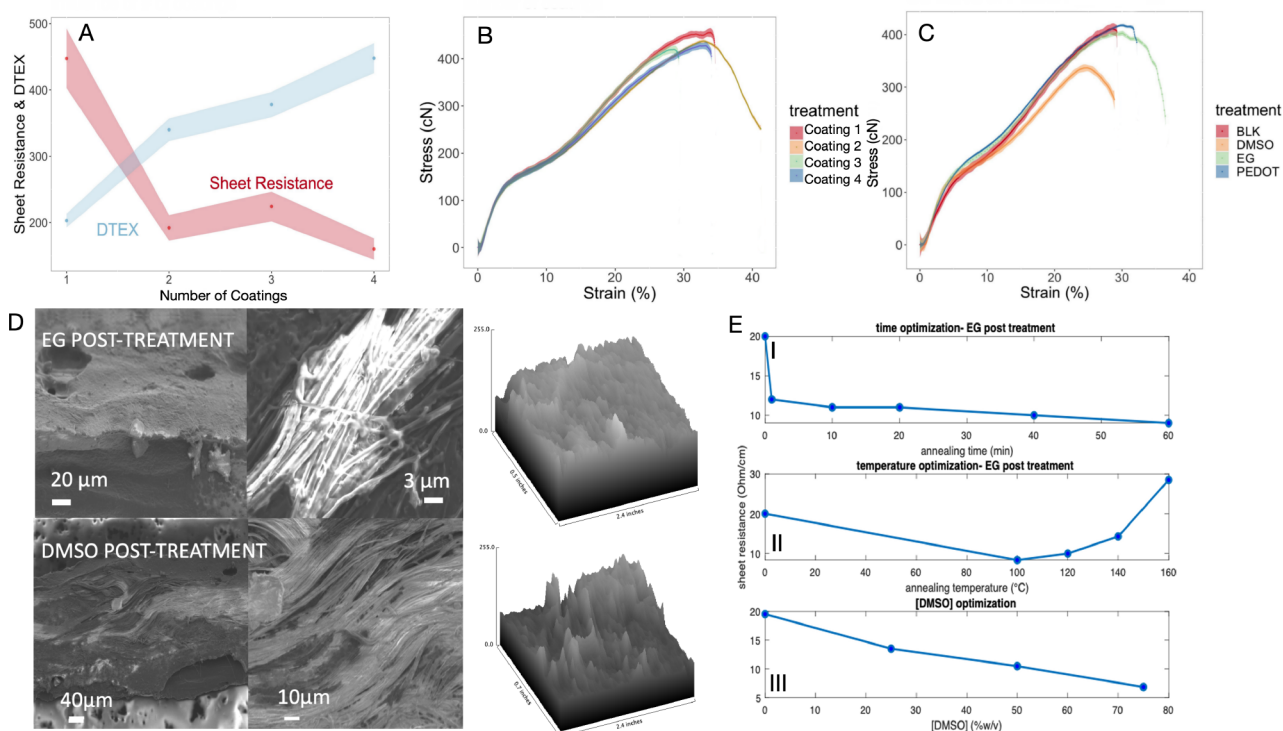
of the conductive composites is addressed, and changes in the formulation of the conductive composites should be introduced. In this way, a self-curing silicone-based textile fixer was tested in order to fix the conductive material in the polyester fibers substrate. *IV* measurements of polyester fibers coated using a self-cross-linking silicone textile fixer (KM) and polyvinyl alcohol (PVA) as fixers were prepared in three different proportions with respect to PEDOT:PSS (i.e., 2:1, 1:1, and 1:2). Then, a simple water resistance test was performed to assess the change in the sheet resistance value after the water exposure (Figure 2A-I and II).

In both cases, the best results were obtained using the PEDOT:fixer 1:1 proportion. Mixtures using PEDOT:PVA 1:2 and 2:1 and PEDOT:KM 2:1 were highly viscous, and the coating of the fibers was ineffective. The PEDOT:KM 1:2 mixture was too fluid, as KM is aqueous-based, and the low viscosity of the mixture also challenged its use as a coating. When a water resistance test was performed on the samples, the PVA-based coating began to dissolve, and a blue colored solution was obtained. The coated fiber after the second test showed an increase of the sheet resistance, evidencing the loss of conductive material by dissolution.

