

# Pigment-Cellulose Nanofibril Composite and Its Application as A Separator-Substrate in Printed Supercapacitors

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## Abstract

Pigment-cellulose nanofibril (PCN) composites were manufactured in a pilot line and used as a separator-substrate in printed graphene and carbon nanotube supercapacitors. The composites consisted typically of 80% pigment and 20% cellulose nanofibrils (CNF). This composition makes them a cost-effective alternative as a substrate for printed electronics at high temperatures that only very special plastic films can nowadays stand. The properties of these substrates can be varied within a relatively large range by the selection of raw materials and their relative proportions. A semi-industrial scale pilot line was successfully used to produce smooth, flexible and nanoporous composites and their performance was tested in a double functional separator-substrate element in supercapacitors. The nanostructural carbon films printed on the composite worked simultaneously as high surface area active electrodes and current collectors. Low-cost supercapacitors made from environmentally friendly materials have a significant potential to be used in flexible, wearable and disposable low-end products.

**Keywords:** cellulose nanofibrils (CNF), pigment-CNF composite, pigment-CNF film, graphene, carbon nanotubes, supercapacitors, energy storage, separator, substrate, pilot scale manufacturing

## Introduction

Here, we present a pigment-CNF composite which has a nanoporous pigment-fiber network structure to enable optimal absorption of ink solvent, but still allow printing on its smooth and closed surface without short circuits. These properties facilitate using the composite as a separator-substrate in printed supercapacitors applications. The composite suitability for printed electronics applications was demonstrated previously by ink-jet with a silver-nanoparticle ink [1]. It was also modelled and demonstrated that in addition to the smoothness, the porosity is the most relevant property for the substrate [2]. Optimal porosity and smoothness properties of substrate are strongly dependent on printing method, ink, solvent and target application related to the absorption, surface charge and binding properties. The selection of raw

materials such as pigment, cellulose micro/nanofibrils, ink solvent and other additives enables varying these relevant properties of the substrate. The production of the composite in laboratory scale is described in [1]. Here, we present the up-scaling method in pilot scale to increase production possibilities of the pigment-CNF composite.

There has been an increasing interest for developing new types of supercapacitors, also called ultracapacitors, to meet requirements of various energy storage applications [3-6]. Supercapacitors are rechargeable electrochemical energy storage devices which offer great advantages of high power capability, high rates of charge and discharge, long cycle life, flexible packaging and low weight compared to other energy storage devices [7]. Future developments are going toward thin, low-cost, lightweight and flexible solutions which can be utilized in wearable and disposable electronics applications [3]. The emerging field of energy harvesting applications [8] for example from light [9], RF fields [10] or vibrations [11, 12] are lacking complementary energy storage solutions. The low-cost, flexible, metal-free, non-toxic and disposable supercapacitors produced by efficient process are needed for application in printed electronics systems [11, 13-15]. Nanostructural carbon materials such as carbon nanotubes (CNT) and graphene are promising future materials to be used in supercapacitors due to their excellent electrical conductivity and high surface area [7, 16-18]. Solution processed supercapacitors prepared from high viscosity CNT inks have been previously demonstrated by the authors [11, 10, 14, 19]. In these cases, a supercapacitor was fabricated so that first, the CNT electrodes were deposited on distinct plastic substrates and second, a commercial paper separator, soaked with the electrolyte, was sandwiched between the CNT-electrodes. In this paper, however, the supercapacitor electrodes are directly printed on the separator-substrate and there is no need for subsequent assembling steps such as lamination.

Inks containing nanostructured carbon materials are usually deposited onto flat and dense substrates such as glass, plastics or metallic films. However, the use of porous materials, for example paper, has many advantages such as strong adhesion of ink onto paper as well as the surface charges and functional groups of the paper material [20]. Paper absorbs solvents easily and binds nanostructural carbon strongly, making the fabrication process simpler than with flat substrates [21, 22]. Here, we take the advantages of highly nanoporous cellulose nanofibrils based substrate in a supercapacitor application.

