Flexible and Printed Electronics

PAPER

Printable cellulose-based electroconductive composites for sensing elements in paper electronics

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Abstract

Conductive flexible hydrogel composites were printed on paper substrates using a functional ink, which was designed and formulated for screen-printing. The inks were prepared using abundant and eco-friendly materials by blending carbon fibers into the matrix of a water-soluble cellulose derivative, carboxymethyl cellulose. For an optimal concentration of carbon fibers (10 wt.%), the printed patterns exhibit a sheet resistance of around 300 Ω/sq without any post-printing annealing process. The resistance of the screen-printed hydrogel patterns is sensitive to variations of relative air humidity through moisture adsorption and swelling of the cellulosic matrix surrounding the carbon fibers. It was found that the sensitivity to temperature and humidity can be triggered by drying the printed patterns at 120 °C. A negative temperature coefficient thermistor with a sensitivity of 0.079 °C−1 at 25 °C and a hygristor, where a variation in the RH from 10% to 60% increases the resistance by 15 times, were screen-printed on paper using the formulated cellulose/carbon fiber based ink.

1. Introduction

Recent developments in the area of printed electronics have been focused on making devices and circuits employing printing techniques as an alternative to conventional silicon-based technology [1–3]. The manufacturing of such devices on flexible substrates, like plastic foils or paper, has gained great importance in aiming to address the needs of the growing market for low cost, disposable, flexible and recyclable electronics. Here, the key issue is to develop reliable eco-materials and processes that must be inexpensive, simple, versatile and target the products’ sustainability.

The use of paper as an eco-friendly material (paper-based electronics [4, 5]) shows great potential to fulfill these demands, either exploring it as a substrate or an active component [6–9]. However, paper exhibits a porous structure and large surface roughness, which results in a series of shortcomings for hosting electronic devices on its surface, making it a challenging substrate compared to those that are smooth, but more expensive, such as non-biodegradable plastic foils, such as polyethylene terephthalate (PET) and polyimide (PI) [4, 8, 10]. To overcome this bottleneck, recyclable multilayer coated paper substrates with relatively high smoothness and good barrier properties can be used [10–12]. Here we have to highlight what has so far been done exploring the potential of paper as a substrate for thermochromic [13] and electrochromic displays [14, 15], nonvolatile resistive memory devices [16, 17], floating gate memory transistors [18], transistors [19, 20], disposable radio frequency identification (RFID) tags [21], batteries [22–24], photovoltaic cells [25, 26], including also sensing, diagnostic and pharmaceutical applications [27, 28].

On the other hand, today several printing techniques are available to be used in the fabrication of electronic devices, such as inkjet and screen-printing [4, 29–31]. The latter has been widely used in the conventional electronics industry due to its simplicity and compatibility with various substrates made of different materials, standing out as a good option also for paper electronics [2, 4, 29]. Like any other printing technique, screen printing deposition of functional materials requires the formulation of suitable inks. Conductive ones are often based on a multi-component system that contains a conducting material in an aqueous or organic solvent and various additives [29, 31]. The preparation of such inks is challenging,
due to the high viscosity required (typically above 1000 cP [2]) in order to avoid excessive spreading and leakage through the mesh, which can be achieved by adding polymer binders. Thus, cellulose can be exploited to provide a stabilizing and film-forming matrix hosting the conductive material that can adhere to a paper substrate [32]. Cellulose is the most abundant natural and renewable biopolymer resource on Earth, which makes sense to use it in the formulation of printable inks applied in paper electronics [33]. Nevertheless, the dissolution of cellulose is a challenge, due to its rigid long-chain and strongly inter/intra molecular hydrogen-bonded structure [34]. For that reason, cellulose is usually converted into derivatives with interesting properties, like carboxymethyl cellulose (CMC), which is a water-soluble anionic polyelectrolyte used in food, pharmaceutical and technical applications as a thickening, water-binding, suspension, stabilizing and emulsifying agent [35].

