PIEZOELECTRIC PAPER: LARGE-SCALE COMPATIBLE MANUFACTURING PROCESS AND SENSOR DEMONSTRATION

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ABSTRACT

Functionalized paper has been used as a substrate for flexible devices for several years now. However, the methods for preparing such paper substrates are typically too complex for integration with large-scale paper manufacturing processes. Here, we demonstrate a simple process for manufacturing piezoelectric paper that is compatible with the conventional papermaking process. This process utilizes microfibrillated wood pulp to achieve paper with high loading (69 wt%) of piezoelectric $BaTiO_3$ particles (~300 nm diameter) that shows high piezoelectric coefficients up to d_{33} = 15.2 pC/N after corona poling. Such a piezoelectric paper composite is used as a simple accelerometer to demonstrate its utility in inertial sensing applications.

KEYWORDS

Piezoelectric, $BaTiO_3$, Paper based sensors, Accelerometer, Nanomaterials, Large scale, Flexible sensors

INTRODUCTION

Paper based substrates have attracted significant attention in the realm of smart materials and electronics due to a growing desire for environmentally sustainable platforms, potential to exploit the fibrous bulk, and opportunity to incorporate other functional materials within the matrix. In addition, paper presents several other advantages that make it a suitable material to be used in sensing devices. It is easy to manufacture at low cost, it is a dielectric material that can be used in numerous sensing mechanisms, and the porous nature allows it to be used as a paper filter where fluids and particles smaller than the pore size can pass through while larger-sized particles are captured [1], [2].

Many attempts have been made in recent years to improve the physicochemical properties of paper by incorporating nanostructured materials onto wood fiber. For example, carbon nanotubes [3] were added to the matrix of wood pup to fabricate conductive paper as well as titanium dioxide functionalized wood fiber [4] was developed by a hydrolysis method. Likewise, polyelectrolytes attract significant interest in the field of making conductive wood fiber for smart paper applications [5]. Recently, multiple researchers developed paper-based sensing devices that have a wide range of applications in the area of bio and chemical sensing [6].

Integrating nanomaterials within the industrial paper production process has the potential to impart useful electronic properties such as piezoelectricity to conventional paper. In past work, wood pulp-based composites for flexible electronics have been achieved by growing ZnO on wood fibers [7], a complex procedure that is incompatible with standard paper making; another study [8] used an approach to electrostatically bind negatively charged $BaTiO_3$ (BT) onto wood fibers, involving electrostatically coating the wood fiber with a total of 3 layers of anionic and cationic polyelectrolytes poly(diallyldimethyl-ammonium chloride (PDDA) and poly(sodium 4-styrenesulfonate) (PSS), respectively, and the addition of the paper strengthening agent carboxymethylcellulose (CMC). The basic idea of this manufacturing process involves embedding BT into a stable matrix of wood fiber; this can be achieved through fiber functionalization. The fiber functionalization process is realized using a layer-by-layer (LbL) approach, and this results in the creation of a positively charged wood fiber surface. Immersion of thus treated fibers into a BT suspension results in electrostatic binding of the BT nanoparticles directly onto each fiber before using these fibers to make paper. Though this process yields a high BT mass loading of wood fiber, it involves complex steps and is rather time consuming.

Recently the production and potential application of microfibrillated cellulose (MFC) fibers have garnered much attention due to their role in enhancing the tensile strength of the paper-based composite, biodegradability, and renewability. MFC is created by refining wood fibers, a mainly mechanical process that partially separates the cellulose fibrils from the wood fiber matrix. There are reports of various applications of MFC -based materials including composites, scaffolds, electronic materials, and solar cells [9].

In this study, we demonstrate that the use of highly refined MFC wood pulp (up to 300 kWh/t specific refining energy, SRE) facilitates BT binding without requiring the time-consuming steps necessary for unrefined pulp. We believe MFC significantly increases the available surface area for better anchoring of BT particles. We form piezoelectric paper from the functionalized MFC and demonstrate the usefulness of such paper for a sensing application.