The best water resistance performance was obtained using the silicone-based fixer (KM), and the proportion 1:1 was chosen for further tests.

The PEDOT:PSS:KM 1:1 coating mixture was also used for depositing conductive coatings on a preknitted nanofiber polyester structure, testing its ability to coat more complex structures. Joule heating of the conductive coating was measured applying different voltages (Figure 2B and C), and Figure 2D shows the increase of the temperature with the applied voltage for PEDOT:KM 1:1. The low viscosity of the PEDOT:PSS:KM 1:2 was inefficient for a neat coating. PEDOT:KM 2:1 was too viscous for the deposition, and no





**Figure 3.** (A) Influence of the number of coatings on the sheet resistance of PEDOT@polyester composites. (B) Stress–strain curves for the samples with different numbers of coatings. (C) Stress–strain curves for the samples with different post-treatments. (D) SEM micrographies of EG and DMSO post-treated samples at different magnifications and surface rugosity obtained using image analysis. (E) Optimization of the annealing time and temperatures for the different post-treatments (EG and DMSO).

homogeneous coating of the fibers was obtained. The sheet resistance values calculated for these coatings were 299, 40, and 193  $\Omega \text{ cm}^{-1}$ , respectively.

#### Doping of the Coatings for Improved Conductivity.

The addition of different compounds in the PEDOT:PSS mixture in non-stoichiometric amounts to improve the conductivity of the polymer is considered a primary doping. Particularly, the addition of polar solvents [e.g., ethylene glycol (EG) and dimethylsulfoxide (DMSO)] enhances the connectivity of PEDOT:PSS grains and thus the conductivity through the improvement of charge carrier transport in the 3D network.<sup>22,24–26,51</sup> However, the amount of the polar solvent should be optimized to avoid a decrease in the conductive material concentration in the coating mixture. The addition of a non-ionic surfactant can improve the  $\pi$ – $\pi$  stacking of the PEDOT molecules and thus the conductivity of the coating according to Yoon et al.<sup>28</sup> Zonyl fluorosurfactant particularly showed a capping effect between the water-soluble PSS molecule and PEDOT, reducing the amount of PSS-doped PEDOT and thus increasing the conductivity.<sup>27</sup> From Figure 2E, the optimized formula under the tested conditions is PEDOT:KM 1:1, EG 5% w/w, DMSO 10% w/w, and surfactant 5% w/w, with a sheet resistance value of 14.5  $\text{k}\Omega \text{ cm}^{-1}$ , which was 560 times lower than the PEDOT:KM coating without primary doping. In Figure 2F, the optimized formula can withstand up to five successive water resistance washing tests without changing significantly the resistance of the material. In the seventh wash test, the resistivity value increased 2.5 times with respect to the initial value (with a confidence level of 95%).

**Number of Coatings.** We hypothesized that the number of coatings applied to the polyester fibers would raise the

conductivity of the composite by increasing the number of homogeneous layers present on the fiber surface. The electrical properties of the composites were tested to corroborate our hypothesis, and also, the tensile measurements were performed to assess the influence of the coatings on the mechanical properties (Figure 3A–C).

From Figure 3B,C and Table 1, it is evidenced that the number of coatings does not affect the mechanical properties

**Table 1. Tensile Parameters Calculated from Stress–Strain Curves<sup>a</sup>**

Number of Coatings	Elastic Modulus (N/tex)	Max. Strain (%)	Max. Stress (cN/Dtex)
1	1.3 $\pm$ 0.3	447 $\pm$ 5	1.5 $\pm$ 0.1
2	1.3 $\pm$ 0.3	447 $\pm$ 5	1.5 $\pm$ 0.1
3	1.2 $\pm$ 0.1	426 $\pm$ 12	1.2 $\pm$ 0.1
4	1.1 $\pm$ 0.1	427 $\pm$ 10	0.9 $\pm$ 0.1