When cellulose or its derivatives are combined with conductive materials, through doping, blending or coating, they have the potential to give rise to new functional composite materials, in the form of microspheres, fibers or membranes, with the electroconductive material dispersed on the surface or within the matrix [32]. Blending cellulose with a conductive material is a current and an extremely attractive, inexpensive and advantageous approach reported in the literature [32, 36, 37]. Moreover it has been demonstrated that CMC is good as a dispersing and stabilizing agent of functional nanostructures [35, 38, 39]. Taking these considerations into account, in this work cellulose-based electroconductive composite inks were designed and formulated with proper specifications for screen-printing, using a simple and eco-friendly method by blending Carbon Fibers (CFs) into the matrix of a water-soluble cellulose derivative such as CMC. CFs were selected as conductive functional material thanks to their relatively low cost for industrial scale production (if compared to carbon nanotubes—CNTs) and high availability [40]. CNTs can be difficult to disperse partly because of their well-known hydrophobicity and intrinsic tendency to form large ropes or bundles due to very strong Van der Waals interactions [29, 41–44]. The use of cellulose derivatives as dispersants of carbon structures was already demonstrated [39, 41, 45–47]. CMC was successfully used as dispersant of single-walled CNTs (SWCNTs) being even more effective than sodium dodecyl sulfate (SDS), a commonly used dispersant for SWCNTs [47].

Sensors are a key component of many concepts of printed electronic systems. Temperature and humidity sensors are of extreme relevance when targeting the fields of smart packaging and internet of things (IoT) for instance. Concerning the last, a plethora of humidity sensing devices can be found, with the most popular relying on the variation of resistance or capacitance. Resistive sensors often present good interchangeability and are cheaper to be manufactured than capacitive-type sensors [48]. Carbon structures based composites have been already explored as sensing elements for temperature and relative humidity (RH) variations, for instance [49–51]. However, to the best of the authors’ knowledge, the combination with CMC in order to formulate inks for screen-printing has not been reported. In the present study, we focus on the physical and rheological properties of the formulated conductive inks, and on the printing quality and electrical properties of the obtained screen-printed patterns. Parameters like the number of printed layers and the influence of temperature and drying time were studied and correlated with the electrical performance of the printed hydrogel cellulose/CFs patterns. Finally, the influence of variation on temperature and RH was studied and successfully used in screen-printed sensor prototypes. In the present case, the sensing ability relies on the reversible swelling of the cellulosic matrix for high and low water contents scenarios. The incorporation of conductive elements in its structure implies that that the electrical conduction takes place through the CFs and herein, variations on resistance are due to changes in percolation through the fibers due to changes in the cellulosic matrix.

2. Experimental

2.1. Materials

CFs were provided by FISIPE [52] while CMC (Mw ~ 250 000, CAS: 9004-32-4) was purchased from Sigma-Aldrich and used as-received. The formulated inks were screen-printed on photographic paper type 3 produced by Felix Schoeller (FS3) [53]. Commercial conductive silver paste (AG-530, Conductive Compounds Inc.) was used to print the electrodes.

2.2. Experimental procedure

2.2.1. Ink formulation and screen-printing

Aqueous solutions of CMC with different viscosities were prepared varying the amount of CMC from 2 to 5 wt.%. After establishing the optimal binder proportion, cellulose-based inks were prepared by blending different contents of CFs, ranging from 1 to 20 wt.%, into an aqueous solution of CMC (3 wt.%). The resulting dark viscous ink was vigorously stirred for 24 h to ensure complete dissolution of CMC in water and improve CFs dispersion in the solution. The formulated conductive inks were deposited by screen-printing using a home-made system and a screen mold made of polyester with the following characteristics: mesh model, 77-55; mesh count, 190 mesh/inch; mesh opening, 81 μm; thread diameter, 55 μm; open surface, 30%; fabric thickness, 88–97 μm.
2.2.2. Characterization of the carbon fibers

Morphology of pristine CFs was examined by scanning electron microscopy (SEM) using a Hitachi TM3030Plus tabletop workstation. An optical microscope (Olympus BX51) equipped with an Olympus DP50 camera and the Cell F View Image System Software was used to estimate the length size of CFs from microscope images with 280 individual fibers, using ImageJ software. The structural analysis of the CFs was done by x-ray diffraction (XRD) using a PANanalytical X’Pert Pro-x-ray diffractometer in a Bragg–Brentano geometry, with a monochromatic CuKα radiation source (wavelength 1.5406 Å). Electrical characterization of the CFs was performed using ribbons with various lengths (from 2 to 10 cm) connected at some point. Conductive silver paint was used for contact electrodes and the resistance of the CFs’ ribbons was measured with a Keithley 617 digital electrometer.