There are a few previous demonstrations of paper-based supercapacitor architectures [4, 21-25]. Hu et al. demonstrated a fully integrated printed supercapacitor on a lightweight paper substrate with single-walled carbon nanotubes (SWCNT) [22]. The electrodes were deposited on both sides of the substrate, with the paper serving also as a separator; however, to prevent the device from short-circuiting due to the micron-sized pores in the paper, a surface treatment was needed to block the ink absorbing into the paper. To prevent the supercapacitor electrodes from short circuits, in our study, only calendaring for pilot scale film casted pigment-CNF substrate was needed. This indicates that nano-sized porosity in the composite allows simpler and roll-to-roll up-scalable manufacturing. Here we demonstrate an integrated structure where the pigment-CNF composite is used as both separator and substrate for screen-printed graphene electrodes as well as spray-coated CNT electrodes. The nano-sized pore structure allows the transport of electrolyte ions through the composite but at same time does not cause short circuit though all components are integrated on same separator-substrate. No metal current collector was used in the supercapacitors. The capacitance and equivalent series resistance (ESR) of the devices were both fairly good ones taking into account rather thin layer of the CNT and graphene inks on the pigment-CNF separator-substrate.

## **Experimental**

### ***Materials***

The Cellulose nanofibrils (CNF) used in these trials was made of Finnish once dried Bleached Hardwood (birch, *Betula L.*) Kraft pulp (BHKP). The fibril cellulose later called VTT CNF (Fig.1) was obtained after eight passes through Masuko Sangyo's (Supermasscolloider type MKZA10-15J) grinder by using decreasing gap width and increasing operating power. Rotation speed was fixed to 1500 rpm. VTT CNF was used in all pilot scale test points. In addition cellulose microfibrils, Celish KY-100g (Daicel Chemicals Ltd., Japan) has been used in samples formed at lab scale.

Pigments used in the pilot scale trials include plate shaped kaolin Capin SP (Imerys), coating grade kaolin Capim DG (Imerys) and aragonite shaped precipitated calcium carbonate (PCC) Opacarb A40 (Speciality minerals Inc.) Rosette shaped Albacar PCC (Specialty minerals) and Intramax 60 kaolin (Imerys) was used in the laboratory scale trials. The plastic carrier material used in pilot tests was 23  $\mu\text{m}$  poly(ethylene terephthalate) (PET) film. The plasma activation was done for the carrier film with argon/nitrogen blend and 50 W/m<sup>2</sup>/min intensity by a Vetaphone Corona-Plus (Type TF-415, CP1C MKII 2.0 kW) device with speed 5 m/min before film casting to increase the surface energy of the PET film.

### ***Pigment-CNF film fabrication***

VTT has used the equipment of Coatema® Coating Machinery GmbH to produce semi-industrial roll-to-roll scale pilot webs and films. Different coating and drying possibilities are available to be applied as a surface treatment process to the webs and films described elsewhere [27]. In this study SutCo environment was used successfully to produce pigment - CNF substrates with 7% dispersions. The dispersions which contained 80% of pigment and 20% of CNF by weight were first dispersed carefully with vigorous mixing with Diaf 100WH dissolver at 50 minutes with 400 rpm. The dispersions were then cast at speed 2 m/min with width of 300 mm and length of 6-8 m. After this, the wet coated film was cut to A4-size samples together with the carrier film and pressed with blotter papers under 0.8 kg weights to remove the excess water.

After slight initial off-line wet pressing, there was a similar variation in the initial dry content, from 20 to 35 %. Drying of PCN substrates was carried out with contact dryer or in oven. The contact dryer is shown schematically in Fig.2. It includes a curved metal plate, heated by electrical coils from the bottom side, and a tensioned dryer fabric. Experiments were carried out at a hot plate temperature of 60 °C during 20 minutes and a constant fabric tension of 2 kg/cm. A commercial dryer fabric made from flat yarns and with a permeability of 1600 m<sup>3</sup>/m<sup>2</sup>/h was used. A more detailed drying study was also done and reported in Timofeev et al. [28]. The pilot manufactured PCN sheets were also dried in an oven at 55°C between glass plates and under 5.6 kPa pressure weights for 48 hours for some measurements.

### ***Pigment-CNF film testing***

After drying, the samples were conditioned under standard climate (25 °C, 50% RH) before calendering and physical testing. The sheets were calendered with a laboratory scale calenderer with hard roll nip once. The calendering was done with approximately 20 MPa pressure and 150 °C temperature. Standard characterization methods were used for sheet testing. The grammage of the samples was determined according to ISO 536:1995. The thickness was determined according to ISO 534:1998 and the density was determined based on the measured values of grammage and thickness. Surface roughness was measured with Dektak 150 Surface profiler (Veeco), with 2.5 µm probe at 1 mg pressure.  $R_a$  is the arithmetic mean roughness,  $R_q$  is the root mean squared roughness and the peak-to-valley value is the height difference between minimum and maximum points in the measured data.

