PIEZOELECTRIC SENSITIVITY MEASUREMENTS OF CELLULOSE NANOFIBRIL SENSORS

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Abstract − Piezoelectric sensitivity of cellulose nanofibril (CNF) film sensors was measured using a mechanical shaker and charge amplifier setup. In-house fabricated CNF film sensors showed 5-7 pC/N sensitivity in ambient conditions. The CNF film used here contained randomly oriented fibrils, and the piezoelectric response is expected to increase remarkably after film polarization and fibril alignment. The results obtained in this study suggest that nanocellulose film is a suitable sensor material for applications in various fields such as material sciences, electronics and biomedical diagnostics.

Keywords: cellulose nanofibrils, piezoelectric sensors, sensitivity measurement.

1. INTRODUCTION

Cellulose based nanomaterials [1], which are also known as nanocellulose, are interesting renewable bio-based nanomaterials which has potential applications for example in electronics and material sciences as well as in biomedical engineering. The nanoscale dimensions and strong ability to form entangled porous networks makes nanocellulose suitable material for membrane applications, for example as a solution-processable and robust separator material in supercapacitors [2]. Fig. 1 describes schematically the fabrication of nanocellulose from a wood cellulose fiber [1]. The piezoelectricity of wood has been known for
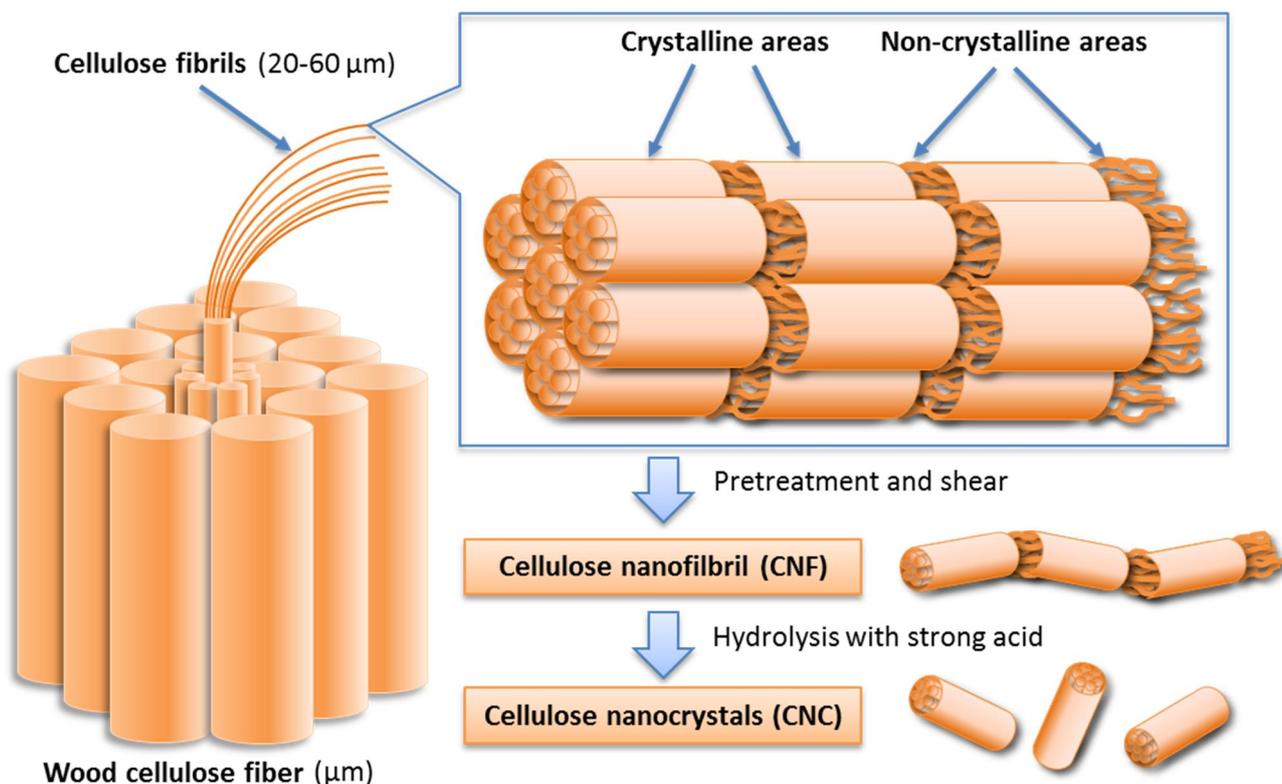