2.2.3. Characterization of paper-based substrates

Morphology of the substrates was examined by SEM and three-dimensional (3D) profilometry. The latter was carried with an Ambios XP-Plus 200 Stylus Profilometer combined with TrueMap software. Hydrophilic nature of paper substrates was analyzed through contact angle measurements with the sessile drop method (Dataphysics OCA-15plus System). A 2 µl liquid drop of deionized water was deposited on the surface of paper-based substrates and at least 3 readings were taken on each sample, for different times.

Thermogravimetric measurements were performed using a Simultaneous Thermal Analyzer (TGA-DSC—STA 449 F3 Jupiter), from room temperature to 550 °C with a heating rate of 5 °C/min, in an aluminum pan, under air atmosphere.

2.2.4. Inks characterization

Viscosity was measured on Bohlin Gemini HRnano rheometer, in parallel plate geometry (20 mm diameter and 500 µm gap) for steady-state measurements. The temperature was kept at 25 °C and, before starting the measurements, samples were subjected to a pre-shearing stage, with a pre-shear of 1 s⁻¹ applied for 30 s, followed by a stabilization time of 180 s. A solvent trap was used to avoid evaporation. The steady-state measurements were performed for shear rates up to 1000 s⁻¹. Thermal degradation of prepared inks was studied in the same conditions described in section 2.2.3.

2.2.5. Characterization of screen-printed patterns

Several samples were prepared to fully understand the influence of the number of printed layers (from 1 to 10) on the electrical properties of the patterns. Each printed layer was dried for 15 min either at room temperature conditions (25 °C and a relative air humidity—RH, of ~50%) or in an oven at 120 °C. These drying conditions were selected considering the results obtained from Fourier transform infrared spectroscopy analysis (FTIR) regarding the water content within the printed patterns. The spectra were acquired at room temperature between 4000 and 550 cm⁻¹ using a Thermo-Nicolet 6700 spectrophotometer from Thermo Electron Corporation operating in attenuated total reflection (ATR) mode.

The continuity and homogeneity of the printed patterns was evaluated using an optical microscope and their thickness estimated by averaging a set of five measurements made using SEM cross section images. The sheet resistance (Rsh) was measured using a four-point probe set-up (Jandel Engineering). The measurements were performed inside a glove box, under an inert atmosphere, controlled temperature (25 °C) and RH (~15%) conditions.

The printed patterns were also subjected to bending deformation (tensile and compressive strain) using cylinders with different radii (18.5, 13.4 and 5 mm, respectively) using a home-made automatic set-up connected to a digital electrometer to monitor the resistance variation. Moreover, repeated bending cycles (up to 1000 cycles) were performed using a cylinder with a fixed bending radius (5 mm).

2.2.6. Electrical characterization under different environmental conditions

The electric properties of the printed patterns films were studied under different conditions of temperature and RH to check their potentialities as sensing elements. Commercial silver ink (PE-AG-530 Flexible Silver Conductive Ink) electrodes were printed on FS3 paper based substrates and dried at 120 °C. Afterwards, the developed CF based ink was also screen-printed into small square patterns of (7 × 10) mm² consisting of 6 printed layers. Each individual layer was dried either at room temperature or in an oven at 120 °C.

The electrical resistance dependence on temperature was undertaken at air atmosphere (~50%RH) and evaluated by heating the films from room temperature to 75 °C using a cryostat (Biorad CS8900) connected to a KEITHLEY 617 programmable electrometer. The influence of RH was evaluated between 10 to 60%RH. The humidity level inside the closed box was controlled by a home-made system consisting of two flow meters (Brooks Instruments) connected to a nitrogen line (for dry air) and to a water bubbler flask (for humid air).

