ELECTROMECHANICAL COUPLING

IN THREE-PHASE FIBROUS PAPER

By

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ABSTRACT OF THE DISSERTATION

Electromechanical Coupling in Three-phase Fibrous Paper

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This work aims to develop a scalable process of fabricating highly porous composite paper with tunable conductivity and put forward an open-source workflow to model a three-phase stochastic fibrous network. In the experimental studies, this work employs a foam-laying method to fabricate composite paper with carbon black (CB) as conductive fillers and cellulose fibers as the matrix. By embossing such paper, its porosity decreases while its conductivity increases. Tuning the porosity of composite paper alters the magnitude and trend of conductivity over a spectrum of concentrations of conductive particles. The largest increase in conductivity from $8.38 \times 10^{-6}$ S/m to $2.5 \times 10^{-3}$ S/m by a factor of $\sim 300$ occurred at a percolation threshold of 3.8 wt% (or 0.36 vol%) with the composite paper plastically compressed by 410 MPa, which caused a decrease of porosity from 88% to 42% on average. Our composite paper showed stable piezoresistive responses within a broad pressure range from 1 kPa up to 5.5 MPa for 800 cycles. The piezoresistive sensitivities of the composite paper were concentration-dependent and decreased with pressure. Composite paper with 7.5 wt% CB had sensitivities of $-0.514$ kPa$^{-1}$ over applied pressures ranging from 1 kPa to 50 kPa and $-0.215$ kPa$^{-1}$ from 1 kPa to 250 kPa. This piezoresistive paper with
embossed patterns enabled touch sensing and detection of damage from darts and punches. Understanding the percolation behavior of three-phase composites (cellulose fibers/conductive particles/air) and their response to damage, pressure, and processing conditions has the potential to enable scalable applications in prosthetics and robotics, haptic feedback, or structural health monitoring on expansive surfaces of buildings and vehicles.

Few theoretical models capture piezoresistive responses of three-phase conductive composites. To interpret the electromechanical coupling of our piezoresistive composite and provide some insight in designing customized composite, we built multiscale models to simulate nanoparticle-nanoparticle interaction and fiber-fiber interaction. We also proposed an open-source workflow for computational generation and finite-element analysis of non-woven fibrous materials. To avoid interpenetration of fibers, we generated a micro-mechanical model with curved fibers in Blender, an open-source 3D computer graphics software, and applied rigid-body physics to fibers to repel each other for stacking. We modeled the paper-making process by simulating the falling and shaking of the fibers. Then, we further analyzed the electrical properties of the fibrous network in the open-source Salome-Elmer software. Overall, the proposed open-source workflow facilitates and speeds up the generation and analysis of the non-overlapping fibrous network.
DEDICATION

To my parents Guiqiang Liang and Laiyou Tan, and my brother Pinzhi Liang.

To Xiyue and Joanna.
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1. Introduction

1.1. Motivation and Objectives

Large-area, skin-like sensors for detecting spatial distributions of touch, pressure, and impact will be useful for a number of applications ranging from civil infrastructure to prosthetics to robotics to structural health monitoring of ground and aerospace vehicles. We envision that paper-based composites may be a good candidate for the large-scale fabrication of skin-like sensors by incorporating a roll-to-roll embossing process for patterning. Meanwhile, few theoretical models capture piezoresistive responses of three-phase conductive composites. Proper modeling at multiscale can facilitate the interpret the electromechanical coupling of our piezoresistive composite and provide some insight in designing customized composite.

In this thesis, we focus on the fabrication and modeling of conductive tunable composite paper suitable for skin-like sensing. This work has three objectives. The first objective is to develop a scalable process to fabricate conductive, three-phase, fibrous composites with tunable electromechanical properties. Second, we aim to explore the processing-property relationships for tunable conductivity of fibrous paper. Thirdly, we pursue to conduct theoretical and numerical analysis of the electrical properties of the piezoresistive material. To accomplish these objectives, we fabricated composite paper with carbon black as conductive particles and cellulose fibers as the matrix, along with detailed electrical characterization and multiscale modeling.

1.2. Background on Paper-based Composite

This section is taken from Chapter 15 of the Handbook of Flexible and Stretchable Electronics. [1]

1.2.1. Paper as a material

Paper has received refreshed attention as a material for advanced electronics because of its wide availability, sustainability, and small environmental footprint[2], [3]. The field of paper-based electronics, papertronics,
refers to electro-chemo-opto-mechanical devices with functionality patterned on or within paper-based substrates. Paper-based substrates are multi-scale, porous mats of fibers that manipulate the flow of fluids, heat, light, charges, magnetic fields, and forces/stresses.

Paper already plays a significant role in writing, printing, packaging, currency, origami, personal hygiene, medicine, and construction. These applications are possible through a diverse set of manufacturing processes and chemical additives. Modification of the fibrous matrix of paper can tune its hydrophilicity or hydrophobicity, porosity, opacity or transparency, and surface roughness [4]–[7]. Paper can be as soft as biological tissue or as strong as Kevlar [8]. Paper is also flexible, porous, lightweight, and biodegradable. Surface treatments and additives can modify the functional properties of paper to make it magnetic, photocatalytic, retardant to flames, antibacterial, deodorizing, electrically conductive, or thermally insulative [9].

Paper is a planar assembly of fibers that lie roughly horizontal, or a mat formed by a nonwoven network of randomly distributed fibers [5], [10]. Printing paper usually contains fillers, such as clay, talc, rosin, or alum to improve brightness, printability, and resistance to water [6]. Other non-cellulose-based “paper-like films” include cellophane, sheets of carbon nanotubes, and sheets of graphene [11]–[13].

1.2.2. Technologies for the Fabrication of Papertronic Devices

Paper is an electrical insulator with a typical dielectric constant of 2.3 and electrical resistivity of $\sim 10^9 \, \Omega \cdot \text{cm}$ [14]. Nevertheless, add-on electronic functionality is attainable, as the fibrous networks and hydrophilic nature of cellulose-based paper enhance the adhesion of functional fillers to its surface or in its porous interior. Electronic traces and components on the surface of a sheet of paper are papertronics on paper. Papertonics in paper tune the electromechanical properties within the volume of the paper substrate. In either class of papertronics, factors that influence electrical properties include conductive fillers, processing, surface roughness, bending stiffness, and absorbency of inks. [15], [16], [2], [3]

1.2.2.1. Electronics on Paper
In this category of papertronics, paper acts as a passive substrate to support functional electronic features. Fabrication involves coating, printing, and writing. For these techniques, formulating an appropriate ink is of prime importance. Inks may contain dispersed nanoparticles (NPs), dissolved organometallic compounds, or conductive polymers. Customized inks balance processability and desired physical properties including conductivity, optical transparency, mechanical strength, and adhesion [17]. How binders and solvents in inks interact with paper is another consideration, as these interactions may lead to swelling, buckling, and shrinking of paper [18].

Techniques for coating thin conductive layers on the outer surfaces of paper include rolling [19], spin coating [20], sputtering [21], and evaporative deposition [22]. Multiple layers of conductive coatings may be necessary for surface homogeneity and uniform electrical conductivity. A typical conductive ink for coating consists of a binder and conductive fillers. Thus, the conductivity of coated paper follows percolation theory in which there is a non-linear relationship between the concentration of a filler in a matrix and the bulk properties of the filler. The threshold of percolation depends on the applied binders and conductive fillers [23]. The binders are typically electrical insulators with low conductivity. Conductive fillers include metals, metal oxides, silicon-based nanomaterials, carbon-based nanomaterials, and conductive polymers [24]. Calendering or annealing can augment the electrical conductivity of the coating. Calendered samples are more compact, less porous, and less vulnerable to crease than uncalendered ones [25]–[27]. Coating techniques are suitable where the application requires complete coverage of functional materials on a surface of the paper with a controlled thickness (e.g., energy storage devices—supercapacitors, batteries, and solar cells) [28]–[30].

Coating techniques coupled with etching or patterned material removal can be effective techniques for patterning 2D features or traces on the surface of a paper-based substrate [31]. This technique is of particular use in capacitive sensing when the patterned conductors benefit from having small gaps between them [32]–[35]. In lab settings with low volumes of produced devices, serial laser-based ablation is effective
in patterning a device in a few minutes. Nonetheless, large-scale manufacturing may require the use of excimer lasers or chemical etching with high-resolution masks. Besides electronic applications, laser treatment can selectively modify the hydrophobic paper (like parchment paper, wax paper, and palette paper) to create hydrophilic patterns with micro/nano-hybrid structures [36]. This method provides a fast and cost-effective way to produce paper-based microfluidics.

To pattern electrical traces and interconnects on paper, techniques include inkjet, stencil, screen, and transfer printing (Figure 1.1). Inkjet printing has a micro-scale resolution with picoliter-sized droplets of ink ejected onto a substrate through one or more nozzles [37]–[39]. Examples of printed functional devices include thin-film transistors, electronic circuits, biosensors, and energy storage devices [40]–[44]. Inkjet printing requires inks with low volatility and low viscosity to avoid clogging nozzles [16]. Therefore, it is necessary to keep the concentration of nanoparticles in ink at a low enough concentration to ease the flow through a nozzle or make the ink thixotropic. A thixotropic or shear-thinning ink has a low viscosity as it experiences high shear rates within a nozzle, and then has a high viscosity after exiting [45]. To keep the ink from penetrating the surface of the substrate, pre-treating the paper is often necessary [41]. Low-temperature thermal, plasma, and photonic sintering processes can reduce the electrical resistance by merging conductive nanoparticles and reducing the porosity of the printed traces [46].

Screen printing involves patterning conductive inks through a mask or mesh onto a substrate[47]. This technique has shown applications in wireless communication antennas on a nanopaper composite, thin-film transistors, and piezoresistive MEMS sensors [48]–[50]. Screen printing typically requires ink of high viscosity (> 1000 cP) to avoid excessive spreading and leakage through the mesh, and some techniques have even included cellulose-based binders to facilitate adhesion to paper [51].

Transfer printing is a technique for picking up traces or devices fabricated on one substrate and placing them on another [51]. Using a soft transfer stamp, the technique leverages rate-dependent adhesion to pick up or deposit targeted components [52]. Often, the transferred electronic components come from
semiconductor-based rigid substrates, and the receptor is a soft, flexible substrate [53], [54]. There is also a non-contact laser-induced forward transfer (LIFT) technique to fabricate three-dimensional (3D) microstructures [55], [56]. Wang et al. used this laser direct-write technique to transfer volumetric pixels of silver nanopastes from donor substrates to the receiving substrates in order to obtain ultra-fine pitch bonds (<10 μm) and interconnects for electronics [57].

![Techniques to fabricate electronics on paper.](image)

**Figure 1.1.** Techniques to fabricate electronics on paper. (A) Inkjet printing (Images taken from [40]). (B) Transfer printing (Images taken from [53]). (C) (D) (E) Stencil-based printing (Images taken from [50]).

Roll-to-roll (R2R) manufacturing is the ultimate strategy to mass-produce flexible electronics over large areas [58]. R2R manufacturing includes gravure printing (with engraved images) and flexography (with raised images). Serial rollers can work together to print images and structures layer by layer [59].
Alternatively, a roll-to-plate (R2P) technique can transfer ink continuously on individual flat sheets of paper (Figure 1.2) [60].

Handwriting is another strategy for fabricating electronics on paper (Figure 1.3). One technique employs pens compatible with highly conductive gallium-based liquid metal, copper ink, silver ink, carbon nanotube ink, enzymatic ink, and zinc oxide nanoparticle-based ink [16], [61]. Another technique uses pencils to produce carbon-based electronics on paper in a solvent-free manner [62]. Pencils represent a simple and low-cost method suitable for rapid prototyping and educational purposes. However, there are many opportunities to explore the reproducibility and scalability of this wear-based (tribological) approach for the potential mass production of papertronics. Analogous to drawing with a pencil on paper, Mirica et al. mechanically abraded a pellet of compressed SWCNTs on the surfaces of paper to form gas sensors. They found that the sensors drawn on paper with smooth surfaces (e.g., weighing paper) had good sensitivity, high signal-to-noise ratio towards NH$_3$, and comparable reproducibility to SWCNT-based devices fabricated by solution-phase methods [63].

Figure 1.2. Large-scale transfer printing techniques: gravure printing and flexography. (A) R2R process (Image taken [59]) and (B) R2P process (Image taken from[60]).
Figure 1.3. Writing techniques for papertronics. (A) A 3D antenna drawn by a silver-ink filled rollerball pen on a sticky paper (Image taken from [64]). (B)(C)(D)(E) A flexible sensing circuit drawn by silver-ink pen (Images taken from [27]). (F)(G)(H) A parallel metal-plate pen depositing ZnO nanoparticles on paper (Images taken from [61]). (I)(J)(K)(L) A pencil-drawn strain gauge (Images taken from [65]).

While electronics on paper are straightforward and promising with their high spatial resolution, there are drawbacks to printing solely on the surface of a substrate. Poor adhesion between paper and conductive inks can affect the long-term stability of produced devices [66]. For a folding substrate, the
tensile or compressive stresses are highest at its surface away from its neutral bending axis. These bending stresses can lead to cracks in patterned circuit architectures, or detachment of electronic components from flexible substrates [67], [68].