Thermogravimetric analysis (TGA) was performed using Mettler TGA 851e thermogravimetric analyser (Mettler Toledo). The measurements were performed in air atmosphere and the air flow was 50 ml/min. The heating rate was 100 °C/min up to 230 or 270 °C.

### ***Supercapacitor fabrication and characterization***

Graphene supercapacitor electrodes were screen printed on both sides of the substrate using a conductive graphene ink (Vor-ink X103 from Vorbeck). Two layers were screen printed on each side, and after printing of each layer, the sample was dried for 2 min at 120 °C in the oven. The samples were additionally dried for 10 min at 120 °C after all layers had been deposited to ensure proper ink drying. CNT supercapacitor electrodes were spray coated on both sides of the substrate using a CNT-xylan nanocomposite ink, the preparation of which is described elsewhere [15]. The ink formulation used here was 3.0 wt-% CNT and 1.5 wt-% xylan in water. A PET mask was used to define the electrode area while spray coating.

Graphene supercapacitors were prepared on the substrates with three different pigment dispersions (PCC-based TP2 and Kaolin-based TP3 and TP4, details of trial points shown in Table 3). CNT devices were prepared only on the kaolin-based TP3 substrate, as the spray-coating method was observed to be unsuitable with the PCN substrates due to the dilute CNT dispersion swelling the composite, resulting in buckling. The electrodes were 3.2 cm by 1.4 cm with an overlap of 1.4 cm, yielding an active device area of 2 cm<sup>2</sup> (Fig.3). The active area of the supercapacitor was soaked in aqueous NaCl (1 M) during measurements.

The supercapacitors were characterized in a 2-electrode configuration with a Zahner Zennium potentiostat/galvanostat. Cyclic voltammetry (CV) was recorded from 0 to 0.9 V at voltage sweep rates 5, 10, 50 and 100 mV/s. Supercapacitor properties were determined from a galvanostatic (constant-current) experiment according to an industrial standard (IEC 62391-1 (2006)). The devices were charged to 0.9 V in 1 min, held at 0.9 V for 30 min, and then discharged with a constant current. The capacitance is calculated from the slope of the discharge curve, and equivalent series resistance (ESR) from the initial IR drop at the beginning of discharge.

## **Results and discussion**

### *Pigment-CNF film material characterization and analysis*

Compatibility of the composite substrate with inkjet printing of silver nanoparticle ink and thermal sintering process was recently demonstrated [1, 2]. The conductivity of silver patterns was similar to those printed on PET film. The best conductivity was obtained for silver nanoparticle patterns, which were inkjet printed on kaolin based sheets. Curing temperatures as high as 220 °C could be used without causing any damage to the sheets. Thermogravimetric analysis (TGA) showed that the substrates can tolerate short exposure to temperatures up to 270 °C and over 12 h exposure to 230 °C shown in Fig.4. These temperatures are much higher than the current substrates for printed electronics, which enables e.g. high sintering temperatures and increase of the production speed. In oven tests it was also observed that PCC based pigments stands better over 200 °C temperatures than kaolin pigments. The kaolin seems to have a tendency to become brittle and dark probably because of ingredients involved on kaolin production process. Similar effects were not seen with PCC grades.

The PCN substrate should meet certain quality requirements in order to be applied as a base for printed supercapacitor applications. The main requirements concern nanoscale porosity, surface smoothness, flexibility and sufficient strength properties of the substrate. The substrate with kaolin pigment particles together with CNF has a suitable structure to be used as a substrate for printed energy storages. The reason for that is the lower porosity as compared to the PCC based substrates [2]. Several methods to upscale the production of pigment-CNF substrates (PCN) were tested: vacuum-assisted hand sheet making, foam forming, solvent casting and spraying. The most promising way for industrial manufacturing turned out to be solvent casting. The controlled adhesion between the pigment-CNF dispersion and the carrier plastic film and high consistency of the dispersion (7 wt-%) in film casting turned out to allow excellent properties for pigment-CNF substrate (Fig 5). The main advantages of the solvent casting method are 1) prevention of shrinkage of substrate during drying, 2) usage of high consistency (over 7%) dispersion and 3) control of toughness and flexibility of substrate by pressing 4) even formation. High resolution SEM images shows that porosity of PCN substrates is in nanoscale shown in Fig.6.