3. Results and discussion

3.1. Structural, morphological and electrical characterization of carbon fibers

Figure 1(a) shows the XRD pattern of CFs, which reveals the characteristic peaks of the hexagonal carbon phase (ICDD file number 00-041-1487), with a
predominant peak near 25.0°, corresponding to (002) planes, and two broad peaks around 43.9° and 51.8° associated with (101) and (004) crystallographic planes, respectively. The SEM image of the as-received CFs (figure 1(b)) reveals a perfect cylindrical shape with a diameter of about 7 μm. An average length size of 123 μm, with a standard deviation of 79 μm, was estimated through a statistical study carried out using 280 randomly selected individual fibers and ImageJ software (figure 1(c)).

Electrical resistance of several pairs of carbon ribbons with different length, interconnected at a single contact point, was measured as depicted in figures 1(d) and (e). The slope of the linear relation represents the fiber’s resistance per length unit and the interception with the y-axis is the contact resistance between fibers (if contact resistance at the silver electrodes is negligible). Using equation (1),

\[ \rho = \frac{RA}{L} \]  

where \( R \) is the measured resistance of the CFs, \( L \) is the length and \( A \) is the transversal area, the electrical resistivity (\( \rho \)) of the CFs and contact point resistance values were estimated to be \( 1.32 \times 10^{-8} \) Ωcm and \( 910 \) Ω, respectively. The first is pretty similar to those encountered in manufacturer specification sheet, which reports a typical resistivity for the fibers of \( 2.2 \times 10^{-8} \) Ωcm\(^{\text{[34]}}\).

3.2. Surface properties and characterization of paper-based substrates

The influence of paper surface characteristics, such as roughness, porosity and wettability on printability of the developed electroconductive inks was evaluated by comparing the multilayer-coated paper FS3 with commercial printing paper. SEM images of the latter are shown in figure 2, revealing a surface composed of randomly dispersed long cellulose fibers of about 5 to 15 μm width. The fibers also appear to be flattened, due to the calendaring step during the manufacturing process. The corresponding cross section image shows packed fibers with a similar structure along the entire paper thickness. In contrast, FS3 paper’s surface exhibits a highly smooth, homogenous and nanoporous surface. From the cross section SEM image it is possible to distinguish different polymeric coating layers as schematically represented in figure 2(b).

There is a bottom and intermediate resin coating layer (RC), responsible by the flattening of the irregular and fibrous surface of raw paper (RP). A nanoporous top-coating layer (NC) assures simultaneously a much smoother and hydrophilic surface in FS3 when compared with conventional printing paper. The 3D surface scan shows that FS3 paper exhibits a peak-to-valley high (PV) and a root mean square roughness (RMS) of 0.80 μm and 0.14 μm, respectively, while commercial printing paper has a PV and RMS roughness of 14 μm and 2.21 μm, respectively.

Figure 2(a) also shows an image of a water droplet profile on the surface of paper substrates at an initial stage and after 5 min. Conventional printing paper reveals a hydrophobic behavior with a contact angle of 100.8°. After only a few seconds, the absorption is particularly large, increasing with time, due to the fibrous and porous nature of the paper and low evaporation rate of water. On the other hand, FS3 paper exhibits a hydrophilic behavior (73.2°), being visible some spreading of the water droplet, confirmed by the decrease of the contact angle to 55.2° after 5 min, while the NC layer slows down the water absorption.

Knowing the range of temperatures in which the paper substrates remain thermally stable is an important point to take into consideration since a post-printing temperature curing process is often required to stabilize the desired properties in the functional printed layer. As shown figure 2(c), both papers are...
stable until 220 °C, then an abrupt mass loss of 40.17% and 53.86% occurs for FS3 and conventional printing paper, respectively, as the temperature increases up to 370 °C, which corresponds to the degradation of cellulose [55].