1.2.2.2. Electronics in Paper

In contrast to electronics on paper, electronics in paper incorporate conductive fillers within a cellulosic network to form intrinsically conductive composites that are less susceptible to cracking and abrasion than inks patterned on the surface of a substrate. Currently, there are three main methods for fabricating cellulose-based conductive paper (Error! Reference source not found. Figure 1.4 (A)(B)(C)): (I) flow-directed filtration [69], (II) dip coating/soaking/deposition, and (III) additive manufacturing (or 3D printing).

Flow-directed filtration begins with the functionalization of fibers by coating treatments or adding fillers during pulping. After pulping, the fibers in solvent pass through a filtering screen or mesh to form a fibrous mat/sheet (e.g., handsheet forming or vacuum filtration). This wet mat then undergoes pressing and drying stages that tune its final morphology and resulting physical properties [70]–[72]. The matted fibers function as a porous and hydrophilic framework to immobilize different types of fillers: (I) carbon-based fillers—carbon black, graphite, carbon fiber, carbon nanotube, reduced graphene oxide, and graphene [72]–[79]; (II) conductive polymers (e.g., poly(3,4-ethylene dioxythiophene) polystyrene sulfonate (PEDOT: PSS)) [80]); and (III) metal nanoparticles (e.g., silver nanowires) [81]. Flow-directed filtration ranges from low-volume fabrication with handsheet forming to medium-volume fabrication with dynamic sheet forming [82] to large-scale manufacturing lines [83].

Simple dip coating, soaking, and deposition embed conductive inks/particles into the fibrous structure of paper [84]–[87]. Usually, it requires repetitive treatments by the selected process to make a uniformly conductive composite paper. These methods are suitable for substrates with varied porosities, such as tissue paper, filter paper, and copy paper [88]. With such paper, rapid prototyping is possible.
However, dip coating, soaking, and deposition may create weak bonds between fillers and fibers, and may also swell the paper. To overcome this, one unique form of deposition uses wax-based printing to form hydrophobic barriers, thus containing the lateral spread of aqueous conductive inks within paper [89].

![Figure 1.4](image)

**Figure 1.4.** Three main techniques to fabricate cellulose-based conductive paper, including (A) flow-directed filtration (Images taken from [76]); (B) Soaking (Images taken from [85]); (C) 3D printing (Images taken from [45]). (D) Carbonization that turns cellulose fibers into conductive carbon networks (Images taken from [90]).

Additive manufacturing (AM) is a technique for the intricate patterning of three-dimensional structures. One AM-based process forms cellulosic structures through the layer-by-layer deposition of a printable conductive composite paste (consisting of cellulose, conductive fillers, and a solvent). This technique achieved complex 3D geometric patterns for capacitors, batteries, and sensors [91]. Previous studies have also demonstrated the printability of cellulose acetate (CA) [92], cellulose nanocrystals (CNC)
[45], composites of silver nanowires, and sodium carboxymethylcellulose (AgNW-CMC) [93], and composites of carbon nanotube and nanofibrillated cellulose (CNT-NFC) [91].

Unlike some printed materials, hot-melt extrusion in typical AM-based processes is problematic for cellulosic pastes. Due to the intramolecular and intermolecular bonds, the hypothetical melting point of cellulose (467 °C) is higher than its degradation temperature (around 315 °C) [94]–[96]. Therefore, cellulose is not compatible with hot-melt extrusion as it degrades upon heating before melting/flowing sufficiently. To print cellulose effectively, current methods include: (I) using a low concentration of cellulose; (II) replacing the hydroxyl groups with other functional groups (e.g., acetate groups) to make the material soluble in volatile solvents, extruding the material, and then reverting the material to cellulose by restoring the hydroxyl groups (e.g. deacetylation)[97], [92]; (III) extruding the spinning solution directly into a coagulating bath and then removing the extruded fibers [91].

The direction of extrusion in additive manufacturing can affect the mechanical properties of printed components. Components containing filaments of oriented particles will result in anisotropic composites. For instance, the reinforcing effects of CNC (an aspect ratio of about 18) in polymer nanocomposites are more significant in the longitudinal direction (LD) than the transverse direction (TD) [45]. Nonetheless, it is possible to minimize the effect of the printing direction with cellulose-based polymers. For printed CA, Young’s moduli (2.2 ± 0.1 GPa in the LD and 2.2 ± 0.2 GPa in the TD) and yield strengths (45 ± 1.9 MPa in the LD and 44.7 ± 2.2 MPa in the TD) were similar in orthogonal directions [92].

Apart from cellulose-based papertronics, another type of electronics in paper utilizes carbonized paper, or a hierarchical porous carbonaceous aerogel (HPCA), which is synthesized from commercial paper by freeze-drying and high-temperature pyrolysis (Figure 1.4 Error! Reference source not found. (D)). Carbonized paper shows promise in energy storage and strain sensors [90], [98]–[100], as it possesses high porosity (up to 99.56%) [99], high specific surface area (63.4 ~ 2200 m2 g−1 ) [90], [100], and moderate...
electrical conductivity (13.6 S/m) [98]. When filled with elastomers, carbonized paper can have foldable and stretchable characteristics which allow it to function as a heater or a strain sensor [98]–[100].

Overall, electronics in paper with inks/particles distributed among insulating cellulosic fibers enable tunable conductive, capacitive, piezoresistive, and piezoelectric properties. There are still opportunities to further understand the process-structure-property relationships of such volumetrically patterned materials. Furthermore, these composite sheets have customizable mechanical properties and keep patterned electrical regions away from exposed surfaces susceptible to scratching and high bending stresses.

1.2.2.3. Typical Paper-based Substrates for Flexible Electronics

Paper-based electronics link distinct fiber morphologies, additives, and surface treatments to target applications. For electronics on paper, copy paper is a common choice for inkjet-based printed electronics due to its printability in conventional printers, availability, and low cost [101], [102]. However, the absorption of ink in copy paper can lead to prints with low conductivity because the resulting tortuous conductive paths may lack complete inter-fiber connectivity along the surface of the substrate. One solution to this problem is to use paper with non-absorptive or hydrophobic surfaces such as glassine paper, parchment paper, or photo paper [103]–[106]. Another approach is to cut and/or etch metallized paper into conductive architectures and devices, as mentioned in Section 1.2.2.1 [32], [33], [35].

In contrast, electronics in the paper are functional conductive composites with inks/particles embedded in the porous paper, such as filter paper and chromatography paper [86], [89]. However, the natural cellulose fibers in such paper have low strength due to their disrupted crystalline (amorphous) regions. In contrast, regenerated cellulose, bacterial cellulose, and nanocellulose fibers consist of only crystalline regions and will result in paper with superior mechanical attributes suitable for applications demanding high strength and endurance [107]–[109], [53]. The nanofibers with high crystallinity can form
densely packed paper that scatters less light than regular paper with fiber bundles and/or pores, which makes such nanopaper transparent and useful for optoelectronic applications [110], [111], [28].

Different materials, grammages, and thicknesses of the paper substrate can achieve desirable mechanical properties for other specific electronic applications. Some paper-like materials made of cellulose derivatives (e.g., nitrocellulose fibers) and synthetic fibers of polyolefins (e.g., Teslin paper) are key components for microfluidics (e.g., lateral flow assays) and printed flexible electronics [112]–[116]. These paper-like substrates have superior mechanical properties to cellulosic paper, fibrous structure, and porosity [117], [41], [118]. Paper made of carbon-based materials such as carbon fibers, carbonized cellulose, carbon nanotubes, and graphene is suitable for energy storage applications due to its resulting conductive and porous morphology [119]–[122]. In addition to the type and material of paper, grammage (mass per unit area) and thickness also affect its overall tensile strength and elastic modulus. Typical tissue paper, copy paper, and filter paper have a grammage of 12–30 gm⁻², 80 gm⁻², and 84 gm⁻², respectively [3], [123]. For paper of similar grammage, filter paper is thicker, less compact, and mechanically weaker than copy paper [123].

1.3. Thesis Overview

This work focuses on the experimental investigation and modeling of three-phase, conductive, cellulose-based paper, along with extensive electrical characterizations. Chapter 1 introduces the motivation, objectives, and background of this work. It presents paper as a material and reviews technologies on fabricating papertronic devices, which include electronics on paper and electronics in the paper. Chapter 2 describes the experimental process to fabricate conductive, porous paper by the foam-laying method. Chapter 3 focuses on the experimental results of the composite paper, including morphology observation under a microscope, detailed electrical characterization, and demonstrations to show the composite paper to be sensing substrates for touch and damage detection. Chapter 4 introduced the computational model of fibrous networks. Chapter 5 summarizes the open-source workflow to generate 3D models of fibrous
networks and analyze the model by finite element methods. Chapter 6 summarizes the completed work so far and makes suggestions for future work. It also reviews some technical issues and potential solutions, as well as challenges from an engineering perspective.

2. Experimental Design of Three-Phase Paper-based Composite

Chapter 2, Chapter 3, and part of the Appendix are taken from our published article in ACS Applied Materials & Interfaces. [124]

2.1. Fabrication of Conductive Composite Paper

To fabricate highly porous and uniform conductive paper, we’ve modified a water-efficient foam-laying process for papermaking compared with the conventional wet-laying process [125]–[127], as shown in Error! Reference source not found.. The foam-laying process uses a foaming agent, or surfactant, to make homogeneous, porous composite paper. Prior uses of surfactants in dispersing carbonaceous particles avoid foaming or bubbling by ultrasonication or by adding antifoaming agents.[128]–[130] However, the surfactant in our foam-laying process helps lower the surface tension of the aqueous suspension containing cellulosic fibers. Then, the suspension foams when mixed with air.[131] The bubbles in the foam separate and redistribute fibers in an enlarged volume, which also prevents flocculation.[132] Vacuum filtration densifies and drains out the bubbles, which helps to form a porous mat of cellulose fibers after drying (Figure 2a, S1). We emboss the samples at room temperature for electrical characterization.
Figure 2.1. Schematic diagram of the process to fabricate composite paper by the foam-laying method and to tune its porosity by embossing. (a) Mixing cellulose fibers and carbon black in water by a Resonant Acoustic Mixer (RAM). (b) Generating foam by a mechanical mixer agitating the aqueous solution of carbon black, fibers, and sodium dodecyl sulfate (SDS). (c) Decanting the foam into the handsheet former through a funnel. (d) Removing bubbles by vacuum filtration with a polished steel plate covering the foam. (e) Composite paper out of a drying ring. (f) Embossing a small sample out of the composite paper.
2.1.1. Fabrication Process: Preparation of Aqueous Dispersions of NBHK Fibers

Uniform dispersion of the conductive filler in the cellulosic matrix is essential to achieving reproducible electrical properties. We used northern bleached hardwood kraft pulp (NBHK) (Prime C, Woodland Pulp LLC) as the matrix material and carbon black Vulcan XC-72R (Cabot Corporation) as the conductive filler. We first disintegrated/agitated a pulp-water suspension (consistency of 1.6%) by a kitchen blender for 3 minutes. After the agitation, the mean width and mean length-weighted length of fibers were approximately 18.9 μm and 762 μm, respectively (measured by MorFi fiber analyzer, Pulp and Paper Services, LLC, Figure S17).

2.1.2. Fabrication Process: Preparation of Aqueous Dispersions of NBHK Fibers and CB

We mixed the agitated pulp suspension with carbon black at an acceleration of ~70 g (686 m/s²) in a resonant acoustic mixer (RAM, ResodynTM Acoustic Mixers, Inc) for 2 minutes to obtain a uniform slurry. We prepared composites consisting of 1 wt% to 40 wt% carbon black based on the dry weight in the ambient environment. We did not go beyond 40 wt% as the conductivity started to level off at high concentrations.

2.1.3. Fabrication Process: Preparation of CB-NBHK Foam by Adding SDS

We diluted the slurry with water to 0.26% consistency (4 g fiber/1.5 L water) and agitated it at 1000 rpm by a mechanical mixer for 3 minutes. Next, we added 0.4 g of sodium dodecyl sulfate (SDS, L4509, Sigma Aldrich) to the slurry, stirring it at 1700 rpm for 15 minutes to entrain air for a stable foam, as shown in Figure S1a. The final air content was around 70%.

2.1.4. Fabrication Process: Preparation of CB-NBHK paper

We decanted the foam via a funnel onto a nylon mesh in a handsheet former with a diameter of 160 mm. To obtain compact structure and uniform surfaces, we covered the foam with a polished steel plate and applied vacuum filtration (88 KPa) for 3 minutes to dewater and filter the bubbles. (Figure S1b-d). We dried the sheet of composite paper in a drying ring for one day in the ambient environment.

2.2. Morphology Observation
We examined the morphology of the prepared composite paper by a scanning electron microscope (SEM, Zeiss Sigma FESEM). We coated the samples with a 20-nm gold layer (Sputter Coater, Model EMS150T ES) and observed them under the conditions of high vacuum at an accelerating voltage of 5 kV.