The web was pressed and dried attached to the carrier plastic with different drying methods described in Timofeev et al. [28]. After drying the sheets were calendered in laboratory scale. Pigment-CNF dispersion was spread at 7% consistency on the plastic carrier material. The method is based on the filed patent application [29]. The grammage of the final wet PCN sheets varied from ~142 to ~221 g/m<sup>2</sup>, and there was a similar variation in the initial solids content in the range of 20 %–35 %. Optimizing the drying conditions turned out to be of extreme importance. Quick drying of the pigment-CMF/CNF web resulted in cracks and the dried structure was hard and brittle. Slow drying at room temperature resulted in a smooth and more flexible structure. The best results were obtained by using pressing of the formed web before or during drying. The smoothest surface was obtained for the sample that was dried in the oven with weight. Interestingly, the excess water can be easily pressed out of the structure, which clearly speeds up the drying process. Pressing also improved further the flexibility of the formed structure.

The effect of different drying conditions on pilot scale manufactured PCN sheet properties was studied (Table 4). The smoothest surface obtained when drying was done in 50 °C in oven under pressure. In these studies to the trial point 1

the contact dryer was not included. Based on drying studies of contact dryer was chosen as the drying method for trial points 2-4 [28]. Drying in room temperature resulted in rougher surface on PCN substrates as shown in Table 4.

Environmental performance of these products was excellent (Fig.7). Evaluation was made by using standardized LCA approach, including fossil greenhouse gases (CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O), expressed as carbon dioxide equivalents (CO<sub>2</sub> eq). For the reference product (PET film) no water consumption data was available. The following assumptions based on the experiments have been made related to the environmental performance of substrates: The composite substrates are compatible with printing methods, such as inkjet, flexo and screen printing, and of suitable quality for low-cost applications, such as disposable personal electronics and diagnostics applications. In this paper, we report the use of CNF as a cellulose material, but the similar pigment-cellulose composite can be composed of cellulose microfibrils (CMF) as well [26]. The composite consists of 80% pigment filler (e.g. CaCO<sub>3</sub>, kaolin) and 20% CMF and it is formed by vacuum filtration, dried under pressure and calendered. However, one must notice that this concept still requires development and especially drying conditions are critical.

### ***Printed nanocarbon supercapacitors on pigment-CNF films***

Supercapacitors were prepared on the PCN calendered substrates of TP2, TP3 and TP4 (Table 3). The calendered substrates were used because it was observed that the uncalendered substrates absorb too much ink which causes short-circuiting of the electrodes on the opposite sides of the substrate. The adhesion of the ink on the calendered PCC-based TP2 was poor: the layer delaminated as soon as the ink had dried and so could not be used for supercapacitors (Fig.8). The sheet resistance of the printed graphene layers, measured with the 4-probe method, was 10 Ω/□, and that of the CNT layers varied between 30 and 70 Ω/□. The large variance of the CNT layer resistance is due to difficulty in depositing layers of similar thickness with a handheld spray coater.

CV curves of typical supercapacitors are shown in Fig.9. The CNT supercapacitor had more rectangular curves, whereas the graphene supercapacitors' are less rectangular. The presence of a voltage maximum indicates the presence of Faradaic reactions [30]. A possible source of reactive species is the graphene ink, which contains different binders and other additives designed to improve the printability. The CNT ink, composed of only carbon nanotubes and xylan polymer [15], does not have this behaviour, but the printability is poorer than that of the graphene ink.

The quantitative properties were determined from galvanostatic measurements and an example curve is shown in Fig. 10. There were no significant differences between the two substrate materials used in the graphene supercapacitors: samples with kaolin-based **TP3** had capacitance 20 mF and samples with kaolin based **TP4** 17 mF. The specific capacitances were 4.9 and 4.2 F/g, respectively, when accounting only for the active material mass on the electrode overlap area. The difference in specific capacitances may be due to uncertainty in weighing the ink layers: the increase in mass of the substrate due to the ink is very small, resulting in inaccuracy of the determined specific capacitance. Based on these results kaolin based substrates worked better compared to PCC based as supercapacitors due to more closed surface and more suitable porosity [2].

While the idea of simple and mass production compatible printable supercapacitor is promising the separator-substrate structure brings some challenges with the encapsulation of the device. Soaking the electrode overlap area in a liquid electrolyte facilitates device characterization in laboratory conditions, but a more robust method is needed for long-term use in an application. As the electrolyte can absorb into the substrate and travel along it, the substrate in the active area needs to be blocked to liquid flow. This could be achieved, for example, by saturating the substrate with a waterproof adhesive. Another way would be to encapsulate the entire freestanding supercapacitor with all the substrate, which then requires a material which does not corrode in aqueous solution. However, the long term encapsulation was not required in the scope of this work where the main focus was in the demonstration of functionality of proposed novel disposable supercapacitor architecture which can be fabricated with low cost and high throughput.