3.3. Ink formulation and characterization

The use of the screen-printing technique for the deposition of electroconductive functional materials demands the formulation of suitable inks, which essentially comprise three main components: conductive functional materials, solvent and additives. To get a good print resolution combined with high electrical conductivity, the optimal combination of each component must be established. The formulated conductive inks are composed of CFs in a non-conductive cellulosic matrix. Thus, a minimum amount of carbon material is required to form percolation paths for charge carriers. For low concentration of CFs (≤5 wt. %), it was not possible to obtain conductive patterns, even after 10 printed layers. To increase conductivity and reduce the number of printing steps, the CFs content was increased up to 10 wt.%. Further increasing in the CFs content (a maximum of 20 wt.% was studied) did not reveal any improvement on the conductivity of the patterns as result of higher concentration of CFs combined with the high length size regarding the screen mold mesh aperture that contributes to the clogging of the mesh openings, resulting in less conductive patterns. For this reason, the CFs content in the ink was fixed at 10 wt.%.

To find out the minimum amount of binder able to result into a continuous and homogeneous film with a good printing definition, several aqueous solutions of CMC with different concentrations (3–5 wt.%) were prepared without adding the conductive functional material. Resolution test lines with a width of 275 μm, spaced by the same distance, were screen-printed using these solutions. The optical micrograph images of the resulting printed test patterns (figure 3(a)) show the actual line width varies depending on solution spreading, which in turn depends on the CMC content, thus their viscosity. Although it is possible to define continuous and narrow lines for solutions with only 2 wt.% of CMC, it tends to drain through mesh openings due to the very low viscosity, even without tangential stress being applied (results are not reported here). It is possible to slightly improve the printability of the solutions by increasing the concentration of CMC binder up to 3 wt.%. By doing so the solution becomes viscous enough to prevent draining through the screen mesh. Higher concentrations did not bring significant improvements on printing quality, being notorious for decreasing on the line resolution. For these reasons, a CMC concentration of 3 wt.% (referred as CMC3) was chosen for the ink formulation.

The resolution allowed by the formulated ink was tested by printing lines with a width of 275 μm in the mesh. The optical micrograph image in figure 3(a) shows that the resulting width of screen-printed line is around 400 μm. The increase in the CMC mass content seems to reduce the resolution of the printed pattern. This can be related to the time that the ink takes
to recover its initial properties once the tangential stress has been removed, which is essential to allow the ink to level up. However, the longer the time, the more spreading occurs, affecting the printing resolution.

The variation of the viscosity as a function of the shear rate for the ink with an optimized content of CMC (3 wt.%) and CFs (10 wt.%) (referred as CMC3 CF10) is represented in figure 3(b), having CMC3 solution as reference. Although the addition of CFs to the ink formulation increases its viscosity from 4.32 to 7.48 Pas for an applied shear rate of 0.1 s$^{-1}$, it is clear that within the CFs concentration range here studied, that the main contribution for the rheological behavior is given by the cellulosic binder. The CMC3 CF10 ink keeps the non-Newtonian behavior of the binder, as the viscosity exhibits a shear thinning behavior with applied shear rate, being classified as pseudo-plastic as desired for screen printing. If on one hand a high viscosity is desirable for the first stage of the printing process, to prevent draining of the ink through the mesh, on the other hand the application of a tangential stress by the squeezing process must allow the ink to pass through the screen mesh openings onto the substrate, by decreasing the ink’s viscosity.

TGA performed on the CMC3 CF10 ink is shown in figure 4(a). An abrupt mass loss occurs before 100 °C, which is related to water evaporation. The ink is stable until around 280 °C; after this temperature further mass losses suggest the beginning of CMC degradation. A detailed study was carried out by FTIR to understand the effects of drying time and temperature on the water evaporation rate of the screen-printed films. For this purpose, CMC3 solution was printed on FS3 paper and the drying temperature limited to 120 °C, to ensure water evaporation while respecting the temperature tolerance of the FS3 paper used as substrate, and thermal stability of the formulated ink. Figure 4(b) shows the FTIR spectra of the screen-printed films, taken for different drying times, either at room temperature or at 120 °C. There, we can identify the following peaks: centered at 2923 cm$^{-1}$ related to stretching of methane ring; 1587 cm$^{-1}$ related to C=O of -COO carboxyl group; 1415 cm$^{-1}$ corresponding to -OH stretching; 1322 cm$^{-1}$ related to C-H stretching in symmetric planes of CMC group; 1263 cm$^{-1}$ and 1064 cm$^{-1}$
corresponding to C-O stretching in the polysaccharide skeleton [56]. The broad band centered around 3260 cm$^{-1}$ corresponds to $-\text{OH}$ stretching and can be associated with the water content within the printed patterns, giving valuable information about the evaporation rate. In general, there is a decrease in the water content with drying time, as this process is faster at 120 °C, as expected. Nevertheless, no major changes occur after 15 min, where FTIR data suggest that the water content is lower within the printed patterns dried at 120 °C while for those dried at room temperature it sets a balance with the environments relative humidity.