### 2.3. Porosity Calculation

The porosity, the ratio of pore volume to total volume, depends on the density of the composite. We deduced porosity by the theoretical composite density $\rho_{ct}$ (the effective solid density by the combination of the filler and the cellulose), and the experimentally determined density $\rho_{ce}$ (mass divided by volume) as Eq. (2.1) and Eq. (2.2) show.[133], [134]

$$\phi = \left(1 - \frac{\rho_{ce}}{\rho_{ct}}\right) \times 100\% \quad \text{(Eq. 2.1)}$$

$$\rho_{ct} = \frac{1}{\sum_{i=1}^{n} \left(\frac{W_i}{\rho_i}\right)} = \left(\frac{W_f}{\rho_f} + \frac{W_m}{\rho_m}\right)^{-1} \quad \text{(Eq. 2.2)}$$

where the density of fillers is $\rho_f = \rho_{CB} = 1.8\,\text{g/cm}^3$ and the density of the matrix is $\rho_m = \rho_{cellulose\ fiber} = 1.5\,\text{g/cm}^3$.

### 2.4. Electrical Characterization

We prepared U-shaped samples by a laser cutter (Versa VLS 2.3) and compressed the samples (Figure S1e) by a hydraulic press (maximum force of 88 kN, Series 3393, Carver Inc.). Before electromechanical characterization, we conditioned the samples in an environmental chamber for 24 hours to achieve the same moisture content within each (Figure S1f). The environmental conditions were 23°C and 50% relative humidity (RH) according to TAPPI Standard T402. We compressed the legs of samples to reduce contact resistance during measurement. Then we measured the samples in the environmental chamber by clamping the compressed legs of the samples with a test fixture (HP14047) as shown in Figures S1g,h. By the admittance spectroscopy method (monitoring the admittance over a wide frequency range),[135] we characterized eight samples of each concentration of composite paper using an HP4192A LF impedance analyzer with a frequency range of 5 Hz to 13 MHz at an oscillator (OSC) level of 1V. From the two components of
admittance (conductance $G$, and susceptance $B$), we calculated the AC conductivity $\sigma$, impedance magnitude $|Z|$, and phase of the sample $\theta_Z$ according to Eq. (2.3) -Eq. (2.5).

$$\sigma(\omega) = |Y(\omega)| = \sqrt{G(\omega)^2 + B(\omega)^2} \frac{L}{Wt}$$
(Eq. 2.3)

$$|Z| = |R + jX| = \frac{1}{|Y|} = \frac{1}{|G + jB|} = \frac{1}{\sqrt{G^2 + B^2}}$$
(Eq. 2.4)

$$\theta_Z = -\tan^{-1}\left(\frac{X}{R}\right) = -\tan^{-1}\left(\frac{B}{G}\right)$$
(Eq. 2.5)

where conductivity $\sigma$, admittance $Y$, conductance $G$, and susceptance $B$ are functions of angular frequency $(\omega)$. Length $L$, width $W$, and thickness $t$ are geometric parameters of the sample. The effective length of our U-shaped samples is 0.79 inch, calculated by COMSOL simulations shown in Figure S18.

2.5. Characterization of Piezoresistive Behavior

To characterize the piezoresistive behaviors of our composite paper, we carried out compression tests using an Instron machine 4411 with a 500-N load cell at 0.02 mm/s at room temperature and 50% RH. We embossed and clamped the two lateral edges of U-shaped samples (Figure S9d), between copper foil for electrical conduction. Then we exerted cyclic pressure by controlling displacement on the unembossed region (0.4 in×0.3 in) and recorded the force and electrical resistance simultaneously. In processing the data, we synchronized the data of pressure and resistance by aligning the peaks and rescaling the machine times. By interpolation, we obtained resistance data according to the range of pressure.
3. Tunable Electrical Properties of Embossed, Cellulose-Based Paper for Skin-like Sensing

The foam-laying method in our paper-making process prevents the flocculation of fibers, which helps to make uniform composite paper. Figure 3.1 compares the front sides and back sides of composite paper made by the foam-laying method and wet-laying method. The foam-laying method can achieve uniform front and back surfaces even with 8-gram fibers, which is twice the mass of the wet-laying method. The composite paper made by the wet-laying method has an uneven, bumpy surface in the backside. Furthermore, the foam-laying method is water-efficient: in our paper-making process, the foam-laying method used 1-1.5 L water, while the wet-laying method used 7 L water.

Figure 3.1. Comparison of composite paper made by the foam-laying method and wet-laying method. 5 wt% CB foam-laying NBHK (8-gram fibers): (A) the front side, (B) the backside. 5 wt% CB wet-laid cotton (4-gram fibers): (C) the front side, (D) the backside.
3.1. Morphology Change of Composite Paper before and after Embossing

Figure 3.2b-g and Figure S2 show scanning electron microscope (SEM) images of the fibrous network. The morphology of the composite paper changed significantly after embossing with decreased porosity. Before embossing, the fibers were sparsely arranged with few contacts per fiber. After embossing, the gaps between fibers became small and even negligible, which narrowed the gaps between the CB particles. Most fibers became flat with an increased top-down, cross-sectional area. Figure S3 shows magnified images of the surface of fibers. As the filler concentration increased, the CB on the fibers evolved from sparse loading to dense loading, which coarsened the fiber surface.
**Figure 3.2.** Picture and SEM images of composite paper. (a) Picture of fabricated composite paper at the concentration of CB from 0 wt% to 40 wt%. (b) - (g) are SEM images of composite paper. (b) and (c) are of 0 wt% CB before embossing and after embossing, respectively. (d) and (e) are of 3.8 wt% before embossing and after embossing, respectively. (f) and (g) are of 10.5 wt% before embossing and after embossing, respectively. (b) has brightness increased by 20% and contrast by 40%, (c) has brightness increased by 20%, (d) has brightness increased by 20% and contrast decreased by 20%, and (f) has brightness increased by 40%.

### 3.2. AC Conductivity of Composite Paper by Admittance/Impedance Spectroscopy

Figure S4a details the impedance-frequency response of composite paper at low concentrations of CB (1 wt%, 1.4 wt%, 2 wt%, and 2.7 wt%). These samples exhibited indistinguishable electrical impedance over the AC frequencies before and after compression, behaving like capacitors with high magnitudes of impedance and negative phase angles (close to -90°). Figure 3.3a illustrates the impedance-frequency response of samples at 3.8 wt% and 5.3 wt% concentrations. Starting from 3.8 wt%, the impedances of the samples were statistically distinct from each other before and after compression. The p-value at 10 kHz was less than $4.2 \times 10^{-5}$ between uncompressed samples and less than $4.4 \times 10^{-5}$ between compressed samples, both significantly lower than 0.05. After compression, the magnitude of impedance decreased, while the phase increased. The magnitude of the compressed samples with 3.8 wt% CB approximated that of the uncompressed samples with 5.3 wt% CB. Figures S5 and S6 show the impedance of characterized samples with high concentrations of CB from 7.5 wt%. For samples from 14.6 wt% and above, the phases of the samples increased to approach 0°, behaving like resistive elements.

Table S1 shows the conductivities of our composite paper. For both uncompressed and compressed samples, the conductivities increased nonlinearly with the concentration of CB, as presented in Figure 3.3b. The conductivity was low before rapidly increasing in the vicinity of 3.8 wt%; then it gradually increased
at high concentrations of CB. For composite paper at each concentration of CB, its corresponding conductivity shifted upward after the embossing process. The greatest shift occurred at 3.8 wt% (or 0.36 vol%, calculated by Eq. (S1) in the SI): its conductivity increased by a factor of 298, i.e., from $8.38 \times 10^{-6}$ S/m to $2.5 \times 10^{-3}$ S/m. This increase in conductivity was concurrent with a decrease in porosity from 88% to 42.4% on average by compression. The compressed, densely packed CB-coated fibers formed more electrically conductive paths than those with higher porosity at the same concentration of CB. Composite paper with 40 wt% CB achieves conductivities of 27.7 S/m before compression and 122 S/m after compression, which are comparable with other works (Table S2).

One can view paper composites as “an effective medium”: an electrical network of resistances/impedance, or a lattice of sites and bonds. Within this network, increasing the volumetric fraction of conductive fillers or particles can lead to dramatic changes in electrical conductivities, dielectric permittivity, and mechanical properties of electronic composites.[137] According to the percolation theory, there is a critical concentration of particles at which the material transitions from low conductivity to significantly high conductivity, which is the electrical percolation threshold. This transition follows the universal scaling law, as shown in Eq. (3.1).

$$\sigma \propto \begin{cases} 
\sigma_f (f - f_c)^t & f > f_c \\
\sigma_m (f_c - f)^s & f < f_c \\
\sigma_m \sigma_f^{1-u} & f \approx f_c 
\end{cases} \quad (\text{Eq. 3.1})$$

where $\sigma, \sigma_f, \sigma_m$ are the conductivities of the composite, fillers, and the matrix, respectively; $f$ is the volumetric fraction of the fillers; $f_c$ is at the percolation threshold; $t, s, u$ are critical exponents for either two-dimensional (2D) or three-dimensional (3D) object-based morphologies. For 2D morphologies, $t = 1.1 - 1.3, s = 1.1 - 1.3$; for 3D morphologies, $t = 1.6 - 2.0, s = 0.7 - 1.0$; $u = t/(t+s)$.[138], [139] According to Eq. (3.1), the log($\sigma$) is proportional to the adjusted CB concentration log($f f_c$) in the region above the percolation threshold. Linear regression analysis confirms the percolation threshold to be 3.8 wt%. Deduced from the slopes of the fitting curves in Figure 3.3c, the critical exponents...
For samples before and after embossing are 3.6 and 2.47, respectively. Further analysis of the slopes is available in Figure S7. Similarly, we obtained exponents \( s \) (0.05 before compression and 0.15 after compression) in Figure S8.

**Figure 3.3.** Impedance-Frequency response and AC conductivity of composite paper. (a) The frequency response of impedance (magnitude and phase) of composite paper at CB concentrations of 3.8 wt\% and 5.3 wt\% before and after compression (8 repetitive samples). The curves are skipping 3 points for clarity. For the phase of 3.8 wt\%, there were only some measurable sporadic values at low frequencies. \( (\theta_Z = -45^\circ \text{ at frequencies of 446 Hz, 562 Hz, and 630 Hz, } \theta_Z = -75.96^\circ \text{ at 14.125 kHz.}) \) The dashed line shows interpolated
phases of 3.8 wt% at the frequencies from 1 kHz to 10 kHz. The data set of 3.8 wt% has one outlier removed. The zoomed-in figures show the error bars. (b) The conductivities of samples over the concentration (weight fraction) of CB at the excitation frequency of 10 kHz. The inset shows the conductivities at low concentrations of CB. (c) Curve fitting of the log-log plot of conductivity over the adjusted concentration of CB for samples above the percolation threshold ($f > f_c, f_c = 3.8$ wt%).

The critical exponents of our composite paper are different from the universal values in the literature. Our composite paper is a three-phase material with cellulosic fibers, CB fillers, and open pockets of air, in which the exponents $t$ (3.6 before embossing, 2.47 after embossing) exceed the typical range of 1.6-2 for 3D morphologies of two-phase materials. The exponents $s$ (0.05 before embossing, 0.15 after embossing) are significantly lower than the literature values (0.7-1.0) for two-phase materials. Our non-universal values of exponents might occur due to frequent tunneling events, contact resistance, or structural imperfections in the conductive media (like the Swiss cheese model).[140], [141]

3.3. Piezoresistive Response of Composite Paper

Figure 3.4 shows the piezoresistive response of composite paper (7.5 wt%, 10.5 wt%, 20.5 wt%) under normal cyclic pressure. For the 10-cycle test, as shown in Figure 3.4a, our composite paper showed stabilized responses to pressure after the first cycle,[142] and exhibited low hysteresis in consecutive loading-unloading cycles. The composite paper displayed negative resistance variation with pressure within a broad pressure range from 1 kPa up to 5.5 MPa (Figure S9ab), which may apply for gentle touch (>10 kPa) and other human dynamic motions.[143], [144] In the pressure-response curves of Figure 3.4a, $S1$ and $S2$ denote the pressure sensitivities ($S = \delta(\Delta R/R_0)/\delta P$, relative resistance change divided by pressure change) of composite paper upon loading in the low-pressure range (1 kPa–250 kPa) and the high-pressure range (250 kPa–up to 5.5 MPa), respectively. The piezoresistive sensitivities of our composite paper decreased with pressure, which is due to the increasing elastic resistance with compression.[145]
The composite paper showed concentration-dependent piezoresistive sensitivity. For the loading state in the low-pressure range, the sensitivities $S1$ to pressure of the composite paper diminished, going from -0.215 kPa$^{-1}$ to -0.035 kPa$^{-1}$, as the concentration of CB increased from 7.5 wt% to 20.5 wt%. In the high-pressure range, the sensitivities $S2$ of the composite paper increased with the concentration of CB but remained comparatively small, with values up to $-0.004$ kPa$^{-1}$. For the unloading state, the sensitivities show similar trends as those upon loading (Table S3). Although our composite paper shows limited sensitivity in these broad ranges, composite paper with 7.5 wt% CB achieves $-0.514$ kPa$^{-1}$ at the loading state and $-0.585$ kPa$^{-1}$ at the unloading state over applied pressures ranging from 1 kPa to 50 kPa (Table S4 and Figure S9c), which exceeds the sensitivities of some graphene-based pressure sensors in this pressure range.[146], [147] Incorporating other nanoparticles in this framework can potentially bring out highly sensitive piezoresistive sensors as Table S5 suggests.