## **Conclusions**

We have demonstrated that low-cost pigment-cellulose nanofibril (PCN) composites can be fabricated in pilot scale. Optimization of drying and wet pressing conditions turned out to be crucial for generation of smooth and flexible structures. The developed nanoporous PCN composite was successfully used as a double functional separator-substrate in printed supercapacitors. The supercapacitor structure was obtained by simply printing the active layers on both sides of the nanoporous separator-substrate. The graphene and carbon nanotube (CNT) based inks were used as high surface area active layer materials and they simultaneously served as current collectors for the supercapacitor. The double functional separator-substrate with kaolin pigments and cellulose nanofibrils (CNF) worked well as an active element in the supercapacitor. The nanoscale porosity of a kaolin based separator-substrate made it more suitable for printing of active electrodes than a PCC-based substrate. The sheet resistance of the printed graphene layers was lower than that of CNT layers mostly due to different coating or printing method. Even though the sheet resistances of graphene and CNT electrodes were different, they resulted in very similar equivalent series resistance (ESR) of the supercapacitors, which suggests that the ESR is mostly caused by the separator-substrate. This type of mass-manufacturing-compatible, low-cost supercapacitor is well suited for energy harvesting applications and personal devices which require only low currents and thus do not suffer excessively from high series resistances. Moreover, they can be safely disposed of after use since they do not contain any toxic materials.

## **Acknowledgements**

The research leading to these results has been partly carried out in the “Efficient Networking towards Novel Products and Processes” (EffNet) research programme of FIBIC Ltd. The EffNet program has received funding from Tekes – the Finnish Funding Agency for Technology and Innovation – and Finnish Bioeconomy Cluster Ltd.

Special thanks to Stora Enso for successful co-operation in EffNet-program. We thank also to VTT colleagues Oleg Timofeev for drying studies, Unto Tapper for SEM images, Timo Kaljunen for semi-pilot trials and Panu Lahtinen for providing CNF material.

S.L thanks the Foundation of Nokia Corporation for support.

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Table 1. Characteristics of cellulose micro/nanofibrils used in in laboratory scale formed sheets measured by Brookfield: 1.5%, vane spindle V73. Detailed description of viscosity, transmittance and visual appearance evaluation used for cellulose micro- and nanofibrils are published in Kangas et al. [26].

| Sample         | Viscosity, mPa·s<br>10 rpm, 1.5% conc. | Transmittance, %<br>800 nm, 0.1% conc. | Visual appearance (optical<br>microscopy) |
|----------------|----------------------------------------|----------------------------------------|-------------------------------------------|
| VTT CNF        | 22502                                  | 60.2                                   | Fine                                      |
| Daicel KY-100G | 15777                                  | 8.1                                    | Coarse, long fibrils                      |

Table 2. Characteristics of cellulose nanofibrils used in pilot tests analysis measured by Brookfield: 1.5%, vane spindle V73.

| Sample ID                  | VTT CNF | STDEV |
|----------------------------|---------|-------|
| Cons. [%]                  | 3.42    | -     |
| pH                         | 5       | -     |
| Apparent yield stress (Pa) | 33      | 1     |
| Viscosity, 0.5 rpm (mPa*s) | 152689  | 517   |
| Viscosity, 10 rpm (mPa*s)  | 19693   | 108   |

Table 3. Pilot manufactured trial points with different pigments.

| Trial point | Pigment 80%                         | CNF 20% |
|-------------|-------------------------------------|---------|
| 1           | Kaolin Intramax                     | VTT     |
| 2           | PCC Opacarb                         | VTT     |
| 3           | Capim SP mass 50% Capim DG mass 50% | VTT     |
| 4           | Capim SP                            | VTT     |

Table 4. Different drying methods influence for sheet properties in trial point 1. RT = Room temperature.