### 3.4. Electrical characterization of screen-printed patterns

As depicted in figure 5(a), the number of printed layers was found to have significant influence on the electrical properties of the screen-printed patterns starting from CMC3 CF10 ink. For a single printed layer, CFs are evenly isolated and distributed within the cellulose matrix (see figure 5(b)), resulting in non-conducting patterns. It is necessary to have at least 4 printed layers in the case of the patterns dried at RT, and 6 layers when dried at 120 °C, to obtain a $R_{\text{sh}}$ of $5.1 \times 10^3$ and $1.8 \times 10^4 \Omega/$sq, respectively. It rapidly decreases with the number of printed layers as more connection points between the CFs, thus continuous percolation paths, are formed. Nevertheless, after 7–8 printed layers enough conductive paths exist and the $R_{\text{sh}}$ stabilizes around $3.1 \times 10^2$ and $1.2 \times 10^3 \Omega/$sq for patterns dried at RT and 120 °C, respectively. This value is much higher than the one expected if considering only the intrinsic resistivity of CFs, since here the interfacial contact resistance between the fibers imposes a limit on the minimum $R_{\text{sh}}$ value that can be obtained.

It is notorious that the patterns dried at 120 °C have the most drastic reduction in $R_{\text{sh}}$ with the number of printed layers, although it is always higher when compared with those dried at RT. This is associated with how the water is removed and how the CMC binder is distributed within the printed patterns. SEM images presented in figure 6 show that CMC is evenly distributed along the entire thickness in the case of the samples dried at 120 °C, while this is not evident for those dried at RT, that simultaneously present some voids. One possible explanation for this is that drying at 120 °C forces the CMC regeneration to occur in a much faster way as the water (solvent) is removed while slow regeneration when drying at room temperature allows the CMC binder to lay down on the substrate. This means CMC will remain at a higher amount at the contact points between CFs in films dried at 120 °C, this being also in line with the high $R_{\text{sh}}$ measured for these patterns when compared with those dried at RT.

The printed patterns were subjected to bending deformation using cylinders with different radius (18.5, 13.5 and 5 mm) for a pattern with 10 printed layers and dried at RT. As shown in figure 7(a), compressive strain leads to a decrease in resistance that reaches 45% of its initial value for a bending radius of 5 mm. On the other hand, an abrupt increase up to 241% is observed under tensile strain for the same bending radius. This is well above the elongation resulting from bending and so cannot be explained only by the geometric change on the patterns. This means that while compressive strain lead to internal rearrangement of the fibers and formation of additional contact points between neighboring CFs, the opposite happens under tensile strain.

Figure 7(b) shows the results of the relative variation in the resistance as a function of the number of tensile bending cycles undertaken by printed patterns using the smallest bending radius (5 mm), which corresponds to the highest bending deformation applied on the sample. The resistance was determined when the samples are taken back to flat conditions. A decrease of about 30% occurs right after the first cycles.

![Figure 5](image1.png)

Figure 5. (a) Sheet resistance of screen-printed patterns as a function of the number of printed layers using CMC3 CF10 ink dried at room temperature and 120 °C. (b) Optical microscope images of the screen-printed patterns after 1, 4, 8 and 10 printing layers on FS3 paper.
Figure 6. Top-view and cross-section SEM images of printed patterns on FS3 paper (10 printed layers) in which each layer was dried for 15 min either at RT or at 120 °C.