Fig. 1. Schematic view of nanocellulose fabrication from a wood cellulose fiber. The cellulose fiber is first cut to fibrils and after various processing steps into cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC). For more details see reference [1].
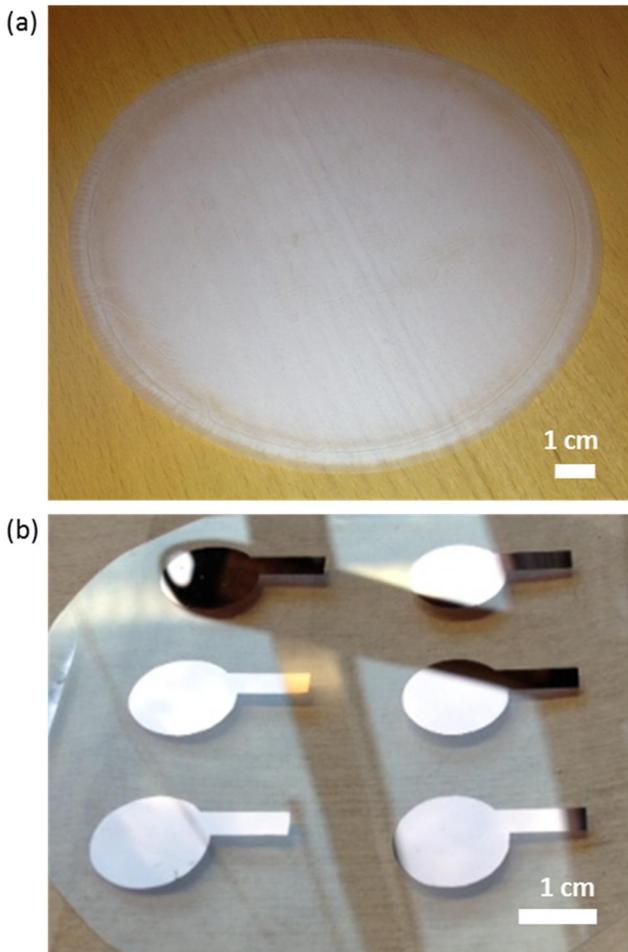
Fig. 2. Photographs of (a) CNF film used in the piezoelectric sensors and (b) copper electrodes on PET substrate.
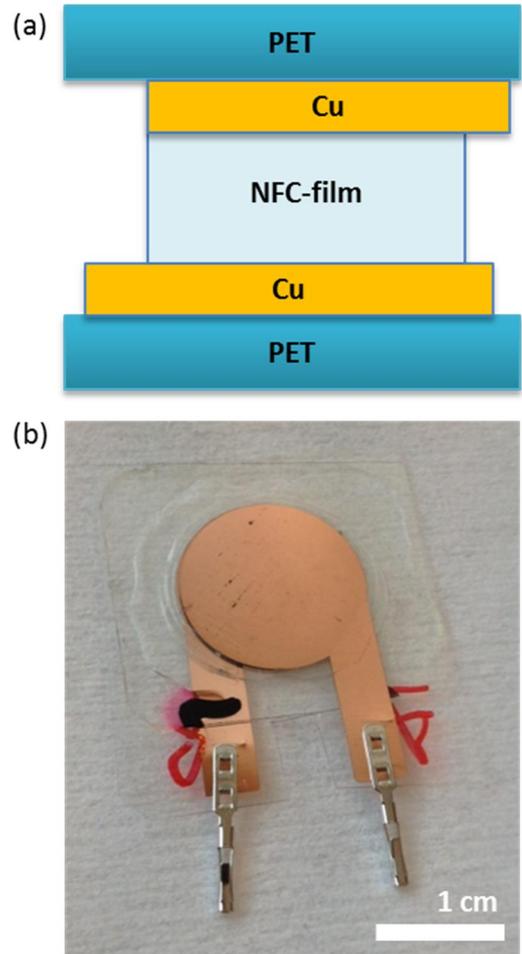