The dependence of piezoresistive sensitivities on the CB concentration of the composite is likely attributable to tunneling effects between CB particles. According to Wang et al., the resistance of CB-rubber composite depends on the resistance between CB particles, which form conductive paths mainly by tunnel currents; compressing such two-phase composite changes the number of effective conductive paths and the electrical resistance of a single effective conductive path.[148], [149] In the low-pressure range, more conductive paths form under compression for the low-concentration CB composites (LCBC) than the high-concentration CB composites (HCBC). Furthermore, due to the greater change of gap/distance between CB particles, the resistance of single effective conductive paths of LCBC decreases more than that of HCBC.[150] Similarly, these two reasons may contribute to the higher piezoresistive sensitivity of our three-phase LCBC than HCBC in the low-pressure range. However, in the high-pressure range, compared with HCBC, LCBC could become more susceptible to the destruction of conductive paths caused by transverse slippage of CB, which decreases the piezoresistive sensitivity.[151]

Our composite paper exhibited repeatable piezoresistivity. Composite paper with 7.5 wt% CB showed stable responses during 800 cycles of compression up to 5.5 MPa (Figure 3.4b). The relative
changes of resistance in the low-pressure range were slightly positive in the first few cycles, gradually dropped to negative values, and stabilized starting from the 40th cycle. Figure 3.4c,d show the magnified cycles at the beginning and at the end of the compression, where the variations of relative change in resistance are neglectable.

**Figure 3.4.** Piezoresistive response of composite paper. (a) Pressure-response curves for composite paper with the mean values and standard deviations based on 9 cycles after 1st-cycle stabilization. For clarity, we plot points at an interval of 0.25 MPa. The right arrows denote loading and left arrows unloading. S1 denotes the sensitivity between 0.001MPa–0.25 MPa, S2 denotes the sensitivity after 0.25 MPa. We only label the sensitivities of the loading state here. Composite paper with 7.5 wt% CB had the steepest slope or the highest pressure sensitivity (−0.215 kPa−1), which was six times larger than that of the 20.5 wt% composite (−0.035 kPa−1). The inset figure shows the resistance over 10 cycles; the inset photo shows the setup of the compression test. (b) The relative change of resistance of 7.5 wt% CB over nearly 800 cycles. (c) The relative change of resistance of 7.5 wt% CB over the first 10 cycles of (b). (d) The relative change of resistance of 7.5 wt% CB over the last 10 cycles of (b).
3.4. Demonstration 1: A Skin-like Touch Sensor over a Curved Surface

To demonstrate the feasibility of composite paper in skin-like sensing, we created a skin-like tactile sensor by embossing composite paper with patterned molds to form conductive traces and regions. The compressed/recessed areas of the paper exhibited higher conductivity than the uncompressed regions. Figure 3.5a-f show a skin-like sensor made of composite paper (diameter of 8 cm, 21.6 wt% CB), which had embossed patterns forming four active electrodes and a central common ground. The common ground had four branches; each branch extended into one electrode to form a capacitive sensing button. The capacitance of these sensing buttons changed when a finger bridged the internal gap (i.e., the uncompressed region of the button). The embossed regions with different porosities divided the composite paper, which helped it conform to curved surfaces. To keep the uncompressed regions from collapsing by human touch, we supported the sensing disk by a cardboard layer with reliefs (Figure 3.5d,e). We then wrapped the disk around a cylindrical cardboard sleeve to form a skin-like sensing pad.

Repetitively touching each button on the sensing pad caused steady increases in capacitance, as shown in Figure 3.5g and Video S1. There was some crosstalk between buttons as they connected through the uncompressed regions (not completely electrically insulating). Touching one button leads to a change in the overall impedance of the sensing pad, which triggered small responses from other buttons as well. Among the four buttons, Button 4 exhibited the highest increase in capacitance. However, touching the uncompressed regions did not generate significant changes in capacitance.
Figure 3.5. A skin-like sensor made of composite paper (21.6 wt% CB) with embossed patterns. (a) Picture of a person wearing a cylindrical cardboard sleeve with the skin-like sensing pad covering on top. (b) The front of the embossed composite paper. (c) The flat back of the embossed composite paper. (d) The supporting layers with relieves are made of cardboard and electrodes made of copper tape. (e) and (f) show
the assembly of the embossed composite paper on top of the cardboard. (g) Relative changes in measured capacitance of the skin-like sensors by human touch.

3.5. Demonstration 2: A Dartboard

To investigate the response of the composite paper to damage, we designed a dartboard with compressed composite paper (21.6 wt% CB). The dartboard consisted of five regions, Rings 1 - 4 and a bullseye (Figure S10a). We shot/dropped darts with metal tips from above the dartboard through a guiding tube (Figure S10b) into the five regions and measured the corresponding changes in resistance. Figure 3.6 a,b and Video S2 illustrate that the resistance of each region increased with damage from the darts. The bullseye displayed the most significant increase in resistance nearly after every shot except the third one, which might be a result of its smaller area compared with the surrounding rings. The third shot at the bullseye overlapped the holes of earlier shots so that it only induced a slight increase in resistance.

The change in resistance of the composite paper reflects the level of damage done to the designated regions by the darts. Damaging the interconnected network of CB-loaded fibers interrupted its electrical functionality. Figure S11 depicts the average increase in resistance for the rings due to the first and second effective hits. The change in resistance caused by the second effective hit nearly doubled the value of the first ones. For Ring 2, we regarded the second and fourth shots as the first and second “effective hits”, respectively; the first and third shots missed the region, but they caused small fluctuations in the resistance due to their substantial impact on the dartboard; the first shot lit the LED on the MATLAB graphic user interface (GUI), due to the low threshold setting of the program. Numerical simulation confirms that the resistance of the sheet increases linearly with the number of holes caused by darts, showing small variations with the distribution of the darts (Figures S12). From the simulation, targeted substrates with a smaller area will experience larger changes in resistance by darts than those with a larger area (Figure S13), which explains why the bullseye has a more significant change in resistance than the surrounding rings.
Figure 3.6. Test of damage on the composite paper. (a) Picture of a dart with a mass of 20 g hitting the bullseye. The inset shows the MATLAB GUI. (b) Resistance changes of the dartboard when hit with darts in different regions. The darts stay in the dartboard for 7 seconds on average before removal. The inset photos show the dartboard before and after shooting. (c) Changes in resistance of the four sensors punctured by holes of different diameters (0.5 mm, 1 mm, 2 mm, 4 mm, 8 mm). The inset shows the 8-mm hole punched in the center of one sensor. (d) The increase in resistance after punching holes of different sizes.
To further investigate how the size of the holes affected the resistance of the composite paper, we punctured composite samples with punches of different diameters. Figure 3.6c,d demonstrate that punches with small diameters (0.5 mm, 1 mm, 2 mm) induced small increases in resistance (~500 Ω). In contrast, subsequent punches of large diameters (4 mm, 8 mm) caused significant increases in resistance (~1850 Ω, ~6900 Ω, respectively). Compared with the 2-mm holes, 4-mm holes cause a 4-fold increase in resistance, while the 8-mm holes cause a 14-fold increase, indicating that our composite paper was capable of detecting, assessing, and classifying damage. The analytical model and numerical simulation verify that the resistance of the composite sheet increases nonlinearly with the hole size (Figures S14-S16).
4. Path-based Modeling of Resistance of Fibrous Network

4.1. Stochastic Modeling of Fibrous Network

Stochastic fibrous network occurs in material prepared by a filtration process, draining, and electrospinning processes, such as softwood-fiber paper, glass-fiber filter, nonwoven carbon fiber mat, and electrospun nylon nanofibrous network. [152]

4.2. The Resistivity of a Fiber Segment Covered with CB Particles by Representative Surface Elements (RSE)

To analyze the resistivity of fiber, we created a computational model of a fiber segment with the representative surface element (RSE) as shown in Figure 4.1 A. First, we set a tiny representative surface element (RSE) on fiber, then we generate a CB footprint according to the volume fraction of CB. We trace conductive paths by finding the closest particles along the Z direction and calculate the resistance of each path based on the interaction between particles. The particles have random diameters within a range (maximum diameter, minimum diameter) and have a uniform distribution. The RSE is defined by a small width and length, radius of fiber, and a small angle α).

The total number of RSE samples, the number of paths per RSE sample, and the size of the RSE are important for a correct prediction of the resistance. For a given RSE, the resistance of each path $R_{\text{path}}$ depends on the relative resistance between particles $R_{1n}$. Combining a significant number $N$ of paths, we obtain the average resistance of the RSE. Calculating $N'$ RSE samples, we can get the average resistance of overall RSEs, as shown in Eq.(4.1)-Eq. (4.6). Dividing the fiber surface into strips and strips into RSEs as shown in Figure 4.1 B, C, D we can estimate the resistivity of the fiber from Eq. (4.7)- Eq. (4.8).

Manipulating the path number and angle of RSE is essential to achieve an accurate representation of CB-coated fiber. Figure 4.2 shows particles and paths on an RSE for different concentrations. At 3.8
wt%, the whole RSE becomes blue as the CB particles can overlap each other. The resistance of RSE goes down with the increased number of simulated paths and saturates after 100 paths, as shown in Figure 4.3.

\[ R_{path1} = R_{11} + R_{12} + \cdots + R_{1n} \]  
(Eq.4.1)

\[ R_{path2} = R_{21} + R_{22} + \cdots + R_{2n} \]  
(Eq.4.2)

\[ \cdots \]  

\[ R_{pathN} = R_{21} + R_{22} + \cdots + R_{2n} \]  
(Eq.4.3)

\[ \frac{1}{R_{RSE}} = \frac{1}{R_{path1}} + \frac{1}{R_{path2}} + \cdots + \frac{1}{R_{pathN}} \]  
(Eq.4.4)

\[ \bar{R}_{RSE} = (R_{RSE} + R_{RSE} + \cdots + R_{RSE})/N' \]  
(Eq.4.5)

\[ R_{strip} = k\bar{R}_{RSE} \]  
(Eq.4.6)

Wherein, \( k = \frac{A_{strip}}{A_{RSE}} \), \( A_{strip} \) denotes the surface area of the strip, \( A_{RSE} \) denotes the surface area of RSE, \( R_{strip} \) denotes the resistance of the strip. We set the specific area of the strip first and calculate how many RSEs on top.

\[ R_{fiber} = \frac{R_{strip}}{n'} \]  
(Eq.4.7)

Wherein, the number of strips \( n' = \frac{A_{fiber}}{A_{strip}} \), \( A_{fiber} \) denotes the surface area of the fiber, \( R_{fiber} \) denotes the resistance of fiber.

\[ \rho_{fiber} = \frac{R_{fiber}}{L_{fiber}} \]  
(Eq.4.8)

We calculated the electrical resistance between carbon blacks considering tunneling resistance and contact resistance between particles according to the tunnel-effect theory presented by Ragnar Holm [153]. The electrical resistance between CB particles consists of tunneling resistance and contact resistance. If the distance between two CB particles exceeds the tunneling gap of the particles, the resistance between these two particles is infinite. If the distance between two CB particles is smaller than the tunneling gap, the resistance will be tunneling resistance, as calculated in Eq.(4.9)-(4.11). If the distance between particles is
smaller than 0, the particles are in contact, and resistance will be contact resistance calculated in Eq. (4.12).

In our model, we set the tunneling gap as 1nm [154].

(1) max distance between particles > tunnel gap: high resistance \( \gg \infty \)

(2) \( 0 < \text{max distance between particles} < \text{tunnel gap} \): Tunneling resistance \( R_T \) [153]

\[
A = 7.32e^5 \left( d_{\text{max}} \times 10^{10} - \frac{7.2}{\varnothing} \right) \quad \text{(Eq. 4.9)}
\]

\[
B = 1.265e^{-6} \times \sqrt{\left( \varnothing - \frac{10}{d_{\text{max}} \times \varepsilon \times 10^{10}} \right.} \quad \text{(Eq. 4.10)}
\]

\[
\rho = \frac{1}{2} \times \left( \frac{A^2}{1 + AB} \right)^{AB} e^{-26} \quad \text{(Eq. 4.11)}
\]

Wherein, \( R_T = \frac{\sigma}{\pi a^2} \), work function \( \varnothing = 4.75eV \) for CB, relative permeability \( \varepsilon = 8 \) for cellulose.

(3) max distance between particles < 0, Contact resistance (constriction resistance) \( R_C \) [155]

\[
R_C = \frac{\rho_1 + \rho_2}{4a} = \frac{\rho_{\text{CB}}}{2a} \quad \text{(Eq. 4.12)}
\]

Wherein, \( \rho_{\text{CB}} \) is the resistivity of carbon black.