<sup>a</sup>Dtex is the linear density of a fiber, calculated from the weight of the fiber for a fixed length (g/10000 m of fiber).

of the composites. The weight of the composites is reflected in the DTex value, defined as the mass in grams of 10000 m-length fiber. The Dtex value increases with the number of coatings and as the sheet resistance of the composite fiber decreases, reaching a plateau from two coatings onward (equivalent to a sheet resistance of 1.6  $\text{k}\Omega \text{ cm}^{-1}$ ). This can be explained considering that successive coatings can lead to a more homogeneous surface around the fibers and the maximum connectivity is reached. Further coatings only increase the thickness and weight of the fiber but do not improve the electrical connectivity of the material. Also, the



samples showed a good linear response in the *IV* measurements, showing the resistive nature of the composites. For further experiments, composites with three coatings were chosen.

Scanning electron microscopy images of the composite fibers with different numbers of coatings are shown in Figure S1. SEM micrographs showed that, when one coating is applied, individual fibers are still visible, with a homogeneous coating among them. The increase in the number of coatings produces an increase in the thickness of the coating and the smoothness of the surface, and the individual fibers appear embedded in the conductive matrix.

**Post-Treatments of the Composites.** The addition of the primary dopants, such as the non-ionic fluorosurfactant, ethylene glycol (EG), and dimethyl sulfoxide (DMSO), produced a decrease in the resistivity of the composite by 1 order of magnitude. However, it is possible to further improve those resistivity values by using the secondary doping approach. Here, EG and DMSO (Figure 2E) were chosen as polar solvents for post-treating the obtained composites and removing the excess PSS from the coated surface.<sup>52</sup> In this way, it is possible to reduce the resistivity of the composite by improving the electrical connection between PEDOT molecules by segregating excess PSS toward the surface of the coating. In Figure 3D, SEM micrographs of the PEDOT coated fibers (three coatings) with EG and DMSO post-treatments are shown. These samples showed a rougher and more porous surface than non-post-treated samples, evidencing the excess PSS segregation. For EG post-treatments, pure EG was chosen, as the effects of diluted EG in ethanol were not satisfactory (data not shown) in terms of improvement in sheet resistance improvement, but also there was a partial dissolution of PEDOT. The different annealing times and temperatures were tested for our samples, reaching optimized conditions at 100 °C and 1 h of annealing time. The temperature and annealing time for DMSO were chosen according to Nagata and co-workers.<sup>53</sup> DMSO 75% w/v was selected as the secondary doping concentration, as pure DMSO yielded partial dissolution of the coating. In this way, DMSO 75% w/v was chosen as the optimized concentration for this secondary doping. The SS curves shown (Figure 3C) did not show a significant difference in the mechanical properties of the post-treated samples with the untreated PEDOT:polyester composites.

**Standardized Washing Test of the Samples.** Washing tests using the same domestic conditions for time, temperature, and soap concentration are crucial, especially when smart textiles are designed for wearable technologies. Ryan and co-workers<sup>39</sup> used PEDOT dyed silk yarns for machine washable fibers and reported no changes in the conductivity of the composite materials up to four washing and drying cycles at 30 °C, 50 min, and spinning at 900 rpm. However, these results are not standardized according to ISO procedures. From the ISO 6330:2012 standard procedures, four conditions for domestic machine washing were chosen according to Table 2. The washing temperature ranged from room temperature to 60 °C during the washing step and using identical washing and rinsing conditions.

The results shown in Figure 4A-I–III show that the number of washings increases the sheet resistance values calculated for all samples due to conductive material loss during the washing step. The EG and DMSO treatment produces a decrease in the resistivity of the composite from 8 Ω·cm to 0.4 and 0.2 Ω·cm,

**Table 2. Washing Conditions Used according to ISO 6330:2012 Procedures<sup>a</sup>**

Washing Condition	Washing Temperature (°C)
1B	room temperature (RT)
2B	30
6B	45
9B	60

<sup>a</sup>*N* = 3, [detergent] = 1 g L<sup>-1</sup>, no bleach containing. Washing time = 12 min, rinsing time = 3 min.