Fig. 3. (a) A schematic side-view of the piezoelectric sensor structure and (b) a photograph of assembled sensor. The electrodes have a circular shape with a diameter of 15 mm.

decades [3]. A classical definition of piezoelectricity is the change of electrical polarization in a material in response to mechanical stress [4]. This phenomenon is expected to be more pronounced in crystalline nanoscale materials, such as crystalline cellulose nanocrystals (CNC) [5]. However, the topic has been poorly covered in the literature and there are only a few very recent reports about the experimental evidence of piezoelectricity of CNC [5, 6]. A polymer-like cellulose nanofibril (CNF) films are composed of amorhous cellulose chains as well as crystalline CNC regions as can be seen from Fig. 1. Due to randomly aligned crystalline regions, also native CNF film is expected to show overall piezoelectric behavior. To our knowledge, the piezoelectric measurements of CNF films have not been reported in the literature before.

In this study, CNF films are used as functional materials in piezoelectric sensors and the sensor sensitivity is measured using a dedicated measurement setup. The sensors are excited with a mechanical shaker providing a sinusoidal input force and the charge generated by the sensor is measured. The sensitivity is defined here as the charge generated by the sensor divided by the normal force used to excite the sensor. This is closely related to transverse piezoelectric coefficient d_{33}.

The structure of this paper is as follows. Section 2 describes the fabrication of CNF sensors. Section 3 introduces the sensor sensitivity measurement setup. Section 4 presents the results and Section 5 concludes the study.

2. FABRICATION

The CNF material was produced by a mechanical homogenizing process, where it underwent 6 passes in microfibrillator equipment (described in more details elsewhere [8]). The CNF film was then fabricated from obtained bleached birch cellulose mass. Films were prepared by pressure filtering (15-30 min) followed by pressing and drying in hot-press at 100 °C for 2 h. The resulting in-house fabricated CNF films presented in the Fig. 2(a) were about 70 μm thick (measured using a micrometer screw).

Electrodes for CNF sensors were fabricated on polyethylene terephthalate (PET, Melinex ST506) substrate by e-beam evaporation (Varian vacuum evaporator). Electrodes were formed by evaporating 100 nm thick copper (Cu) layer through a laser-cut stencil shadow mask. The resulting circular shape electrodes of 15 mm in diameter are presented in Fig. 2(b).
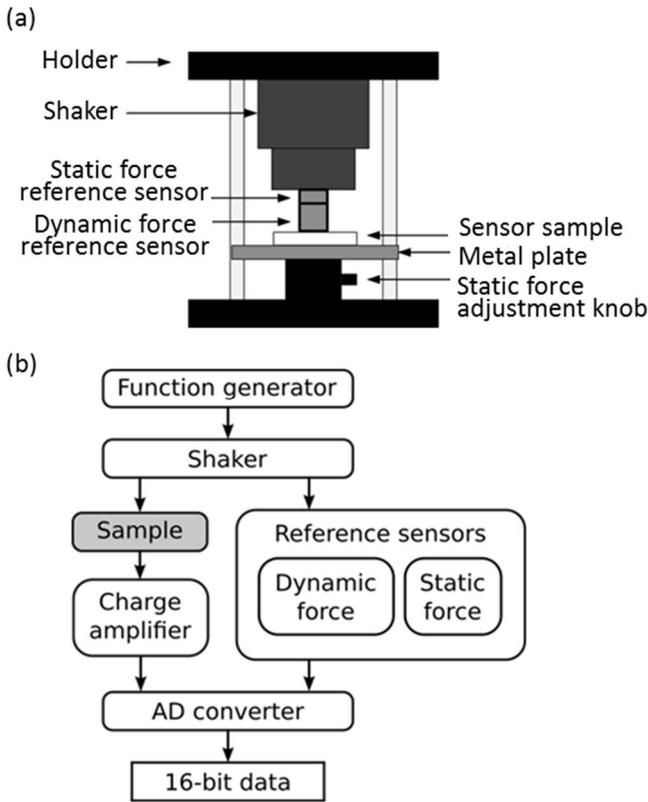
Fig. 4. Schematic view of (a) the sensitivity measurement setup and (b) the block diagram of the sensitivity measurement setup.