Figure 7. (a) Normalized resistance with increasing bending radius for compressive (pink) and tensile (blue) strain (Inset: schematic representation of the printed patterns under compressive and tensile strain). (b) Normalized resistance with increasing number of bending cycles under tensile strain for a fixed curvature radius of 5 mm. (c) Schematic model of the indenter used to perform the bending cycles and rearrangement of the CFs within the printed patterns. (d) Cross-section images (SEM) of the printed patterns on FS3 paper before and after 1000 bending cycles.
while the resistance reaches around 50% of its initial value after 1000 bending cycles. The vertical compression along the direction perpendicular to the surface when the films are strained promotes the rearrangement of the CFs creating more contact points between fiber right after the first cycle. Figure 7(c) shows the schematic representation of the fibers rearrangement within the film after bending while cross-section SEM images after 1000 cycles in figure 7(d) confirms it.

3.5. Carbon fiber-based films as temperature and humidity sensing elements

As seen in section 3.3 the drying conditions affect the electrical resistance of the printed patterns, which was attributed to how water is extracted from the cellulose matrix and CMC regenerates. This means that these patterns have great potential to be explored as sensing elements for temperature and humidity. While CFs have a semiconductor-like resistivity dependence on temperature, the CMC distribution within the printed patterns determines water adsorption/desorption in function of RH.

The schematic on figures 8(a) and (b) shows each step of the fabrication process for temperature and humidity sensors. The variation of electrical resistance of the patterns consisting of 6 printing layers, each one was dried for 15 min either at RT or at 120 °C, was registered from 25 to 75 °C and backwards using a heating/cooling rate of 2.5 °C min⁻¹. A period of 120 s was found to be sufficient for the stabilization of temperature upon a step of 5 °C. As shown in figure 9(a), both samples present a negative temperature coefficient and non-linear dependence of resistance with temperature, typical of semiconducting materials (thermistors) and is similar to what has already been reported in the literature regarding carbon and carbon fiber composites [49, 50, 57]. The cooling curve shows that the resistance variation presents some hysteresis, more pronounced on patterns dried at 120 °C. However, after 24 h, sensors dried at RT and 120 °C had already recovered 75 and 37% of the initial resistance value, respectively.

The Arrhenius plot for both samples with different drying conditions presented in figure 9(b) shows a logarithmic dependence of the electrical conductivity (assuming the printed patterns as solid slabs) versus the reciprocal of the absolute temperature. Two different slopes (i.e. conduction regimes) are present with the transition temperature staying around 40 °C. The activation energy was estimated from the slope of

Figure 8. (a) Schematic representation of the procedure for sensor fabrication. (b) Image of the printed sensors.

Figure 9. (a) Comparison of relative resistance variation between 25% to 75 °C for patterns dried either at RT or 120 °C (heating/cooling cycles, represented by solid/open symbols, respectively.) (b) Linear fittings (red line) of the ln(σ) versus 1000/T for each pattern. (c) Sensitivity dependence on temperature for samples dried at RT and 120 °C.
Arrhenius plot through equation (2).

$$\sigma = \sigma_0 e^{-\frac{E_a}{k_B T}}$$

where $\sigma$ is the electrical conductivity, $\sigma_0$ is a pre-exponential factor, $E_a$ is the activation energy (related to charge carrier hopping within the composite), $k_B$ is the Boltzmann constant, and $T$ is the temperature.

The existence of a few CFs only slightly above the percolation threshold within a non-conducting cellulosic matrix means that electrical conduction is governed not only by the intrinsic properties of CFs but also by the contact between themselves. At low temperature, the difference in $E_a$ is high when comparing both the drying conditions (0.33 eV versus 1.38 eV for RT and 120 °C, respectively). The highest sensitivity (and hysteresis) of the latter is attributed to the presence on CMC along the entire thickness of the printed patterns. Assuming the existence of CMC, the energy for hopping plays a most significant role in this case, by allowing charge transfer between neighboring fibers and thus, triggering the conductivity of the film.

The Arrhenius plots show that above 40 °C a second regime starts to dominate, where the difference in $E_a$ is not so high for both drying conditions (0.16 eV and 0.31 eV for RT and 120 °C, respectively), meaning that the electrical behavior becomes dominated by the intrinsic properties of the CFs, while at the same time the increasing temperature reduces the influence of the potential barriers existing at the contact points between fibers.