FABRICATION OF PIEZOELECTRIC PAPER

Highly refined wood pulp refined at 200 kWh/t and at 300 kWh/t denoted Fiber(200) and Fiber(300), respectively, was obtained from CANFOR Ltd. (British Columbia, Canada) along with unrefined pulp (Fiber(0)). Prior to the functionalization, zeta potential measurements are taken to identify the surface charges of the wood fiber and the BT particles. The measurements on the pristine wood fibers (-23 ± 2.5 mV) and BT particles (-24.7 ± 1 mV) show the necessity of an intermediate layer; hence, the attachment of BT particles onto wood fibers can be enabled through a positive polyelectrolyte interlayer.

In this study, the piezoelectric paper is prepared by functionalizing the wood fiber with the help of cationic polymers to create a uniform positively charged surface to enable the anchoring of 300 nm sized BT particles onto wood fiber. First, an aqueous solution of positively charged PDDA (1 wt % in 0.5 M NaCl) and an aqueous solution of negatively charged PSS (1 wt % in 0.5 M NaCl) are prepared. Here the NaCl serves to avoid coiling up of polyelectrolytes. Different batches of these wet state fibers with a fiber dry weight of 3g per batch are processed in different sequences of steps before forming handsheets according to TAPPI standard T-205. For a 3-layer LbL process as in [8] and shown in Fig. 1 (top) a batch of F(200) fibers is immersed in a PDDA solution (400 mL- for 1 hour), followed by a PSS solution (400 mL- for 1 hour) and again in a PDDA solution (400 mL for 12 hours) to create a positively charged surface on the wood fibers. The wood fibers are then immersed in a BT suspension (1 wt % of BT sonicated in 400 mL of distilled water for 10 minutes) for 12 hours adsorption. Followed this, the functionalized fibers are transferred to

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400 mL of 5 wt % of CMC dissolved in distilled water and left for 12 hours adsorption under magnetic stirring at 500 RPM.

Other fiber batches undergo much simpler processes employing at most one polyelectrolyte layer as shown in Fig. 1 (bottom). For a single layer process a batch of fibers is immersed in a solution of 1 wt % PDDA dissolved in 0.5 M NaCl (400 mL-for 1 hour). Then the wood fibers are transferred to 1 wt % of BT dispersed in 400 mL of distilled water and left for 12 hours adsorption under magnetic stirring at 500 RPM. In one case, the functionalized fibers are also transferred to 400 mL of 5 wt % of CMC and left for 12 hours adsorption under magnetic stirring at 500 RPM. One batch of refined pulp is also directly immersed in the same BT suspension as above, without prior deposition of a polyelectrolyte. The process using a single polyelectrolyte layer is also applied to non-fibrillated-Fiber(0) pulp to compare the properties of the resulting paper sample with paper based on refined MFC pulp.

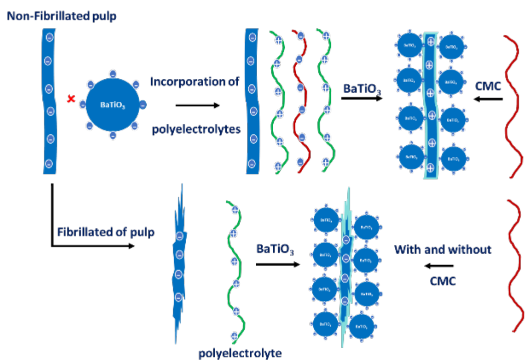

Figure 1: Schematic of a 3-layer LBL process [8] (top) and the simplified fiber functionalization process (bottom)

CHARACTERIZATION AND POLING

The piezoelectric paper is characterized using a scanning electron microscope (SEM) to image the distribution of particles on the fibers, and thermal gravimetric analysis (TGA) allows determining the mass fraction of BT in the paper composite. The paper is subjected to corona poling (Milman Thin Film Systems Pvt. Ltd.) to render it piezoelectric at 122°C (Curie temperature of BT) for 1 hour with a needle voltage of 63 kV and a grid voltage of 25 kV. The piezoelectric coefficients of the hybrid paper samples are measured with a PiezoTest PM300 d_{33} meter (Piezotest Pte. Ltd. Singapore). The piezoelectric paper is characterized by X-ray diffraction (XRD) before and after poling to understand the influence of poling on the tetragonality of the BT lattice structure.