A principle structure of fabricated piezoelectric sensor is presented in Fig. 3(a). Before the sensor assembly, CNF film was cut into round shape pieces of a diameter a bit larger than the electrodes to avoid short-cutting. The CNF pieces were then sandwiched between two electrodes and fixed together from outside the electrode edges using a sticker film (2 way glue, manufactured by Kuretake Co.). In total, four sensors were assembled and measured in this work. A photograph of one fabricated sensor is presented in Fig. 3(b).

3. MEASUREMENTS

The Brüel & Kjaer Mini-Shaker Type 4810 was used in the sensor sensitivity measurements. The shaker generates a dynamic excitation force with force rating of 10 N sinusoidal peak and has a frequency range from DC to 18 kHz. A sinusoidal input for the shaker was provided with a Tektronix AFG3101 function generator. A commercial high sensitivity dynamic force sensor (PCB Piezotronics, model number 209C02) was used as a reference sensor for the dynamic excitation force. The sensor was connected to a sensor signal conditioner (PCB Piezotronics, Model 442B06) with a low-noise coaxial cable. A load cell (Measurement Specialties Inc., model number ELFS-T3E-20L) was used as reference sensor to measure the static force between the sample and shaker's piston. A pretension, which is producing static force, is needed to keep the sample in place and to prevent the piston jumping off the surface
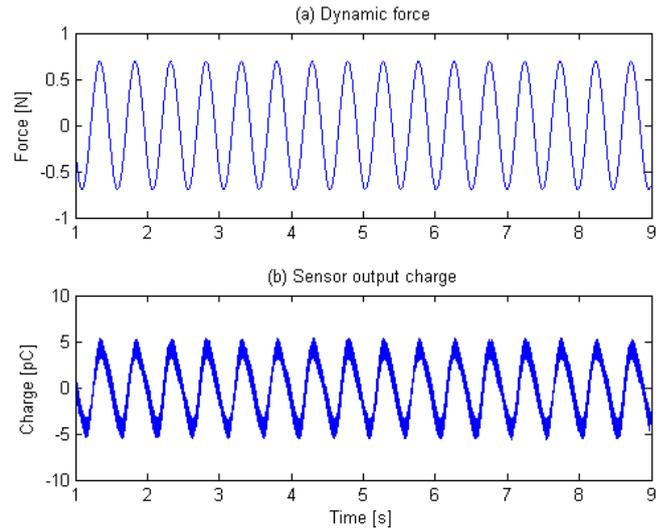

Fig. 5. An example of measured (a) dynamic force and (b) sensor output charge signals. The signals are measured from sensor S1.

during the measurement. Fig. 4(a) shows the sensor sensitivity measurement setup in details. The components of the measurement system are marked in the figure. In Fig. 4(b) the schematic view of the measurement setup is presented.

The sensitivity is defined here as the charge generated by the sensor divided by the normal force used to excite the sensor. This is closely related to transverse piezoelectric coefficient d_{33}. Generally, the piezoelectric coefficient d_{ij} is related to the electric field produced by a mechanical stress; the first subscript refers to the electrical axis and the second to the mechanical axis [7]. The main axes 1, 2 and 3 correspond to length, width and thickness and the shear about these axes is represented by 4, 5 and 6 [7]. Thus, in the transverse piezoelectric coefficient measurement, the electrodes are located on the top and the bottom of the sensor material film and the film is excited with a dynamic force in thickness direction.

To measure the sensor sensitivity in transverse direction, the sensor was placed horizontally on the metal plate. A static force of approximately 3 N was used. The sensor was excited with a dynamic, sinusoidal 2 Hz input signal of 1000 mV (peak to peak), resulting in an approximate force of 1.3 N. The excitation was done by applying the force in the middle of the sensor. The measurement was repeated three times; between the measurements the static force was relieved and the sensor was re-positioned on the metal plate for the new measurement. The same measurements were conducted from both sides of the sensor, resulting in a total of six excitations per sensor. The same measurement principle has been previously used to evaluate the sensor sensitivities of piezoelectric polymer film (polyvinylidenefluoride, PVDF) sensors [9-14].