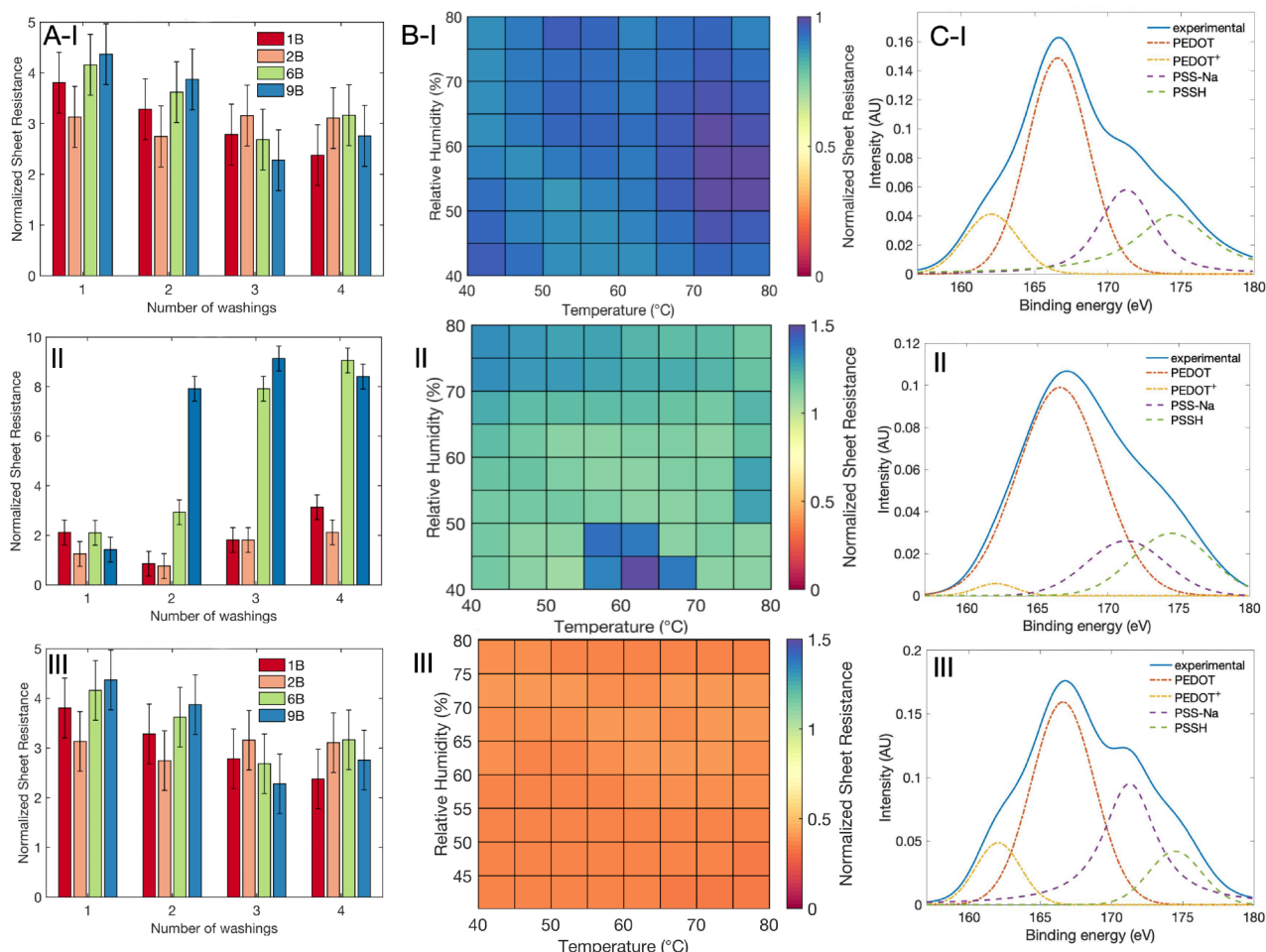
respectively (non-washed samples). After the first wash in cold water (*T* < 30 °C), the resistivities increased 6, 2, and 2 times with non-treated, EG-treated, and DMSO-treated samples. However, after the fourth wash at 60 °C (condition 9B of ISO 6330:2012), the increase in the sheet resistance values was 10, 12, and 4 times for non-post-treated, EG post-treated, and DMSO post-treated samples, respectively. Even though several authors explained the decrease in the solubility of PEDOT:PSS in water when using EG as a post-treatment secondary doping reagent in films<sup>52</sup> due to the increase of the interconnections of PEDOT molecules, in the SEM micrographs shown in Figure 3D, there was an increase of the roughness of the coating after the post-treatments. These pores could enhance the water–surface interaction and accelerate the conductive material loss, especially at higher washing temperature cycles. In this study, DMSO-treated samples showed the better performance in terms of improving the resistivity values due to secondary doping and an extended range of temperatures and washing cycles in which the sheet resistance has small changes. Considering these results, the most favorable laundering conditions for extending the lifetime of the composite would be those at lower temperatures, like room temperature or 30 °C (washing condition 1B).