The piezoelectric paper is finally used to construct an accelerometer and this device is characterized by using a sinusoidally driven voice coil actuator (VCA) along with a reference accelerometer (ADXL203EB by Analog Devices). The charge response of the paper-based accelerometer is measured using a Kistler 5015A charge-voltage converter.

RESULTS AND DISCUSSION

Table 1 shows the BT mass fraction and the piezoelectric coefficient of paper samples made according to Fig. 1. The samples with one polymer layer and without CMC show the highest BT loading, and the highest d_{33} value among these samples is achieved for Fiber(300), while the lowest mass loading and d_{33} is achieved for unrefined pulp.. The addition of CMC appears to slightly reduce the BT mass loading while not significantly affecting the piezoelectric properties. The omission of the polyelectrolyte layer does not affect the BT mass loading is a meaningful manner but leads to a significant reduction of the piezoelectric properties of the sample. This shows that MFC eliminates the need for additional functional layers while achieving higher BT loading compared to previous work [8].

Table 1: BT mass loading and piezoelectric coefficient of paper samples; Fiber(SRE) indicates the specific refining energy in kWh/t

Sample	wt% BT	d_{33} [pC/N]
Fiber(0) + PDDA + BT	26	2.0
Fiber(200) + BT	61	4.3
Fiber(200) + PDDA+ BT	64	8.0
Fiber(200) + PDDA +BT+ CMC	53	10.1
Fiber(200) +PDDA +PSS + PDDA +BT +CMC	43	4.7
Fiber(300) + PDDA+ BT	69	15.2

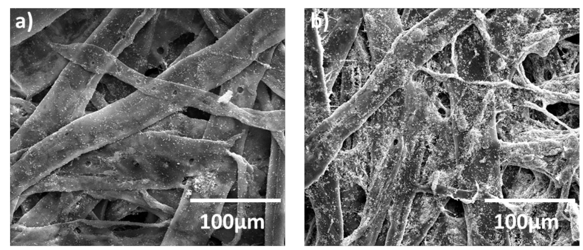

Figure 2: SEM images of a Fiber(0)+PDDA+BT and Fiber(300) + PDDA+ BT paper sample showing a significance difference in the loading of $BaTiO_3$ onto wood fiber.

The SEM images in Fig. 2 clearly elucidate the loading efficiency of MFC over non-fibrillated pulp through its external fibrils which enhances the physical adsorption of particles on the fiber surface. Fig. 3 shows SEM images of the highly loaded piezoelectric paper made from Fiber(300). The BT particles tightly coat the fibrillated wood fibers. The cross section of the fiber matrix also shows that the paper is highly loaded with BT particles.

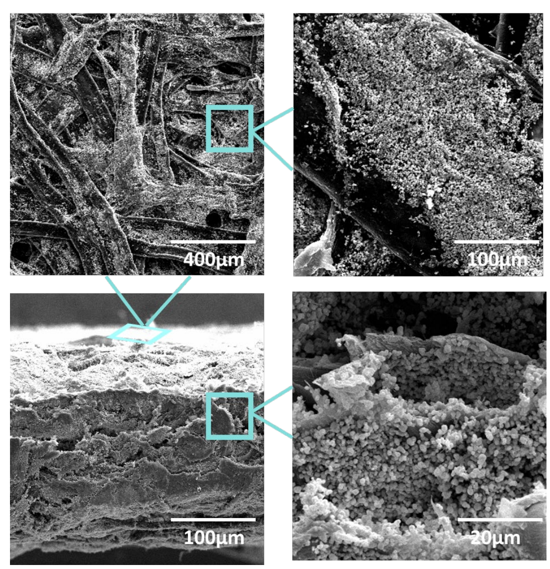

Figure 3: SEM images of a Fiber(300) + PDDA+ BT paper sample showing high loading of $BaTiO_3$ in the wood fiber matrix