**Figure 4.1** Computational Model of CB-fibers (A) representative surface element (RSE) with a small angle \( \alpha \). (B) Multiple RSEs along the strip of fiber. (C) Multiple strips around the fiber. (D) cross-section of fiber coated with CB.
Figure 4.2. The representative surface element of a fiber surface with particles (blue dots). The shortest electrical paths from one side to the other are searched (red lines). Particles and paths on an RSE for different concentrations: (A) 1 wt% CB, (B) 3.8 wt% CB, (C) 10.5 wt% CB.

Figure 4.3. Resistance of representative surface element with an increasing number of simulation CB paths in modeling.
4.3. **Finite Element Analysis of Nanoparticle-Nanoparticle Interactions on the Surface of a Fiber**

The previous section calculates the resistivity of the representative surface element of fibers depending on the number of paths, which may over-estimate the resistance between two endpoints due to the neglect of the branches of paths. As the particles can overlap each other, which may not represent reality. In this section, we built 2D models by finite element analysis to calculate the resistivity of representative surface element (RSE) of carbon black-coated fibers. As carbon black form aggregates easily, we approximate the carbon black as two-layer ellipses — hard cores representing the carbon blacks and soft shells representing the tunneling layer. We generated the cores of ellipses randomly one by one in MATLAB and use *Inpolygon* function to detect intersections between the cores. It took around 4000-5000 trials to generate non-overlapping elliptical cores at 40% area fraction and above. With the positions and orientations of elliptical cores exported, we constructed the 2D models of cores and shells (the semi-axes are 1.25 times that of the cores). Figure 4.4 shows three aspect ratios of ellipses at different CB area fractions. The electrical percolation of the RSE depends on the aspect ratio and the area fraction of CB aggregates. Large aspect ratios and high-area fractions of CB aggregates improve the connectivity between aggregates. For CB aggregates of the aspect ratio of 2, the RSE does not percolate at 30% but at 40%, as shown in Figure 4.4 A, B.

López-de-Uralde et al. has pointed out CB aggregates have four types of morphologies according to the aggregate length/width ratio ($\alpha = \frac{L}{w}$) and irregularity. According to their experiments, the spheroidal aggregates ($\alpha < 1.5$) takes up 3.38% of the whole aggregates, ellipsoidal aggregates ($2 \leq \alpha \leq 3.5$) 32.33%, linear shapes ($3.5 < \alpha$, low irregularity) 19.17%, and branched shapes ($3.5 < \alpha$, high irregularity) 45.11%, as shown in Table 4.1 [156]. We approximate these four types of morphologies by changing the aspect ratio of ellipses as shown in Table 4.2. We have run seven simulations to generate a random distribution of CB aggregates of different area fractions, as shown in Figure 4.5. Figure 4.6 shows the seven configurations of CB aggregates at 50% area fraction. A simulated material is considered percolating when
more than 50% of simulations for a given size percolate [157]. We summarized the percolation probability of RSE with different area fractions of CB aggregates in Figure 4.7. In our simulation, the percolation threshold of CB aggregates is around 37% area fraction. As the CB concentration in aggregates is not 100%, the percolation threshold of CB will be lower than the 37% area fraction.

**Table 4.1.** Morphological Categorization of carbon black nano-aggregates in [156]

<table>
<thead>
<tr>
<th>Shape of CB aggregates</th>
<th>Aspect Ratio</th>
<th>Occurring Probability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spheroidal</td>
<td>$\alpha &lt; 1.5$</td>
<td>3.38%</td>
</tr>
<tr>
<td>Ellipsoidal</td>
<td>$2 \leq \alpha \leq 3.5$</td>
<td>32.33%</td>
</tr>
<tr>
<td>Linear</td>
<td>$3.5 &lt; \alpha$</td>
<td>19.17%</td>
</tr>
<tr>
<td>Branched</td>
<td>$3.5 &lt; \alpha$, high irregularity</td>
<td>45.11%</td>
</tr>
</tbody>
</table>

**Figure 4.4.** Representative surface element with elliptical aggregates of CB. We have simulated two aspect ratios of ellipses at different CB area fraction. The area fraction only considers the elliptical cores. (1) aspect ratio =2: (A) 30 vol % CB, (B) 40 vol % CB, (C) 50 vol % CB; (2) aspect ratio =4: (D) 30 vol % CB, (E) 40 vol % CB, (F) 50 vol % CB. (3) aspect ratio =6: (G) 30 vol % CB, (H) 40 vol % CB.
Table 4.2. Probability of aspect ratios of ellipses representing CB aggregates in RSE.

<table>
<thead>
<tr>
<th>Aspect Ratio of Ellipses</th>
<th>1.5</th>
<th>2</th>
<th>2.5</th>
<th>3</th>
<th>3.5</th>
<th>4</th>
<th>4.5</th>
<th>5</th>
<th>5.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Occurring Probability (%)</td>
<td>3</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>16.25</td>
<td>16.25</td>
<td>16.25</td>
<td>16.25</td>
</tr>
</tbody>
</table>

Figure 4.5. Representative surface element with ellipses of different aspect ratios at 50% area fraction.

Figure 4.6. Seven simulations of CB aggregates of different aspect ratios at 50% area fraction.
This model has not yet received sufficient refinement to provide accurate surface resistivities for the following simulation. Nevertheless, we are going to assign approximate surface resistivities for the subsequent modeling.

### 4.4. Calculations of Resistance of Fibrous Network

According to Akin’s 2D model, starting at the cathode C, the electrical current flows along a possible fiber path \((C, P_i, A)_j\), comprised of nodes \(P_i\) and the center axes of the fiber segments \((P_i, P_{i+1})\), towards the anode A. Each axis of the fiber segment is characterized by a length \(l_i\) and an in-plane orientation angle \(\phi_i\) such that \(\phi_i = \text{atan} \left( \frac{d_2^i}{d_1^i} \right)\), \(\overrightarrow{d_i} = (d_1^i, d_2^i)\) is the orientation vector of the fiber segment. [158]

In a 3D space, we modeled curved cellulose fibers as chains of line segments linked by the nodes across the representative volume in MATLAB. First, we preset the size of the representative volume. Then, we randomly generated the starting points/nodes on one side of the representative volume.
To create a chain of line segments to represent curved fibers, we extended Akin’s model to include two Euler angles (in-plane orientation angle $\phi_i$ and out-of-plane orientation angle $\theta_i$) and length $l_i$ to determine the positions of nodes along the fiber path. The length $l_i$ of each segment $(P_i, P_{i+1})$ follows the Rayleigh-like distribution, and both the two Euler angles follow uniform distribution, see Figure 4.8.

We generated nodes along the fiber path in a slightly enlarged volume and stopped the generation once the line segment reaches the boundaries. For those line segments that went out of the boundaries, we trimmed them at the boundaries and only consider the parts inside the representative volume (Figure 4.9). In Figure 4.10, we created fibrous skeletons by polygon curves in COMSOL by linking the nodes and drew circular cross-sections on the work planes that are normal to the starting edges of the curves. Assuming a specific circular cross-sectional area, we calculated the volume fraction of fibers and generated fibers until predestined volume fraction.

This model allows the fibers to intersect or penetrate each other and gives a rough estimation of the electrical properties of the stochastic fibrous network. We have evaluated the effective resistivity of the composite at three different fibrous volume fractions with seven repetitive tests. With several repeated tests, we can get the average resistivity of the fibrous network.

To simulate compression, we only consider compression that occurs in z-direction only assuming no contraction or extension in x and y. Compressed fiber segments are approximated using straight lines, i.e., buckling is not considered. Compression can be either linear (Eq. 4.13) or quadratic (Eq.4.14).

$$D_{compressed} = az + b = \begin{cases} 0, & @Z = 0, \\ -d, & @Z = c \end{cases} \quad (\text{Eq. 4.13})$$

$$D_{compressed} = az^2 + bz + e = \begin{cases} 0, & @Z = 0, \\ -\frac{d}{3}, & @Z = \frac{c}{2} \\ -d, & @Z = c \end{cases} \quad (\text{Eq. 4.14})$$

Wherein, $D_{compressed}$ denotes compressed displacement, $a, b, c$ here denote constants.
The modeling steps are as follows:

1. Start with a bounding box of the paper sheet with dimensions \( ax \times by \times cz \) along x, y, and z directions, respectively.
2. Define minimum and maximum fiber thickness \( fibth_{min} \) and \( fibth \).
3. Define \% porosity \( volpor \) and maximum segment length \( randdis \).
4. Define \% of compression \( dis \) in z-direction
5. Loop until \% porosity \( volpor \) is reached:
   i. Generate paths of fibers in increasing x-direction such that:
      a. The electrodes lay on the opposite faces of the bounding box \( x=0 \) and \( x=a \),
      b. Each path is formed of fiber segments,
      c. Fiber segments are generated one at a time with the spherical coordinates \( r \), \( \theta \), \( \phi \) such that \( r \) is rayleigh distributed and \( \phi \) and \( \theta \) are uniformly distributed,
      d. \( r \), \( \theta \), and \( \phi \) are then converted to cartesian \( x \), \( y \), and \( z \).
      e. Generate a fiber thickness \( th \) per segment such that \( th \) is uniformly distributed
   ii. If the fiber segments lay outside the bounding box, force the fiber segments to lay within the box by generating \( r \), \( \phi \) and \( \theta \) at the faces of the bounding box.
   iii. For the non-compressed and compressed states:
      a. Calculate the volume of each fiber segment (a cylinder of radius \( 0.5*th \)) and the intersection of each new fiber segment with all existing fiber segments.
      b. Deduct the volume of intersection from the total volume.
      c. This is still an estimation as a closed form solution for finite cylinder-cylinder intersection does not exist.

We generate the microstructure realizations for this study using path-based modeling in Figure 4.11. The fibrous network generated by this method has an overlapping nature, which means fibers can penetrate each other. And the fibers have sharp turns, which affect the finite element analysis. For the
compressed model, the cross-section remains unchanged. Figure 4.12 shows the electrical characteristics of six fibers in COMSOL. More fibers will lead to nonconvergent results. Adding fillets to the sharp turns may smoothen the network for convergent results.

**Figure 4.8.** Structural modeling of curved fibers. (A) SEM image of curved fibers of 10% composite CB paper. The scale bar is 1000 μm. (B) Model of one fiber with segments. (C) Location of Node $Q$ is defined by orientation angles and length.
Figure 4.9. Fibrous network of 20% porosity.
Figure 4.10. Creation of 3D solid fibers using Livelink for MATLAB in COMSOL. (A) Create fibrous skeletons by polygon curves in COMSOL by linking the nodes and draw circular cross-sections on the work planes that are normal to the starting edges of the curves. (B) (C) Sweep across the curves with the circular cross-sections. (D) The fibrous network after sweeping.
Figure 4.11. 3D solid model of a fibrous network built by COMSOL. (A) Before compression. (B) After compression.

Figure 4.12. Finite element analysis of the electrical characteristics in COMSOL.
5. Open-source Computational Generation and Finite-Element Analysis of Non-overlapping Fibrous Materials

To model the characteristics of fibrous networks, two main strategies are continuum and microstructural models. Continuum models compute average geometrical properties of constituents and their variations over representative volume elements (RVEs). The accuracy in continuum models relies on the RVE size and the approximation of material details in RVEs. Continuum models are suitable to analyze systems that do not prioritize material details. Microstructural models simulate geometrical and physical properties of individual constituents separately at a higher computational cost than continuum models. Microstructural models can directly correlate each constituent and determine the stresses and strains in each constituent [159]. To understand the electromechanical properties of three-phase fibrous networks, we aim to use the second approach—to build microstructural models of fibrous networks.

5.1. Background for 3D Modeling of the Stochastic Organization of Non-overlapping Fibrous Networks

There are three families of methods for numerically generating random-fiber composite RVEs, namely, the random sequential adsorption (RSA) schemes, the Monte Carlo procedures, and image reconstruction technique [160]. These random-fiber composites may contain overlapping fibers. The RSA algorithms involve tedious looping calculations to determine the position and orientation of a new fiber to avoid overlapping with previously deposited fibers.

To build non-overlapping or hardcore fibrous networks, previous efforts focused on modifying overlapping models. Yi et al. and Karakoç et al. have generated non-overlapping fibrous composites by reforming intersecting fibers. They determined fiber intersections based on planar projection and curved up the newly-generated fiber along Z-axis at the fiber crossings over the previously generated ones [159], [161].
This method may not work for networks that have more out-of-plane, protruding fibers. Heyden has created 3D fibrous networks by random walks and created bonds at the crossings of fibers [162]. By representing fibers as chains of spheres, Gaiselmann et al. has relocated spheres on fibers if they are too close to the spheres of the other fibers based on an iterative avoidance algorithm [163]. Chapelle et al. have applied a force-biased algorithm to chains of spherocylinders: a repulsion force to suppress the overlapping between two fibers and a bending and stretching force to maintain fibrous structures [164].

5.2. Using Rigid Body Dynamics to Create the Morphology of Fibrous Networks

We aim to build non-overlapping fibrous networks by Blender, an open-source modeling software. The physics engine in Blender can perform collision detection, soft body, and rigid body dynamics. Previous studies used Blender to generate packed-bed reactors with particles in different shapes and applied the structures for subsequent CFD simulation [165]–[167]. All these publications show that Blender is an easy-to-use open-source tool for the synthetic generation of a stack of particles with a high degree of automation.