**Influence of Temperature and Humidity on Composite Electrical Properties.** The usage of wearable technologies should consider the difference in weather conditions and situations in which the user is exposed. For this reason, it is important to assess the behavior of the materials under varying temperatures and relative humidity (RH) conditions (Figure 4B-I–III and Figures S2–S4).

Figure 4B-I–III shows that the post-treatments affect the response of the composite material to different temperature and humidity conditions. In all cases, samples showed a decrease in the sheet resistance as temperature increases with a typical behavior of disordered semiconductors with a negative temperature coefficient of resistance,<sup>54</sup> particularly at % RH above 60%. This phenomenon is explained considering the partial removal of water and solvent molecules from the coatings at higher temperatures. At a fixed temperature and increasing the % RH, there is an increase in the resistivity due to the adsorption of water molecules by PSS, which is highly hydrophilic. PSS molecules have two types of sulfonic groups:  $-\text{SO}_3^-$  and neutral  $-\text{SO}_3\text{H}$ . The anionic sulfonic groups are responsible for the ionic interaction with PEDOT molecules, while the neutral sulfonic groups are mainly responsible for the adsorption of water.<sup>50</sup>

In the samples, for a fixed temperature and increasing % RH, a maximum value of resistivity is achieved with a decrease at higher RH due to a water meniscus layer formation.<sup>55</sup>

However, the extent of temperature and RH ranges in which the resistivity changes vary in each sample. In Figure 4B-I, the response surface to *T* and RH shows minimal changes up to 80



**Figure 4.** (A) Sheet resistance variation as a function of the washing condition (1B, room temperature; 2B, 30 °C; 6B, 45 °C; 9B, 60 °C; [detergent] = 1 g L<sup>-1</sup>, no bleach containing; washing time, 12 min; ringing time, 3 min) and the number of washings (*N*: 1–4). (B) Normalized sheet resistance under different temperatures (40–80 °C) and relative humidity conditions (40–80% RH). (C) XPS measurements and peak deconvolution for the S 2p core-level spectra. (I) No post-treatment, (II) EG post-treatment, (III) DMSO post-treatment.

°C and 80% RH, where the resistivity decreases 21% from initial conditions at 30 °C and 30% RH.

In Figure 4B-II, the resistivity does change significantly in the region of low temperatures and high % RH with a variation of 10% at 40 °C 40% RH and 80% RH. The counteractive effects of irreversible polymer backbone changes due to air and moisture and the increase of conductivity due to polymer crystallinity explain the localized increase in the resistivity at low % RH and temperatures between 55 and 70 °C.<sup>56</sup>

In Figure 4B-III, resistivity changes more dramatically around 60–70% RH at all temperatures assayed.

All of the samples showed excellent durability during these measurements, withstanding more than 330 measurement cycles under the different humidity and temperature conditions. Also, they were resistant to the handling, without peeling of the coating. Further plots of normalized sheet resistance measurements with different temperatures and % RH at each washing condition and post-treatment are available in the Supporting Information (Figures S2–S4).