| Pressing & drying of<br>Trial point 1                   | Thickness,<br>[ $\mu\text{m}$ ] | Grammage,<br>[ $\text{g}/\text{m}^2$ ] | Density, [ $\text{kg}/\text{m}^3$ ] | Ra, [ $\mu\text{m}$ ] | Rq,<br>[ $\mu\text{m}$ ] | Peak-to-<br>Valley,<br>[ $\mu\text{m}$ ] |
|---------------------------------------------------------|---------------------------------|----------------------------------------|-------------------------------------|-----------------------|--------------------------|------------------------------------------|
| TP1, pressing 10min,<br>drying +50°C, under<br>pressure | 102.0 $\pm$ 1.7                 | 143                                    | 1398 $\pm$ 23                       | 0.15                  | 0.19                     | 1.2                                      |
| TP1, pressing 10min,<br>drying RT                       | 161.2 $\pm$ 0.3                 | 209                                    | 1297 $\pm$ 2                        | 0.60                  | 0.70                     | 4.4                                      |
| TP1 pressing 10min,<br>drying +50°C                     | 124.7 $\pm$ 5.2                 | 178                                    | 1425 $\pm$ 60                       | 0.20                  | 0.25                     | 2.0                                      |
| TP1, no pressing,<br>drying RT                          | 179.1 $\pm$ 3.0                 | 221                                    | 123 $\pm$ 21                        | 0.45                  | 0.60                     | 4.0                                      |

## Figures

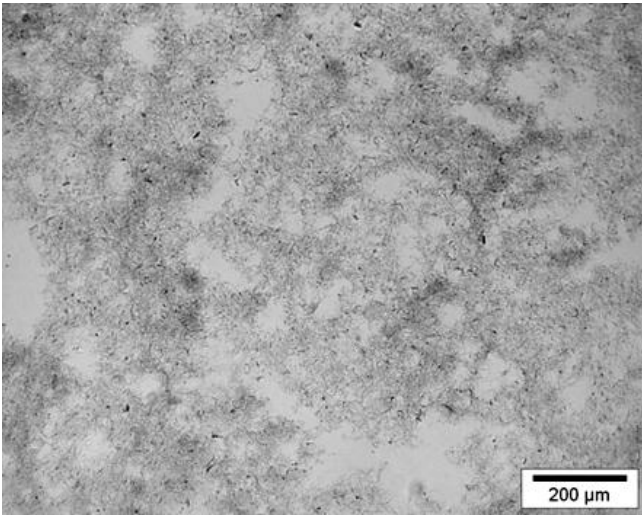


Fig.1 SEM image of VTT's cellulose nanofibril (CNF) grade.

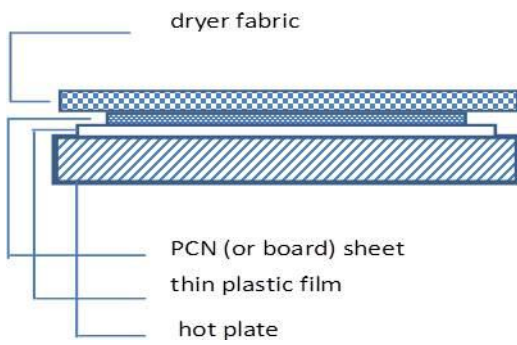


Fig.2 Schematic view of a contact dryer.

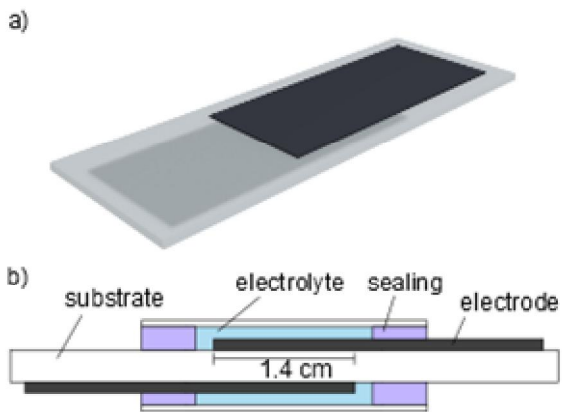


Fig.3 Schematic overview (a) and cross-section view (b) of the supercapacitor device configuration and assembly.

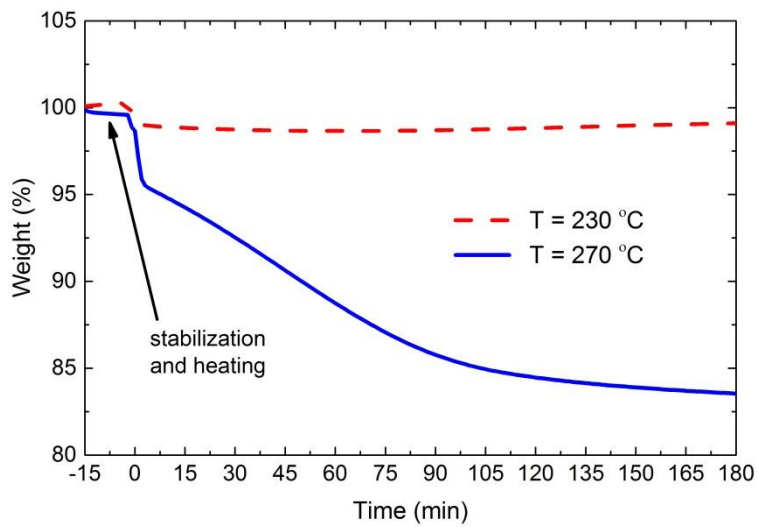


Fig.4 Thermogravimetric analysis of pigment-CNF sheets shows that the substrate can stand temperatures as high as 230°C (red) for hours.