The charge developed by the sensor was measured with a custom-made combination of a charge amplifier and a 16-bit AD-converter. The connection to the AD-converter from the sensor was provided via coaxial wires and crimp connectors (Nicomatic Crimpflex). The AD-converter had additional channels for sampling also the voltage signals from the reference sensors.

The measured data was processed to solve the sensitivity of the sensor to the force. The sensitivity was obtained by dividing the charge generated by the sensor with the force obtained with the dynamic force sensor. The unit of sensitivity is thus pC/N. Since the excitation force was sinusoidal, the sensitivity can be calculated simply by dividing the amplitudes of the respective signals. Possible baseline drift in the signals was removed with high-pass filtering before the sinusoidal amplitudes were solved by fitting sinusoidals to the signals as described in the IEEE Standard for Digitizing Waveform Recorders (IEEE Std 1241) [15]. Fig. 5 shows an example of the measured signals of (a) measured dynamic force and (b) measured sensor output charge. The signal is measured from sensor S1, and a sensitivity of about 6.1 pC/N can be calculated from the signals (sensor output charge of 8.6 pC (peak-to-peak) divided by dynamic force of 1.4 N (peak-to-peak)).

4. RESULTS

The operation of four nominally identical CNF sensors was evaluated with sensitivity measurements. Table 1 presents the results of the sensitivity measurements. The values are presented as mean sensitivities ± standard deviations for each sensor side.

All four measured CNF sensors showed quite similar sensitivity values as can be noticed from Table 1. These results suggest that the nanofibrils are homogeneously distributed inside the film and the sensitivity values are reliable. The sensor S3 showed quite high deviation, but only on the side 2. This may result from non-uniformity of the electrode or the sensor material surfaces, causing contributions from other than normal direction forces. The average sensitivity values for the sensors S1, S2, S3 and S4 were (5.3 ± 1.4), (5.2 ± 1.0), (7.0 ± 3.7) and (6.0 ± 1.9) pC/N, respectively.

Table 1. Average force sensitivities for each sensor side.

Sensor name	Sensitivity (pC/N), side 1	Sensitivity (pC/N), side 2
S1	4.7 ± 1.1	5.8 ± 1.6
S2	5.9 ± 0.9	4.5 ± 0.5
S3	5.3 ± 1.2	5.3 ± 4.8
S4	4.6 ± 0.4	7.4 ± 1.6

5. CONCLUSIONS

The piezoelectric sensors were fabricated from nanofibrillated cellulose (CNF) film. The sensitivity of fabricated sensors was measured using a dedicated measurement setup. The fabricated four piezoelectric sensors made of 70-μm-thick CNF film showed d_{33} sensitivities from 5 to 7 pC/N. One should point out that the CNF film measured here was in its native state, as fabricated, and not polarized which is a general method for piezoelectric material fabrication. In comparison, a polarized 28-μm-thick PVDF film has a piezoelectric coefficient d_{33} of -33 pN/C [7]. This is about four times larger than non-polarized CNF film measured in this work.

The sensitivity of the CNF films is expected to increase after polarization. In the polarization stage, the film exposed to a high electric field to generate piezoelectric properties. The poling procedure, in general, consists of applying an electric field for a certain period of time. The polarization of the CNF film should lead to orientation of crystalline CNC regions inside the CNF film leading to a remarkable increase of piezoelectric effect due to the large piezoelectric coefficient of CNC [5, 6]. However, polarization of dry film is difficult due to the entangled and stiff structure of the film and thus, further fabrication process development is required in order to increase the CNF film sensitivity.

To conclude, functional piezoelectric sensors were fabricated from CNF film. The results obtained in this study suggest that nanocellulose film is a suitable sensor material for applications in various fields such as material sciences, electronics and biomedical diagnostics.

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