Figure 4C-I and II shows the S 2p core-level XPS spectra for the samples and their respective peak deconvolutions (peak assignment corresponding to neutral PEDOT, cationic PEDOT<sup>+</sup>, PSS salt or PSS-Na, and protonated PSS-PSSH). DMSO post-treatment removed the excess PSS molecules from the polymeric structure, evidenced by the change in the

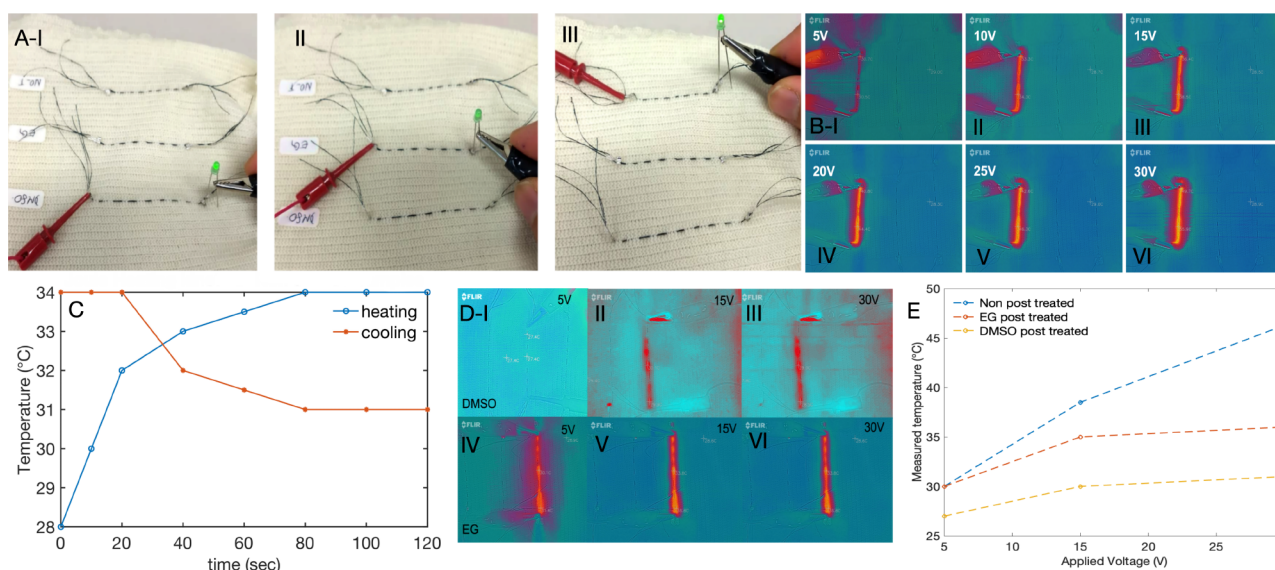
ratio PEDOT/PSS (calculated from the sum of PEDOT related peaks to PSS related peaks). The ratio values were 1.3, 1.3, and 2 for non-post-treated, EG post-treated, and DMSO post-treated samples, respectively.

In Figures S5–S7, the Si 2s and Si 2p core-level spectra are shown for the samples, indicating the silicone-based textile finisher used as a fixer of the PEDOT:PSS to the fiber surface.

Regarding the washed samples, the sheet resistance measurements of non-post-treated samples (Figure S2), with EG and DMSO post-treatments (Figures S3 and S3, respectively) with the optimized washing conditions (1B, Table 2) at temperature and % RH conditions are shown for one to four successive washings.

This fact is evidenced in the S 2p core-level XPS spectra (Figure 4C-I–III, Figures S5–S7), where the PEDOT/PSS ratios calculated from the deconvoluted areas of each peak were 1.6, 1.9, and 2.3 for non-post-treated, DMSO post-treated, and EG post-treated samples, respectively.