The generation of straight or curved fibers is by means of rigid body dynamics in Blender. The module for rigid body dynamics uses a Newton-Euler solver to compute both translational and rotational motions of rigid bodies, along with relevant constraint/contact equations to deal with joints and contacts [168].

We developed a stacking model to automatically fill a digital space with straight fibers or curved fibers. The model consists of several steps:

1. Define parameters (number of fibers, diameters of fibers, length of fibers)
2. Create a collection of fibers and a digital box (B_X, B_Y, B_Z)
3. Generate straight fibers or curved fibers above the box
4. Apply rigid body physics to fibers and box to stack up fibers in the box
5. Shake the box to achieve the final fibrous configuration
6. Separate the layers of fibers and fill the caps of the layers
7. Export stereolithography (.stl) files of fibers

8. Measure porosity (Only consider the shells and cores inside the RVE box, without taking bridges into account, which has negligible effects on porosity).

9. Repeat steps (3) to (7) to predict morphologies.

In generating the fibers, we take a two-layered model into account. The two layers are the conductive shell representing CB and the insulating core representing the cellulose fibers as shown in Figure 5.1. The curved fibers are based on Nurbspath which follow the 3D skeleton contours and have a round bevel – the bevel depth is the radius of the fibers. The shell and core of fiber have the same central line. To reduce the computational cost, the resolutions of the fibers are set to small numbers (in our case: 2) along the peripheral direction and axial direction. The generated fibers have octagonal cross-sections. We have a collection of three curved fibers to produce the whole network of fibers. The geometric parameters are in Table 5.1. In Blender, we used metric units and applied coordinate scales in Salome to do microscale simulations. For the simulation, the average length of curved fibers is 760 μm and the diameter of the cores is 23 μm, which are close to the measured value in Section 2.1.1. Changing the coordinate scale in Salome, we can model nanoscale composite as well.

For the rigid body simulation, we joined the shell and core of fibers first and make them fall together under gravity with their origins set to the center of mass (volume). The fibers have mesh-based collision shapes. By changing margin in the sensitivity setting of the rigid body, there may be a gap between fibers when piling up. After piling up the fibers in a box, inserting keyframes of rotation in the graph editor triggers the box to shake the fiber to form the final configuration. The shaking process can distribute the fibrous network, which approximates the paper-making process (Figure 5.2).

Fibrous networks with a large number of fibers are achievable with the above-mentioned workflow in Blender. We first used the particle system in Blender to generate random curved fibers from a collection of curved fibers, which are overlapping, then converted the fibers into individual objects, and assigned rigid
body physics to all the fibers before deposition (Figure 5.3). Figure 5.4 shows a network of 1250 straight fibers and a network of 500 curved fibers.

**Table 5.1.** Geometric parameters of the fibrous network.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Box Internal Dimensions ((B_X, B_Y, B_Z))</td>
<td>1000, 1000, 760 (unit in Blender)</td>
</tr>
<tr>
<td>Collision Margin of Fibers</td>
<td>1 (unit in Blender)</td>
</tr>
<tr>
<td>Diameter of Shells</td>
<td>46 µm</td>
</tr>
<tr>
<td>Diameter of Cores</td>
<td>23 µm</td>
</tr>
<tr>
<td>“Straightened” Length of Curved Fibers</td>
<td>596 µm, 786 µm, 895 µm</td>
</tr>
<tr>
<td>Diameter of Bridges</td>
<td>16.6 µm</td>
</tr>
<tr>
<td>Height of Bridges</td>
<td>&lt;=0.8 µm (gap)</td>
</tr>
</tbody>
</table>

![Figure 5.1](image)

**Figure 5.1.** A collection of curved fibers in Blender. (A) The fibers consist of two layers: shell and core (highlighted). (B) The rendered fibers have an octagonal cross-section. (C) Fill the caps/endfaces of the two layers.
**Figure 5.2.** Shaking fibers in Blender to achieve final configuration. (A) Fibrous network before shaking (B) Fibrous network after shaking for 200 frames and settling down at 300th frame. The animated shaking of the box is Z Euler Rotation with noise modifier setting (scale: 1, strength:1.5, offset: 0, phase:1, frame range:0-200)

**Figure 5.3.** Creation of a large number of fibers in Blender by particle system. (A) Using particle system in Blender to generate random curved fibers which are overlapping. (B) Converting fibers into individual objects. (C) Assign rigid body physics to all the fibers before deposition.
Figure 5.4. Fibrous network generated by rigid body simulation. (A) a network of 1250 straight fibers. (B) part of the network of (A). (C) part of the network of 500 curved fibers.

5.3. Bridging Electrical Paths between Components in Fibrous Network for Finite Element Analysis

Salome is an open-source Pre- and Post-processing platform for numerical simulation, which is programmable with Python scripts. Pichler has inserted bridges between neighboring particles in Salome to simulate contact points to analyze the thermal conductivities of packed beds. [169] Similarly, to simulate tunneling conductance between fibers, we have inserted bridges between neighboring fibers to fill the gaps by the following procedure (see also Figure 5.5):

1. Load the fibers into the geometry module (GEOM) of SALOME
2. Create cylindrical bridges with a given diameter at small gaps/contact-points
3. Cut bridges by fibers to get capped bridges
4. Repair/clean CAD models and perform the boolean operation
5. Compute bounding box of fibrous network and build RVE box
6. Perform partition (no tool object)
7. Create mesh of the fibers and bridges using SALOME’s mesh module (SMESH)
Figure 5.5. Bridge method in Salome. (A) Imported unshaken fibers without bridges. (B) Fibers linked with bridges (circled by red lines).

5.4. **Sampling Box to Create Representative Volume Element (RVE) for Finite Element Analysis**

For electrical simulation, a plus-sampling method corrects edge effects by using a sampling box RVE box (highlighted as yellow in Figure 5.6A), [170] which is 20% smaller in X and Y direction than the bounding box (indicated by the blue dashed line) of fibrous network and 2% larger in the Z direction. Two electrode plates connect the fibrous network to impose electrical potential (1V on one end, 0V on the other end). The shells and the cores have different conductivity, and the sampling box has a low conductivity, close to air. The bridges have modest conductivity. For simplification, we used the conductivities listed in Table 5.2 for the simulation.
Figure 5.6. Setup for electrical simulation of fibrous network. (A) a sampling box highlighted in yellow, and two electrode plates on two ends of the fibrous network. The blue dashed line indicated the bounding box of the fibrous network (10% transparency). The volume fraction of fibers in the sampling box is 7.6%, i.e. 92.4% porosity. (B) Potential distribution of the fibrous network with the sampling box (the box has a low conductivity of 1E-9 S/m). (C) Potential distribution of the fibrous network without the sampling box. (D) Zoom-in image showing bridges connecting fibers.

5.5. Calculation of Electrical Bulk Properties from RVEs through Finite Element Analysis

We solved the steady-state electrical conduction equation for a fiber network model placed between two electrode plates using the open-source finite element (FE) software Elmer, which has a plugin in Salome. To model microscale fibers, we need to set the coordinate scale by a constant. The mesh of the whole
geometry used tetrahedron as elements based on NETGEN 3D-2D-1D algorithms: the bridges have moderate meshes, and the rest have coarse meshes.

Electrical potential is applied at the end face of one electrode plate the network of three fibers shown in Figure 5.6B and Figure 5.6C has a 92.4% porosity within the sampling box and a resistivity of 0.092 $\Omega \cdot m$ (based on the cross-section of the RVE box). Network with more fibers shows less electrical resistance. Figure 5.7 shows a fibrous network of six fibers with 92% porosity and resistivity of 0.046 $\Omega \cdot m$. Figure 5.8 shows the fibrous network of nine fibers with 83% porosity and resistivity of 0.031 $\Omega \cdot m$. Table 5.3 summarizes the porosity and resistivity of these networks. As we can see, the porosity of the RVE box decreases with more fibers and the resistivity of the RVE goes down. The decreased resistivity may also come from the increased effective number of electrical paths connecting electrodes. This method can generate and analyze fibrous networks with more fibers in the future. Combining the RVEs in series or parallel, we may simulate large-scale fibrous networks or systems.

**Table 5.2.** Conductivities of each material in simulation.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Conductivity (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shells</td>
<td>1000</td>
</tr>
<tr>
<td>Cores</td>
<td>1</td>
</tr>
<tr>
<td>Bridges</td>
<td>100</td>
</tr>
<tr>
<td>RVE Box</td>
<td>1e-9</td>
</tr>
<tr>
<td>Electrodes</td>
<td>59.59e6 (copper)</td>
</tr>
</tbody>
</table>
Figure 5.7. Fibrous network of six fibers. The porosity of the network is 92%. (A) Fibrous network in the geometry module in Salome (10% transparency). The blue dashed line indicated the bounding box of the fibrous network. The yellow area indicated the sampling box. (B) Mesh module of Salome (40% transparency for the RVE box). (C) (D) Potential distribution of the fibrous network in the Paravis module of Salome.
Figure 5.8. Fibrous network of nine fibers in simulation. The porosity of the network is 83.1%. (A) %.

(A) Fibrous network in the geometry module in Salome (10% transparency). The blue dashed line indicated the bounding box of the fibrous network. The yellow area indicated the sampling box. (B) Potential distribution of the fibrous network in the Paravis module of Salome.

Table 5.3. The porosity and resistivity of simulated fibrous networks

<table>
<thead>
<tr>
<th>Numbers of fibers</th>
<th>Porosity</th>
<th>Number of effective electrical paths</th>
<th>Resistivity (Ohm*m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>92.4%</td>
<td>2</td>
<td>0.092</td>
</tr>
<tr>
<td>6</td>
<td>92.0%</td>
<td>3</td>
<td>0.046</td>
</tr>
<tr>
<td>9</td>
<td>83.1%</td>
<td>4</td>
<td>0.031</td>
</tr>
</tbody>
</table>

5.6. Additional Strategy that Needs Further Development

To investigate the degree of network compression on the piezoresistive sensitivity of composite, we can manipulate the previously generated fibrous network in Section 5.2.1 by soft-body physics. We set the fibers after shaking to be soft bodies and place the fibers between two rigid plates for compression as shown in Figure 5.9. The morphological changes of fibers depend on the setting of the simulation. For a proof of
concept, we set the bending coefficient of fibers as 0.3. The compression is controllable by the displacement of the top plate. With the compressed morphology, we can run the electrical simulation to see how the conductivities of the network change compared with that before compression in the future.

Figure 5.9. Compressing fibers with soft-body physics. (A) Place fibers between two rigid plates. (B) fibers before compression. (C) fibers after compression.

6. Conclusions and Future Work

6.1. Summary of Results and Contributions of the Research

This thesis developed a scalable process of fabricating highly porous composite paper with tunable conductivity and established an open-source workflow to model a three-phase stochastic fibrous network. The conductivity of the nanocomposites increased non-linearly with the concentration of CB, which followed the universal scaling law from the percolation theory but with different critical exponents. Embossing the composite paper increased its conductivity and caused a maximum change of ~300 fold at the percolation threshold (3.8 wt%, or 0.36 vol%). Our composite paper showed stable piezoresistive responses within a broad pressure range from 1 kPa up to 5.5 MPa for 800 cycles.
This piezoresistive composite paper functioned as a tunable platform for creating capacitive and resistive sensors through embossed patterns, showing promise in applications for skin-like sensing for touch and pressure, intelligent packaging protection, and fabrication of other flexible electronics. The increasing resistance of the material during the damaging process has the potential to detect and assess the impact on applied surfaces, monitor the structural health of buildings and vehicles, and alert people of danger. Overall, this work presents a potentially scalable process for manufacturing sheets of uniform porous composite paper with tunable electrical conductivity and piezoresistivity, adaptable for new applications on flexible substrates.

For the computational model, we developed a path-based modeling method to bridge nanoscale to mesoscale of three-phase conductive composite paper. We have built a nanoscale model to calculate the resistivity of the representative surface elements (RSEs) of CB-coated fibers by direct calculation and finite element analysis. With this resistivity of RSE, we modeled a 3D fibrous network by generating fibers with random lengths and orientational angles. This method allowed fibers to penetrate each other. To generate a fibrous network with non-overlapping fibers, we developed an open-source workflow using Blender as a modeling platform, and Salome as Pre-processing, analyzing, and Post-processing platform for a 3D fibrous network. This open-source workflow deposited straight fibers or curved fibers with rigid body physics into a box and shake them to achieve the final configuration. Bridges are created between fibers to simulate tunneling conductance between fibers. This open-source workflow facilitates and speeds up the generation and analysis of the non-overlapping fibrous network. It can contribute to the design of and optimization of composite structures with different fillers in the future.