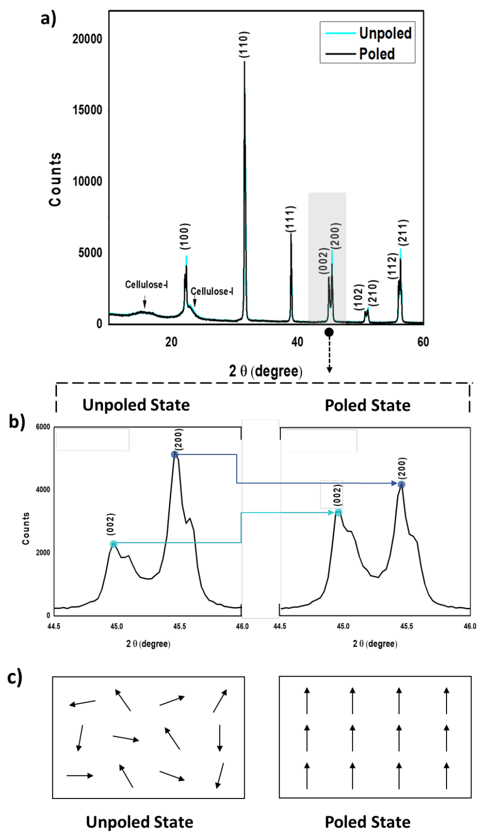

Figure 4: XRD analysis of Fiber(300) + PDDA+ BT piezoelectric paper and influence of poling on domain orientation

XRD characterization allows assessing the effect of poling on domain orientation of BT in the piezoelectric paper. The XRD pattern of the hybrid paper exhibits peaks in the range of 2θ=44.5°-47° corresponding to BT (Fig. 4a) allowing analysis of the structural changes related to corona poling. The peaks at (200) and (002) in both unpoled and poled states suggest that the BT is tetragonal [3]. Tetragonal structures with random orientation show a (200) plane peak intensity twice the intensity of the (002) plane peak. The relative intensity of the (002) plane peak increases by 32.6 % with poling and the relative intensity of the (200) plane peak simultaneously decreases by 18.8 % (shown in Fig.3b); this indicates domain wall reorientation of the ferroelectric domains with the poling process; the domain orientations are schematically depicted in Fig. 3c [10].

DEMONSTRATION OF ACCELEROMETER

The Fiber(300)-based piezoelectric paper is used as a substrate to build an accelerometer to demonstrate its suitability as a substrate for sensing applications. An accelerometer is constructed using the piezoelectric paper by attaching parallel copper electrodes and adding a seismic mass of m = 30 g to one of its sides. This setup is then mounted to a 3D printed cube which is mounted to a VCA as shown in Fig. 5.

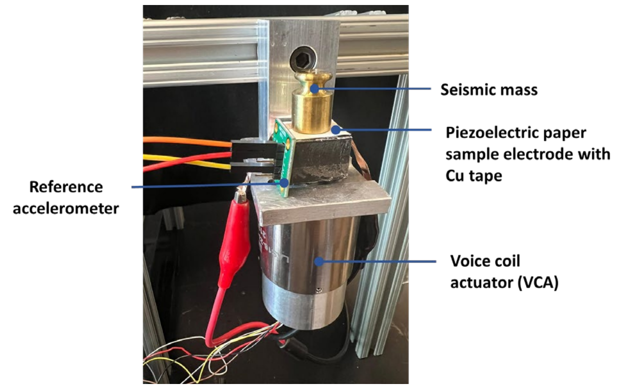

Figure 5: Photograph of an accelerometer set up used in the experiments

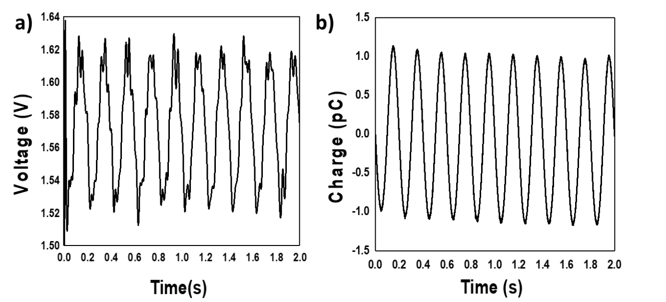

Figure 6: Output signal at 5 Hz from a) commercial reference accelerometer and b) paper accelerometer

The time-dependent output signals of the reference accelerometer and the paper accelerometer for excitation at 5 Hz are acquired simultaneously, and they are shown in Fig. 6.