On samples with DMSO post-treatment, up to the third washing the same trend is found, and the fourth washing showed a slight increase in the normalized sheet resistance due to the loss of conductive material. This assumption is supported by the analysis of the XPS signals corresponding to the silicone fixer and the PEDOT:PSS in the coating, which



**Figure 5.** (A) LED test for the conductive PEDOT@polyester fibers ( $n = 3$ ). (I) With DMSO post-treatment, (II) EG post-treatment, (III) non-post-treatment. (B) (I–VI) Thermo-camera images of non-post-treated fibers at 5, 10, 15, 20, 25, and 30 V. (C) Kinetic measurements of the heating and cooling rates of non-post-treated samples at 10 V. (D) Thermo-camera images of DMSO post-treated samples (I–III) and EG post-treated samples (IV–VI) at 5, 15, and 30 V. (E) Measured temperatures at different applied voltages for the different PEDOT@polyester composites measured at the experimental setup shown in A1–AIII.

indicates that the silicone fixer is not lost during the washing procedures but the conductive material is lost.

In the post-treated samples, an increase in the sensitivity toward % RH and the temperature is observed, particularly with the elimination of excess PSS with washings. FE-SEM and EDX measurements are shown in Figure S8. The EDX mapping of the washed and non-washed fibers showed an increase in the S signal on the surface with respect to the Si signal of the conductive coating. Also, the washed fibers showed some naked polyester fibers, exposed after the successive washings. The surfaces of the composites were smoother than the non-washed ones, in accordance with the previous observations using XPS. The variability of the sheet resistance with successive washing with  $T$  and % RH found was non-post-treated > EG > DMSO. Therefore, the sample with DMSO post-treatment showed the best water and washing resistance with a lower degree of variability up to three successive washing.

**Joule Heating of the Coated Fibers.** For the application of the composite fibers as all-organic conductive heaters with water and washing resistance, a simple setup was developed (Figure 5A). A 10 V voltage was applied to each bundle of fibers ( $n = 3$ ), and a green LED was connected to them. This simple conductive test lit the LED just by contact with the conductive fibers. A double flat knitted wool fabric was used as a base material to limit the heat dissipation during the heating test. The various temperatures observed using a thermo-camera are shown in Figure 5B for non-post-treated samples and Figure 5D for DMSO and EG post-treated samples. As seen in Figure 5C, the increase of the temperature was clearly visible and stable in time in a few seconds. The cooling time was approximately 20 s after the applied voltage stopped. In Figure 5E, the less conductive fibers showed the better Joule heating performance for the same applied voltages.<sup>57</sup>

## CONCLUSIONS

In this work, we developed PEDOT:PSS coatings over polyester submicron sized fibers with excellent electrical and mechanical properties in only one step. The primary doping during the coating and secondary doping produced as a post-treatment of the composites along with the silicone-based textile fixer produced highly conductive washable composites maintaining their electrical properties even after successive washings. The conductive performance and the Joule heating properties of the composites were assessed under different temperature and humidity conditions mimicking the different environments where the composites could be utilized embedded as part of wearable devices. Their responses under such extreme conditions showed that the composites are highly stable over time (e.g., more than 330 measurement cycles, over weeks of continued measurements), resistant to the touch or handling with particular emphasis when a secondary doping through post-treatments is performed. The as-obtained composite materials would become suitable conducting yarns for wearable technologies showcasing flexibility, durability, and electrical reliability upon washing under domestic conditions, also featuring their possible application as all-organic heaters. As currently there are no standards or regulations setting the limits of washability of e-textiles, all efforts aimed at pushing the boundaries of performance for such all-organic conductive fibers could be of great interest to the community, triggering future developments and applications.

In future work, the quantification of microplastics during laundering of these composites will be assessed, as the environmental and health impacts of these pollutants in aqueous ecosystems can damage the flora and fauna in the long term.