6.2. Future Work

We have only fabricated conductive composite paper with cellulose and carbon black. With this promising foam-laying method, future composite paper can have different matrices and fillers. For the modeling, we have a nearly automatic programmatic approach during the modeling building and finite element analysis. In the future, a fully automatic process can be achieved by Python scripts linking Blender and Salome.
platforms. Limited by our knowledge and tools, we make many simplifications in modeling the fibrous structure. Accurate representation of a realistic fibrous network requires curved fibers generated by a more random collection of fibers, which is obtainable by particle system in Blender. Tuning the curvature of fibers can also be useful to simulate other fibrous networks, like carbon-nanotube networks. Optimizing the bridging (shapes and numbers) between the fibers can better simulate tunneling effects between fibers.

The dynamics of fibers in rigid-body configuration may depend on the initial height of the fibrous network, which needs further investigation. This work can combine with Monte-Carlo simulation for repeatable tests in the generation of the fibrous network to predict likely outcomes and expected variability for the distribution of fibers. Changing the morphology of fibrous networks will be essential for the investigation of electromechanical properties, which may be achievable by the soft-body simulation in Blender. Future work based on this thesis can help understand the effect of the porosity of paper and the degree of network compression on the piezoresistive sensitivity of composite.
Appendix

This section has material taken from the supporting information from our published article in ACS Applied Materials & Interfaces. [124]

Converting from weight fraction to volume concentration for CB

We convert the weight fraction into volume concentration for CB by Eq. (S1) or Eq. (S2), [171], [172]

\[ V_{CB} = \frac{v_{CB}}{v_c} = \frac{m_{CB}}{\rho_{CB} \times v_c} = \frac{m_{CB}}{\rho_{CB} \times m_{C}/\rho_{C}} = \rho_{C} \times W_{CB}/\rho_{CB} \]  
\[ (S1) \]

where \( V_{CB} \) and \( W_{CB} \) represent the volume concentration and the mass concentration of carbon black, respectively. Symbols \( m, v, \rho \) represent mass, volume, and density, respectively. The subscript \( CB \) indicates carbon black particles, while the subscript \( C \) indicates composite paper (including fibers and CB). \( \rho_{CB} = 1.8 \text{ g/cm}^3 \). For our composite paper, before compression \( \rho_{C} = 0.17 \text{ g/cm}^3 \), the CB concentration 3.8 wt\% corresponds to 0.36 vol\%; after compression \( \rho_{C} = 1.08 \text{ g/cm}^3 \), the CB concentration 3.8 wt\% corresponds to 2.29 vol\%. This approach has taken porosity into account by using the experimental density \( \rho_{C} \).

The other approach starts from the calculation for two-phase composites, we can convert the weight fraction into volume concentration by as Eq. (S2). [172], [133], [173] For three-phase composites that include air, we take porosity into account by using Eq. (S3).

\[ V_{CB} = \frac{W_f \rho_m}{(W_f \rho_m + (1-W_f)\rho_f)} \]  
\[ (S2) \]

\[ V_{CB} = \frac{W_f \rho_m}{(W_f \rho_m + (1-W_f)\rho_f)} \times (1 - \emptyset) \]  
\[ (S3) \]

where \( W_f \) represents the mass fraction of fillers (i.e., \( W_{CB} \)), \( \rho_m \) is the density of the matrix (cellulosic fibers in our case, i.e., 1.5 g/cm\(^3\)), \( \rho_f \) is the density of the fillers (i.e., \( \rho_{CB} = 1.8 \text{ g/cm}^3 \)), \( \emptyset \) is the porosity of the composite.
Figure S1. (a) Picture of the foaming process by a mechanical mixer. (b) Picture of decanting the foam into the handsheet former through a funnel. (c) Picture of foam in the handsheet former. (d) Handsheet covered with a steel plate for vacuum filtration. (e) Picture of samples at the concentration of 10.5 wt% CB before embossing (left, 1 mm thick) and after embossing (right, 0.2 mm thick). (f) Picture of testing in an environmental chamber with constant temperature and humidity (23°C and 50% RH). (g) Picture of U-shaped composite sample in an HP4192A LF impedance analyzer. (h) Dimensions of the U-shaped sample.
Figure S2. SEM images of Composite paper before and after compression. (a) and (b) are of 2 wt% uncompressed sample and compressed sample, respectively. (c) and (d) are of 20.5 wt% uncompressed sample and compressed sample, respectively. (e) and (f) are of 28.6 wt% uncompressed sample and compressed sample, respectively. (g) and (h) are of 40 wt% uncompressed sample and compressed sample, respectively. (a) and (f) have brightness increased by 20%, (c) has brightness increased by 40%, and (g) has brightness decreased by 20%.
Figure S3. Magnified SEM images of foam paper of different CB concentrations before and after compression. (a), (c), (e), (g), (i), (k), (m) are uncompressed samples of 0 wt%, 2 wt%, 3.8 wt%, 10.5 wt%, 20.5 wt%, 28.6 wt%, and 40 wt%, respectively. (b), (d), (f), (h), (j), (l), (n) are compressed samples of 0 wt%, 2 wt%, 3.8 wt%, 10.5 wt%, 20.5 wt%, 28.6 wt%, and 40 wt%, respectively. (i) has brightness increased by 40%, (a), (h), and (k) have brightness decreased by 20%, (l) has brightness increased by 20%, and (m) has brightness decreased by 40%.
Table S1. Average conductivity of composite paper at 10kHz before and after compression

<table>
<thead>
<tr>
<th>Mass Concentration of CB (wt%)</th>
<th>Average conductivity (before compression) (S/m)</th>
<th>STD</th>
<th>Average conductivity (after compression) (S/m)</th>
<th>STD</th>
<th>Ratio of Conductivity (before compression/after compression)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.59E-06</td>
<td>9.28E-08</td>
<td>3.19E-05</td>
<td>5.49E-06</td>
<td>5.71</td>
</tr>
<tr>
<td>1.4</td>
<td>5.60E-06</td>
<td>9.13E-08</td>
<td>2.98E-05</td>
<td>5.77E-06</td>
<td>5.32</td>
</tr>
<tr>
<td>2</td>
<td>5.58E-06</td>
<td>1.02E-07</td>
<td>2.71E-05</td>
<td>3.06E-06</td>
<td>4.86</td>
</tr>
<tr>
<td>2.7</td>
<td>5.34E-06</td>
<td>1.22E-07</td>
<td>2.68E-05</td>
<td>2.98E-06</td>
<td>5.02</td>
</tr>
<tr>
<td>3.8</td>
<td>8.38E-06</td>
<td>1.11E-07</td>
<td>2.50E-03</td>
<td>4.25E-04</td>
<td>298.37</td>
</tr>
<tr>
<td>5.3</td>
<td>6.69E-04</td>
<td>2.78E-04</td>
<td>8.19E-02</td>
<td>1.36E-02</td>
<td>122.39</td>
</tr>
<tr>
<td>7.5</td>
<td>1.30E-02</td>
<td>8.18E-04</td>
<td>3.43E-01</td>
<td>8.86E-02</td>
<td>26.38</td>
</tr>
<tr>
<td>10.5</td>
<td>1.03E-01</td>
<td>4.36E-03</td>
<td>8.84E-01</td>
<td>1.07E-01</td>
<td>8.59</td>
</tr>
<tr>
<td>14.6</td>
<td>1.99E+00</td>
<td>2.34E-01</td>
<td>1.18E+01</td>
<td>2.16E+00</td>
<td>5.93</td>
</tr>
<tr>
<td>20.5</td>
<td>5.24E+00</td>
<td>1.78E-01</td>
<td>3.11E+01</td>
<td>2.93E+00</td>
<td>5.94</td>
</tr>
<tr>
<td>28.6</td>
<td>1.20E+01</td>
<td>1.02E+00</td>
<td>6.54E+01</td>
<td>7.92E+00</td>
<td>5.46</td>
</tr>
<tr>
<td>40</td>
<td>2.77E+01</td>
<td>1.66E+00</td>
<td>1.22E+02</td>
<td>8.05E+00</td>
<td>4.41</td>
</tr>
</tbody>
</table>
**Table S2.** Comparison of the electrical conductivity of carbon-black composite paper

<table>
<thead>
<tr>
<th>Composite paper</th>
<th>Conductivity (S/m)</th>
<th>Sheet resistance (Ω/sq)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vulcan XC 72R CB (40 wt%)-cellulose</td>
<td>27.7 (1 mm thick) 122 (0.35 mm thick)</td>
<td>36.1 (1 mm thick) 23.4 (0.35 mm)</td>
<td>Our work</td>
</tr>
<tr>
<td>SR511 CB (33 wt%)-kraft fibers</td>
<td>9 (~0.28mm)</td>
<td></td>
<td>[174], [175]</td>
</tr>
<tr>
<td>23 wt% CB/77 wt% cellulose*</td>
<td>229 (0.268mm)</td>
<td></td>
<td>[176]</td>
</tr>
<tr>
<td>copy paper coated by ink (XC-72R CB (67 wt%)-cellulose acetate)</td>
<td></td>
<td>250</td>
<td>[177]</td>
</tr>
<tr>
<td>filter paper dip-coated in suspension (CB (67wt%)-CMC)</td>
<td></td>
<td>38.1 **</td>
<td>[178]</td>
</tr>
<tr>
<td>commercial paper made of recycled fibers coated by 30 vol% carbon black/starch</td>
<td></td>
<td>4.5 ***</td>
<td>[179]</td>
</tr>
</tbody>
</table>

*(use a fixer of 2% cationized starch water solution), **127 Ω for a sheet with dimensions of 40 mm×12mm×0.2mm), ***calculated by a given formula and confirmed by plotted data

Conductivity: [7] > our work > [5,6] > [10]

Sheet resistance: our work < [9] < [8].
Figure S4. Comparison of composite paper at 1 wt%, 1.4 wt%, 2 wt%, and 2.7 wt% CB concentration from 8 samples. The small error bars based on standard deviation show the uniformity of the samples. (a) The frequency response of impedance magnitude with standard deviation as error bars. The curves are skipping 6 points. (b) The frequency response of phases with standard deviation as error bars. The phases slightly increase with frequency but remain at around -90°. The curves are skipping 3 points.
Figure S5. Comparison of composite paper at 7.5 wt%, 10.5 wt%, and 14.6 wt% CB concentration from 8 samples. The slightly large error bars of 7.5 wt% compressed samples rise from different porosities of the samples. (a) The frequency response of impedance magnitude with standard deviation as error bars. The curves are skipping 6 points. (b) The frequency response of phase with standard deviation as error bars. The curves are skipping 6 points.
Figure S6. Comparison of composite paper at 20.5 wt%, 28.6 wt%, and 40 wt% CB concentration from 8 samples. (28.6 wt% and 40 wt% samples each have one outlier removed (Sample 6 and Sample 4, respectively). The small error bars based on standard deviation show the uniformity of the samples. (a) The frequency response of impedance magnitude with standard deviation as error bars. The curves are skipping 6 points. (b) The frequency response of phase with standard deviation as error bars. The curves are skipping 6 points.
Further analysis of conductivity with CB concentration beyond percolation threshold

In Figure 3c, the fitting curves seem to have two trends above or below the fourth point, which corresponds to 14.6 wt% CB, as shown in Figure S7(a). Here, we fit curves for four cases (Figure S7(b)): $Y_1$ (high porosity, low CB concentrations below 14.6 wt%), $Y_2$ (high porosity, high CB concentrations above 14.6 wt%), $Y_3$ (low porosity, low CB concentrations below 14.6 wt%), and $Y_4$ (low porosity, high CB concentrations above 14.6 wt%). The slopes of the curves indicate the rates of change of conductivity ($\Delta \sigma / \Delta (f - f_c)$), among which $Y_1$ has the steepest slope or highest rate of change of conductivity.

Based on the theory of tunneling current[148], we assume that the rate of change of conductivity depends on the gaps between CB particles, which are determined by the porosity of the composite paper and the concentration of CB. As high porosity and low concentration of CB contribute to separate CB particles, large changes in conductivity may occur as the proximity between particles decreases during compression. Lowering the porosity of the paper substrate brings the fibers closer to each other as well as the CB particles on the fibers, and increasing the concentration of CB densifies the CB particles on fibers. Therefore, the rate of change of conductivity is more significant for $Y_1$ than others. Due to the increased resistance to pressure with CB concentration, the samples of $Y_4$ have slightly higher porosity than $Y_3$, which explains the slight higher slope of $Y_4$ than that of $Y_3$. 
Figure S7. Further analysis of conductivity with CB concentrations beyond the percolation threshold. (a) Curve fittings of the log-log plot of conductivity over a concentration of CB larger than the percolation threshold ($f > f_c, f_c = 3.8 \text{ wt%}$) (8 samples). (b) Schematic drawing of CB paper network for four different cases: (1) high porosity and low concentration of CB, (2) high porosity and high concentration of CB, (3) low porosity and low concentration of CB, (4) low porosity and high concentration of CB.

Figure S8. Curve fitting of conductivity of composite paper at CB concentrations less than the percolation threshold ($f < f_c, f_c = 3.8 \text{ wt%}$) (8 samples).
Table S3. Pressure sensitivities of composite paper during loading and unloading at pressure ranges of 1 kPa–250 kPa and 250 kPa–5.5 MPa.