Fig.5 Smooth layer of pigment-CNF dispersion was spread on top of the support material.

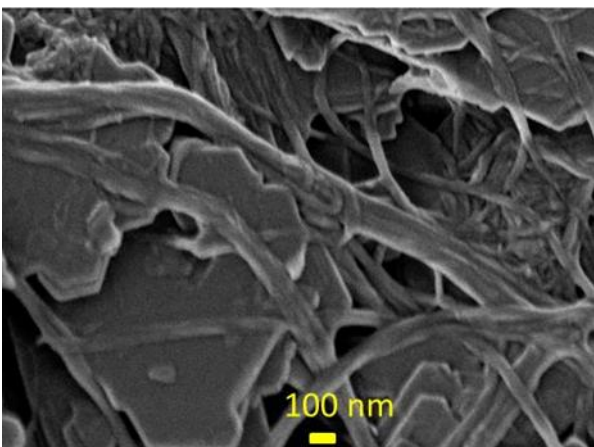


Fig.6 High resolution SEM image of the PCN sheet before calendering.

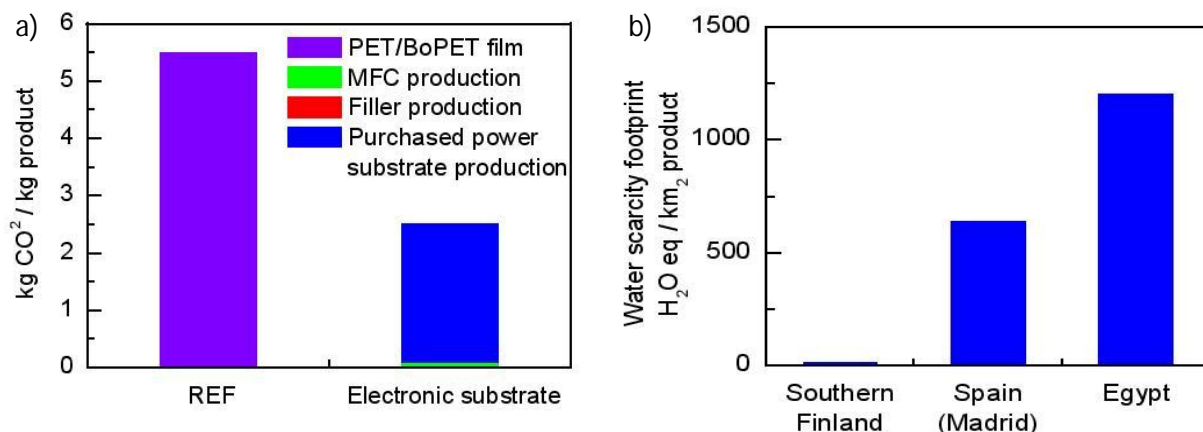


Fig.7 Environmental performance screening for the substrates of printed electronics: Calculated cradle-to-gate carbon footprint for printed electronics substrate in comparison with PET/BoPET film reference (range 5-8 kg CO<sub>2</sub>/kg from literature) (a) and water consumption of substrate production weighted with local scarcity indices (b).