## EXPERIMENTAL SECTION

**Sample Preparation.** Polyester fibers of 700 nm diameter were purchased from Teijin Limited (Japan). Samples were treated using an atmospheric plasma generator (Sakigake



YHR-S, Japan) for 800 s and uniformly coated with a mixture of PEDOT:PSS 10% w/v in water which was prepared by proper dissolution of PEDOT:PSS pellets purchased from Agfa (Orgacon dry), self-cross-linking silicone emulsion KM-2002-L-1 (KM) from Shin-Etsu Chemical (Japan) in the ratio 1:1 with the addition of dimethyl sulfoxide (DMSO) 10% w/w, ethylene glycol (EG) 5% w/w, and zonyl fluorosurfactant (Sigma-Aldrich) 5% w/w. Poly(vinyl alcohol) (PVA, Kuraray Co. Ltd., Tokyo, Japan) 16% w/v was dissolved in a water bath at 60 °C. The polyester fibers were homogeneously coated by immersing the fibers on the coating mixture, and then, the fibers were wound in a cone and a thermal treatment at 70 °C for 1 h was applied. Silver paint Dotite D-550 was purchased from Fujikura Kasei Co. LTD (Japan). The conductive paste was applied to the ends of each fiber sample and cured at 70 °C for 4 h or at room temperature overnight for further electrical measurements.

**Mechanical Characterization.** Tensile testing was performed using a tabletop universal tester (Shimadzu, EX-SX, Japan) with a 50 mm gauge length and a strain rate of 10 mm min<sup>-1</sup> until failure.

**Electrical Characterization.** The electrical resistance of the coated yarns was determined using a Keithley 2401 sourcemeter in a two-point probe configuration, using samples of 10 cm contact with silver paste and crocodile clips. *IV* curves were measured from 0.5 V with steps of 0.2 V (triplicate measurements).

**Fourier Transform Infrared (FTIR) Measurements.** The plasma-treated samples were characterized using a Bruker Alpha II FTIR.

**X-ray Photoelectron Spectroscopy (XPS).** The non-post-treated and post-treated samples with EG and DMSO (with and without washing) were measured using XPS (Kratos, Axis Ultra DLD) with a binding energy range up to 1100 eV, 100 meV step, charge neutralizer in, dwell time of 200 ms, and 35 sweeps.

**Field Emission Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (FE-SEM and EDS).** FE-SEM and EDS images were obtained using a JEOL JSM-IT800 without any further treatment of the samples. The beam energy was set to 15 kV, and the working distance was between 1 and 39 mm. EDS mapping was performed with scanning energies between 0 and 20 kV and a working distance of 10 mm. The surface smoothness of the samples was analyzed using ImageJ software.

**Water Resistance Tests.** Samples were soaked in deionized Milli-Q water at room temperature for 1 h, under constant magnetic stirring at 100 rpm. Then, the samples were air-dried overnight before further testing.

**Washing Tests.** Samples were washed using the Domestic Washing and Drying Procedures for Textile testing (ISO 6330:2012),<sup>43</sup> in particular using procedure numbers 1B, 2B, 6B, and 9B. For each condition, samples were washed up to four times with triplicate samples.

**Reliability Performance Tests.** Samples with silver contacts and a length of 10 cm were exposed to high relative humidity and high temperature using a benchtop type environmental chamber (Espec Corp., Japan). The temperature was varied from 25 to 80 °C and the relative humidity (RH) from 30 to 80%. Electrical measurements (*IV* measurements) were performed *in situ* once the *T* and RH conditions were stabilized (after 40 min).

**Joule Heater Demonstrator.** The setup of the all-organic Joule heater demonstrator was created using a double layer of 100% merino wool flat knit for thermal insulation purposes. Three PEDOT:polyester fiber composites were bundled and bound together with a metallic crimp. The fibers were hemstitched by hand into the top layer of the wool knit. Different voltages were applied using a sourcemeter, and a green LED was used as a fast conductive test. The generated heat was detected and measured using a Flir Thermocamera (Teledyne FLIR LLC, USA), and the images were collected on an Ipad (Apple Inc., USA).

All confidence intervals were calculated with a 95% confidence level, with *N* = 5, unless stated otherwise.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c06671>.

SEM micrographs, normalized sheet resistance measurements of non-washed and washed samples at different humidities and temperatures, and XPS measurements and FE-SEM-EDX measurements of non-washed and washed samples (PDF)

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### Notes

The authors declare no competing financial interest.

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