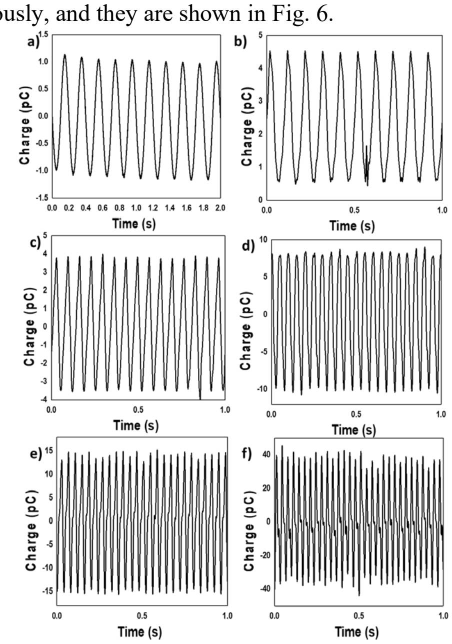

Figure 7: Output signal at different frequencies a) 5 Hz b) 10 Hz c) 15 Hz d) 20 Hz e) 25 Hz f) 30 Hz

To test the frequency response of our paper-based accelerometer, we measured the charge output at frequencies from $f = 5$ Hz to 30 Hz in 5 Hz intervals. As shown in Fig. 7a-f, the charge output increases with an increase in frequency for a nearly constant displacement amplitude A_d = 1 mm, corresponding to an increasing acceleration amplitude $A_a = A_d\,(2\,\pi\,f)^2$.The sensitivity of the accelerometer $S = A_C / A_a$ (with the charge amplitude A_C) remains approximately constant around 5.82 pC/ms^{-2} in the frequency range; a constant sensitivity is expected as the mechanical resonant frequency of this device most likely occurs above this frequency range. Below resonance, the sensitivity [11]

$$A_C/A_a = d_{33} * m \quad ---- (1)$$

allows calculating the piezoelectric coefficient independently to verify consistency. Based on the sensitivity obtained in this frequency range, the d_{33} = 19.7 pC/N is comparable to the value of d_{33} = 15.2 pC/N measured using the d_{33} meter (Table 1).

In addition to the above experiments, one of the Fiber(300)-based paper sample was repeatedly poled for three times at the same poling conditions mentioned in the experimental section to induce the maximum polarization. This yielded the highest piezoelectric coefficient of 32.8 pC/N. However, it decayed to 8 pC/N after 24 hours. Our future work will focus on understanding the mechanisms behind this decay of piezoelectric coefficient in the paper-based composite.

CONCLUSION

We have demonstrated the manufacturing of a piezoelectric paper composite through the electrostatic interaction of polyelectrolyte coated MFC wood pulp with BT nanoparticles. The use of MFC wood pulp enhances the loading of BT nanoparticles on to wood fibers and upon corona poling, yields a piezoelectric coefficient of the composite of up to 32.8 pC/N. As a proof-of-concept demonstration, a piezoelectric paper-based accelerometer was constructed and its time series response at different frequencies was recorded, demonstrating the utility of piezoelectric paper composites for inertial sensing. Our initial experimental results indicate that functionalizing microfibrillated wood fibers with BT nanoparticles is a promising approach to integrate piezoelectric functionality into conventionally manufactured paper and enhance its piezoelectric performance by significantly improving the loading of BT nanoparticles. Such piezoelectric paper composites are expected to open greener avenues for applications in diverse niches such as energy storage, nanogenerators, accelerometers, strain sensing, microfluidic devices, biosensing, tactile sensors and speakers, to name a few.

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