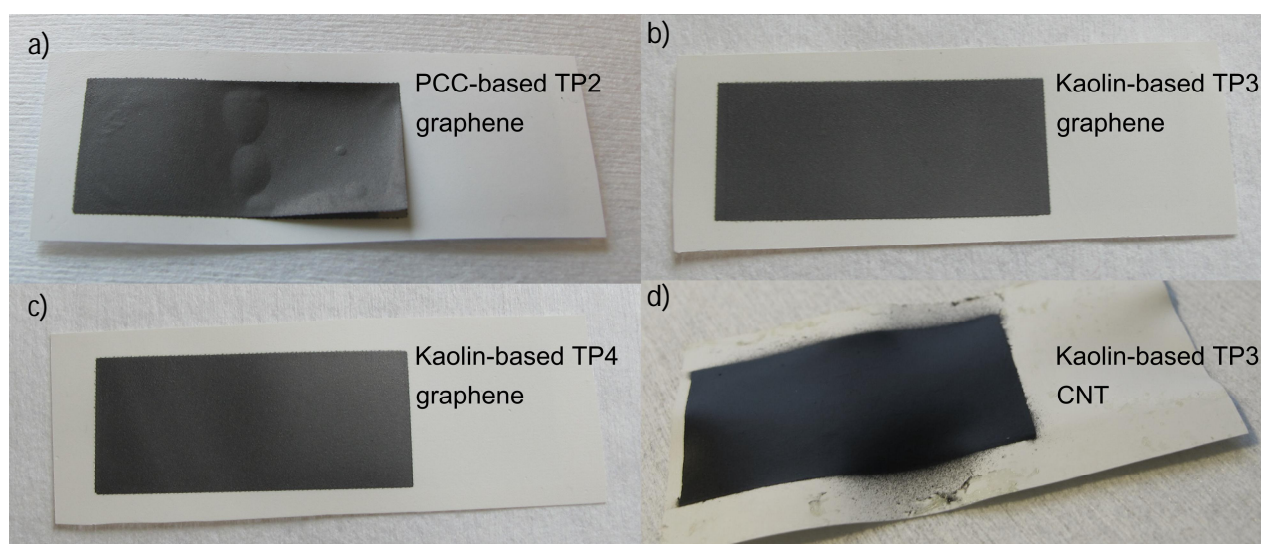


Fig.8 Printed graphene and CNT layers on the substrates. Good results were achieved for kaolin-based substrates when printed with graphene ink. The adhesion of ink to the PCC-based substrate was poor, resulting in delamination of the printed electrode layer. Spray-coating the CNT ink resulted in the sheet buckling due to absorption and the ink spreading under the mask.

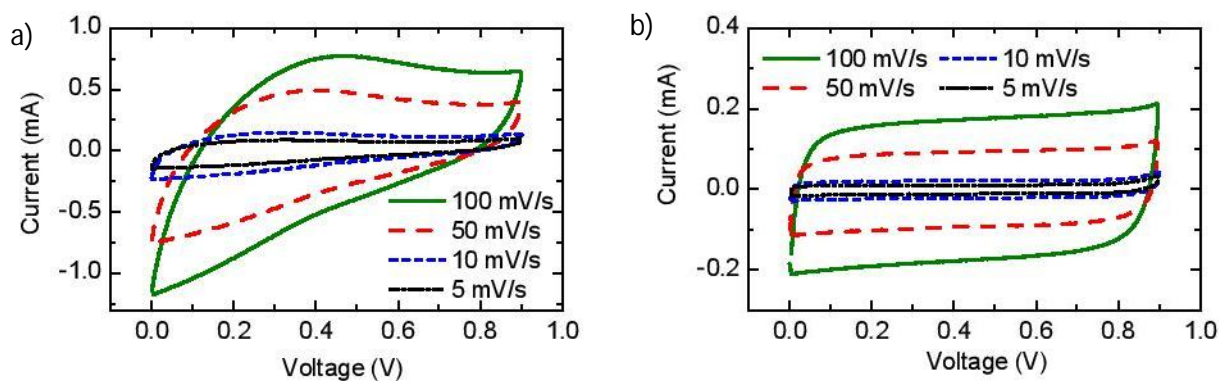


Fig.9 CV curves of the devices with a) graphene and b) CNT electrodes.

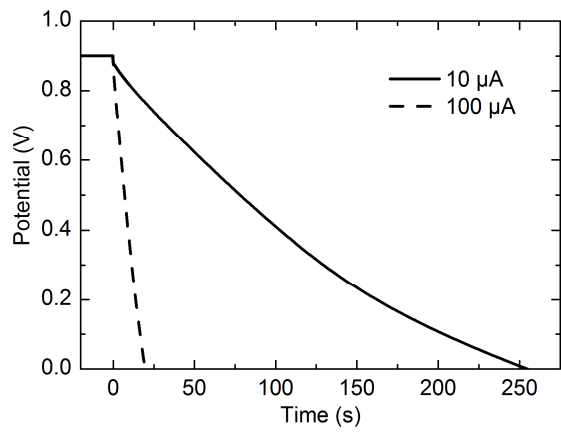


Fig.10 An example of standard supercapacitor characterization by galvanostatic discharge curves in the case of CNT supercapacitors.