<table>
<thead>
<tr>
<th>CB concentration</th>
<th>State</th>
<th>Sensitivities S1 (/kPa) (1 kPa–250 kPa)</th>
<th>Sensitivities S2 (/kPa) (250 kPa–5.5 MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5 wt%</td>
<td>loading</td>
<td>−0.215</td>
<td>−0.002</td>
</tr>
<tr>
<td></td>
<td>unloading</td>
<td>−0.169</td>
<td>−0.001</td>
</tr>
<tr>
<td>10.5 wt%</td>
<td>loading</td>
<td>−0.063</td>
<td>−0.003</td>
</tr>
<tr>
<td></td>
<td>unloading</td>
<td>−0.116</td>
<td>−0.001</td>
</tr>
<tr>
<td>20.5 wt%</td>
<td>loading</td>
<td>−0.035</td>
<td>−0.004</td>
</tr>
<tr>
<td></td>
<td>unloading</td>
<td>−0.042</td>
<td>−0.003</td>
</tr>
</tbody>
</table>

Table S4. Pressure sensitivities of composite paper during loading and unloading at a pressure range of 1 kPa–50 kPa.

<table>
<thead>
<tr>
<th>CB concentration</th>
<th>State</th>
<th>Sensitivity S (/kPa) (1 kPa–50 kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5 wt%</td>
<td>loading</td>
<td>−0.514</td>
</tr>
<tr>
<td></td>
<td>Unloading</td>
<td>−0.585</td>
</tr>
<tr>
<td>10.5 wt%</td>
<td>loading</td>
<td>−0.262</td>
</tr>
<tr>
<td></td>
<td>unloading</td>
<td>−0.378</td>
</tr>
<tr>
<td>20.5 wt%</td>
<td>loading</td>
<td>−0.184</td>
</tr>
<tr>
<td></td>
<td>unloading</td>
<td>−0.196</td>
</tr>
</tbody>
</table>
Table S5. Comparison of some pressure sensor

<table>
<thead>
<tr>
<th>Paper-based pressure sensor</th>
<th>Absolute sensitivity value (kPa)</th>
<th>Pressure range (kPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tissued paper with reduced graphene oxide (rGO) by soaking</td>
<td>17.2</td>
<td>0-2</td>
<td>[146]</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>2-20</td>
<td></td>
</tr>
<tr>
<td>MXene/tissue paper</td>
<td>0.55</td>
<td>0.023-0.982</td>
<td>[180]</td>
</tr>
<tr>
<td></td>
<td>3.81</td>
<td>0.982-10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.52</td>
<td>10-30</td>
<td></td>
</tr>
<tr>
<td>SWNT/tissue paper</td>
<td>2.2</td>
<td>0.035-2.5</td>
<td>[181]</td>
</tr>
<tr>
<td>Tissue paper coated with silver nanowires (AgNWs)</td>
<td>1.5</td>
<td>0.03–30.2</td>
<td>[144]</td>
</tr>
<tr>
<td>Tissue paper coated with gold nanowires</td>
<td>1.14</td>
<td>0.013-50</td>
<td>[182]</td>
</tr>
<tr>
<td>GO-PEDOT:PSS modified cellulose paper</td>
<td>0.878</td>
<td>0.032-0.343</td>
<td>[183]</td>
</tr>
<tr>
<td>Carbon black/cellulose composite paper</td>
<td>0.514</td>
<td>1-50</td>
<td></td>
</tr>
<tr>
<td>(7.5 wt% CB, loading state)</td>
<td>0.215</td>
<td>1-250</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.002</td>
<td>250-5500</td>
<td>This Work</td>
</tr>
<tr>
<td>Filter paper with multiwalled carbon nanotubes (MWCNTs)</td>
<td>0.077</td>
<td>0.08–5</td>
<td>[184]</td>
</tr>
<tr>
<td></td>
<td>0.012</td>
<td>~5-50</td>
<td></td>
</tr>
<tr>
<td>Pressure sensors based on EGaIn droplets, sponge rubber, and copy paper substrates with and without MWNT thin films.</td>
<td>0.014</td>
<td>0-100</td>
<td>[185]</td>
</tr>
<tr>
<td>Graphene deposited on copper foil</td>
<td>0.0045</td>
<td>0-50</td>
<td>[147]</td>
</tr>
</tbody>
</table>
Figure S9. (a) Pressure-response of 7.5 wt% CB composite paper over time interval of 250 s. (b) Pressure-response of 7.5 wt% CB composite paper over time interval of 5 s. (c) Pressure-response curves for composite paper at pressure range (1 kPa–50 kPa). (d) A prepared sample for piezoresistive tests.
Figure S10. Setup for shooting darts into the dartboard. (a) Picture of the circuit layer. (b) Picture of the shooting system using a tripod and a guiding tube.

Figure S11. The average increase in resistance of Rings 1-4 after the first and second effective hits at the dartboard.
Figure S12. Electrical potential changes of a 0.5-mm thick plate with 2-mm holes to model darts. (a) Seven tests of the same number of darts. Here the number of darts is 3. (b) One of the seven tests showing an increasing number of darts/holes from 1 to 10.
Figure S13. FEA simulation results of resistance change of composite sheet caused by darts in seven tests: (a) absolute change of resistance, (b) relative change of resistance for targeted substrates with two areas: 20 mm × 20 mm, 15 mm × 15 mm.
Theoretical description of the response of the material to punches and darts

Previously, Mendelson and Karioris punched same-sized holes in conductive paper and showed that the conductivity change of the paper increased linearly with area fraction of small circular holes, which is proportional to the square of the hole radius.[186], [187] Naghashpour and Van Hoa drilled holes in composite plates and found that change in electrical resistance went up with the hole size nonlinearly.[186], [187] There are few explanations in this nonlinear behavior. Here, we describe the behavior qualitatively through a simplified analytical model and quantitatively with a numerical model.

Figure S14. A simplified model of a square plate with a hole for the punctured composite paper: (a) a whole plate, (b) a quarter of the plate with resistance $R'$, (c) equivalent circuit of the composite paper.

Analytically, we model the composite paper in the punching experiments by a square plate with a hole of radius $r$ in the center, as Figure S14(a) shows. We divide the plate into four parts and view the resistance of the perforated plate as four resistors $R'$ in parallel and series configurations, as shown in Figure S14 (b)(c):

$$R = \frac{R' R'}{R' + R} + \frac{R' R'}{R' + R} = R' = \int_0^{L/2} \frac{\rho}{A(x)} \, dx = \int_0^{L/2} \frac{\rho}{w(x) t} \, dx \quad (S4)$$
wherein, \( w(x) \) is the width of the plate in the first quadrant, as Figure S14(b) shows. \( w(x) = \frac{W}{2} \) \( y(x) = \frac{W}{2} - \sqrt{r^2 - x^2} = \frac{W}{2} - r\cos\theta \), when \( x \in [0, r] \); and \( w(x) = \frac{W}{2} \) when \( x \in \left[ r, \frac{L}{2} \right] \). Converting Cartesian coordinates \((x,y)\) to polar coordinates \((r,\theta)\) \( x = r\sin\theta \), \( dx = r\cos\theta \, d\theta \), Eq. (S4) becomes:

\[
R = \int_{x=0}^{x=r} \frac{\rho}{(\frac{W}{2} - r\cos\theta)} \, dx + \int_{x=r}^{x=\frac{L}{2}} \frac{\rho}{W} \, dx = \frac{\rho}{t} \int_{\theta=0}^{\theta=\frac{\pi}{2}} \frac{1}{\frac{W}{2} - r\cos\theta} r\cos\theta \, d\theta + \frac{2\rho}{Wt} \left( \frac{L}{2} - r \right) \tag{S5}
\]

Applying integral substitution \( u = \tan\frac{\theta}{2}, \cos\theta = \frac{1-u^2}{1+u^2}, d\theta = \frac{2 \, du}{1+u^2} \) yields:

\[
\frac{\rho}{t} \int_{u=0}^{u=\frac{1}{2}} \frac{1}{\frac{W}{2} - r(\frac{1-u^2}{1+u^2})} \, r(1-u^2) \, du = \frac{2\rho}{t} \int_{u=0}^{u=\frac{1}{2}} \frac{r(1-u^2)}{(\frac{W}{2}-r+\frac{W}{2}+ru^2)(1+u^2)} \, du \tag{S6}
\]

Substituting Eq. (S6) in Eq. (S5), the total resistance of the plate \( R \) will be:

\[
R = \frac{2\rho}{t} \int_{u=0}^{u=1} \frac{r(1-u^2)}{\left( \frac{W}{2} - r \right) + Wu^2 + \left( \frac{W}{2} + r \right) u^4} \, du + \frac{2\rho}{Wt} \left( \frac{L}{2} - r \right) \tag{S7}
\]

As the initial resistance of the plate without holes is \( R_0 = \frac{\rho L}{Wt} \), the relative change of resistance \( \frac{\Delta R}{R_0} \) caused by a hole of radius \( r \) is

\[
\frac{\Delta R}{R_0} = \frac{R - R_0}{R_0} = \frac{2\rho}{t} \int_{u=0}^{u=1} \frac{r(1-u^2)}{\left( \frac{W}{2} - r \right) + Wu^2 + \left( \frac{W}{2} + r \right) u^4} \, du + \frac{2\rho}{Wt} \left( \frac{L}{2} - r \right) - \frac{\rho L}{Wt} = \frac{2W}{L} \int_{u=0}^{u=1} \frac{r(1-u^2)}{\left( \frac{W}{2} - r \right) + Wu^2 + \left( \frac{W}{2} + r \right) u^4} \, du - 2\frac{r^2}{L} \tag{S8}
\]

Eq. (S8) indicates that the relative change of resistance only depends on the length and width of the plate and the radius of the hole.
For our case, $L = W = 0.02$ m, and the effective resistivity is 4.78 $\Omega \cdot$ m, which takes account of contact resistance between the electrodes in the demo. The resistance and relative change in resistance of the plate with a hole of radius $r$ are:

$$R = \frac{2 \times 4.78}{0.0005} \int_{u=0}^{u=1} \frac{r(1-u^2)}{(0.01-r) + 0.02u^2 + (0.01+r)u^4} \, du + \frac{2 \times 4.78}{0.02 \times 0.0005} (0.01 - r) \tag{S9}$$

$$\frac{\Delta R}{R_0} = 2 \int_{u=0}^{u=1} \frac{r(1-u^2)}{(0.01-r) + 0.02u^2 + (0.01+r)u^4} \, du - 100r \tag{S10}$$

By MATLAB symbolic calculation of Eq. (S9) and Eq. (S10), we obtain the analytical value of resistance and calculate the change of resistance. Meanwhile, we also acquire the numerical solution by finite element analysis (FEA) (Figure S15). Figure S16 shows the results of the experiment, FEA simulation, and analytical calculation. All three results show that the resistance of the composite paper changes nonlinearly with increasing hole size. The effect of the hole size on the resistance of the paper becomes evident starting from 2 mm. However, the experimental values are higher than those from the other two approaches. The discrepancy between experiment and theoretical results is likely due to the cracks and fractures that occur within the composite paper during the punch experiments, which potentially break the conductive paths in the paper and cause larger changes of resistance than theoretically predicted.

Similarly, for the dartboard demo, the holes caused by the dart (~ 2 mm diameter) provoke small, discrete changes in resistance that accumulate to significant values after several hits. In Figure S12, we simulate the darts by randomly removing a specific number (1-10) from the square sheet. For each number, we run seven tests with different positions of holes. As the number of darts/holes increases, the resistance of the sheet increases linearly (Figure S13a). In the actual dart demo, the darts can overlap each other, which explains why the change is not uniform after each hit. Furthermore, the small error bars indicate the position/distribution of the darts has little effect on the resistance of the sheet for the same number of darts. We also simulate substrates with different areas and find that resistance changes by darts are greater in the smaller substrate than the larger one (Figure S13b), which explains why the bullseye has a more significant change in resistance than the surrounding rings (Figure 6b).
Figure S15. Electrical potential changes of a 0.5-mm thick plate with holes in diameter $D$ ranging from 0 mm to 12 mm.
Figure S16. The resistance change of punctured composite paper verse the radius of the hole by experiment, simulation, and analytical calculation: (a) absolute resistance with cubic polynomial fitting \( Y_1 = 43.4X_1^3 + 178.7X_1^2 + 282.8X_1 + 9705.5, R^2 = 0.99; Y_2 = 25X_2^3 + 37.1X_2^2 + 137.2X_2 + 9537.8, R^2 = 0.99; Y_3 = 27.5X_3^3 - 27.2X_3^2 + 127.3X_3 + 9537.2, R^2 = 0.99),(b) relative resistance change.
**Figure S17.** Optical images of cellulosic fibers taken by MorFi fiber analyzer (credit: Pulp and Paper Services, LLC).
Figure S18. Effective length of U-shaped samples determined by COMSOL simulation. Assuming bars with legs (a) and without legs (b) (1×0.3×0.04inch, same resistivity 27.7 S/m), applying an equal voltage (1 V) across both bars allows determination of resistance. The effective length of the U-shaped samples will be the length of the straight bar (1inch) multiplied by the ratio of resistance (95.32/120.34≈0.79). Therefore, for U-shaped samples, the effective length of conductance is 0.79 inch instead of 1 inch.
Bibliography


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