Sensitivity ($\alpha$) was calculated through equations (3) and (4), where $\beta$ is a constant related to the thermistor’s curvature and $R$ and $R_0$ are the resistance values ($\Omega$) at temperatures $T$ and $T_r$ (K), respectively [53]. Sensitivity is higher at lower temperatures, presenting a maximum value of 0.026 and 0.079 °C$^{-1}$ for samples dried either at RT or at 120 °C, respectively, near 25 °C. While the value obtained for sample dried at RT is slightly low, the sensitivity of sample dried at 120 °C is like that typically presented by thermistors for temperature variations centered around 25 °C.

$$\alpha = -\frac{\beta}{T^2}$$

$$R = R_0 e^{\beta \left(\frac{1}{T} - \frac{1}{T_r}\right)}$$

Electrical resistance under different RH conditions was determined using a home-made system consisting of two flowmeters controlling the volume of dry air (directly from the N2 line) and wet air (from the water bubbler flask) inside a closed box (see figure 10(a)). Electrical resistance was registered 5 min after reaching the required percentage of humidity inside the box, from 20% to 60% RH and backwards. This period was found to be sufficient for stabilization, indicating a relatively fast response. The values obtained for both samples are presented in figure 10(b) where it is clear that resistance increases with RH. The adsorption of water molecules by the CMC hydrogel matrix promotes the swelling of the film structure and affects the contact between CFs. Resistance presents a non-linear dependence on moisture content, increasing about 3 and 15 times when changing RH from 10% to 60%, for printed patterns dried at RT and 120 °C, respectively. Once again, samples dried at 120 °C present a higher sensitivity than samples dried at RT related to the higher moisture absorption/desorption associated with the distribution of the hydrogel CMC matrix along the thickness of the printed patterns, as already discussed. Resistance variation was also registered as the RH is brought back to the initial value. The response time of the sensor was found to be similar, with less than 5 min required to stabilize its resistance value, with small hysteresis.

The increasing interest in the field of printed sensors has been largely driven by the development of cost effective devices for the concept of the internet of things (IoT), where continuous monitoring is essential for interaction between humans and objects [48, 58]. The authors believe that a positive contribution has been made with the present work, where fully screen-printed cellulose based sensors on a paper substrate have been developed. While most humidity sensors rely on ceramics or polymers as sensing materials [48], the use of a biopolymer-like cellulose directly contributes to the achievement of low-cost and sustainable sensing systems. The relative low response time and hysteresis (namely in the case of humidity sensors), combined with the low cost of raw materials and production techniques and potential scalability to mass production, makes these sensors suitable for several types of applications, including smart tagging and packaging for the monitoring of food and other goods with regards to an IoT era [48].

4. Conclusions

Screen-printed printed conductive patterns were obtained from a water-based electroconductive ink compatible with paper substrates. The ink was formulated using CMC (3 wt.%) as binder and CFs (10 wt.%) as the functional conductive material. Printed patterns dried at room temperature have a $R_{48}$ of $3.1 \times 10^4 \Omega$/sq (measured at 25 °C and 15%RH) after 10 printing layers without any annealing process.

It was observed that patterns dried at 120 °C show a more uniform distribution of the CMC matrix after regeneration which is believed to affect the contact between fibbers and results in an increase in the resistance. However, the presence of CMC along the entire thickness of the printed patterns enhances the interaction with ambient humidity through water adsorption/desorption. This improves the sensitivity of these patterns when explored as sensing elements for both temperature and RH. The temperature sensor is a
thermistor with non-linear NTC behavior, and it was found that drying the films at 120 °C triggers its sensitivity from 0.026 to 0.079 °C⁻¹, around 25 °C, but with associated high hysteresis. For this reason, they are suitable for integration in disposable or slow rate/sporadic monitoring type of intelligence. On the other hand, patterns dried at RT are more suitable for use as temperature sensors in reusable systems. Resistance dependence on moisture is also non-linear and increases up to 15 times for patterns dried at 120 °C when the RH changes from 10% to 60%. In this case, hysteresis is small and so these patterns are more suitable for use as humidity sensors.

Finally, the absence of degradation of these sensing elements after 1000 bending cycles demonstrates the great potential for using them in flexible and printed electronics.

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