Chapter 1

Nanocellulose as a Piezoelectric Material

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Additional information is available at the end of the chapter

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Abstract

Cellulose-based nanomaterials, which are generally known as nanocelluloses, are interesting renewable biomaterials which have potential applications for example in material science, electronics and biomedical engineering and diagnostics. Cellulose has a strong ability to form lightweight, highly porous and entangled networks that make nanocellulose suitable as substrate or membrane material. Recently, also studies related to piezoelectric behavior of nanocellulose have been published. The piezoelectricity of wood was proposed already in 1955 by Eiichi Fukada, but only very slightly studied since then. Here, we show the experimental evidence of significant piezoelectric activity of different types of nanocellulose films. Wood-based cellulose nanofibril (CNF) and cellulose nanocrystals (CNC) films, and bacterial nanocellulose (BC) films have been studied. The recent results suggest that nanocellulose is a potential bio-based piezoelectric sensor material.

Keywords: nanocellulose, bacterial cellulose, cellulose nanofibril, piezoelectric sensor, cellulose nanocrystal

1. Introduction

Cellulose, the most abundant biopolymer on earth, is generally obtained from plant sources. Cellulose-based nanomaterials, such as wood-based cellulosic nanofibrils (CNF) and cellulose nanocrystals (CNC) as well as bacterial cellulose (BC), are also known as nanocelluloses [1]. These interesting bio-based and renewable nanomaterials have potential applications in many different fields. Their nanoscale dimensions as well as a strong ability to form entangled porous networks make nanocelluloses suitable source materials for lightweight membranes, films and nanopapers. Importantly, these materials can be processed in aqueous media, which ensures low cost and high throughput manufacturing of functional devices for electronics [2–4], sensing [5], and optics [6]. Further, combining of nanocelluloses with water-processable carbon

nanomaterials, such as carbon nanotubes or graphene, open routes to fabricate flexible and disposable electronic devices, such as supercapacitors [7–9].

Figure 1 describes fabrication of CNF and CNC from wood cellulose fibers. In principal, wood-based nanocellulose is fabricated by cutting the wood cellulose fibers into smaller units until its dimensions become into nanoscale, referring to 'top-down approach'. CNF can be obtained, for example, from birch wood by sulfate digestion and subsequent bleaching, followed by miniaturization processing through a Masuko grinder and homogenization by microfluidizer [10].

On the other hand, BC films are produced through oxidative fermentation of polysaccharides by certain bacteria such as *Komagataeibacter xylinus*, which can be considered as 'bottom-up approach.' In comparison with wood-based cellulose, bacterial cellulose (BC) holds interesting properties such as biodegradability, high purity, water-holding capacity, and superior mechanical and structural properties. The free-standing films can be obtained from wood-based nanocellulose (CNF and CNC) by solution casting methods [11], while the BC films are produced as such as free-standing films.

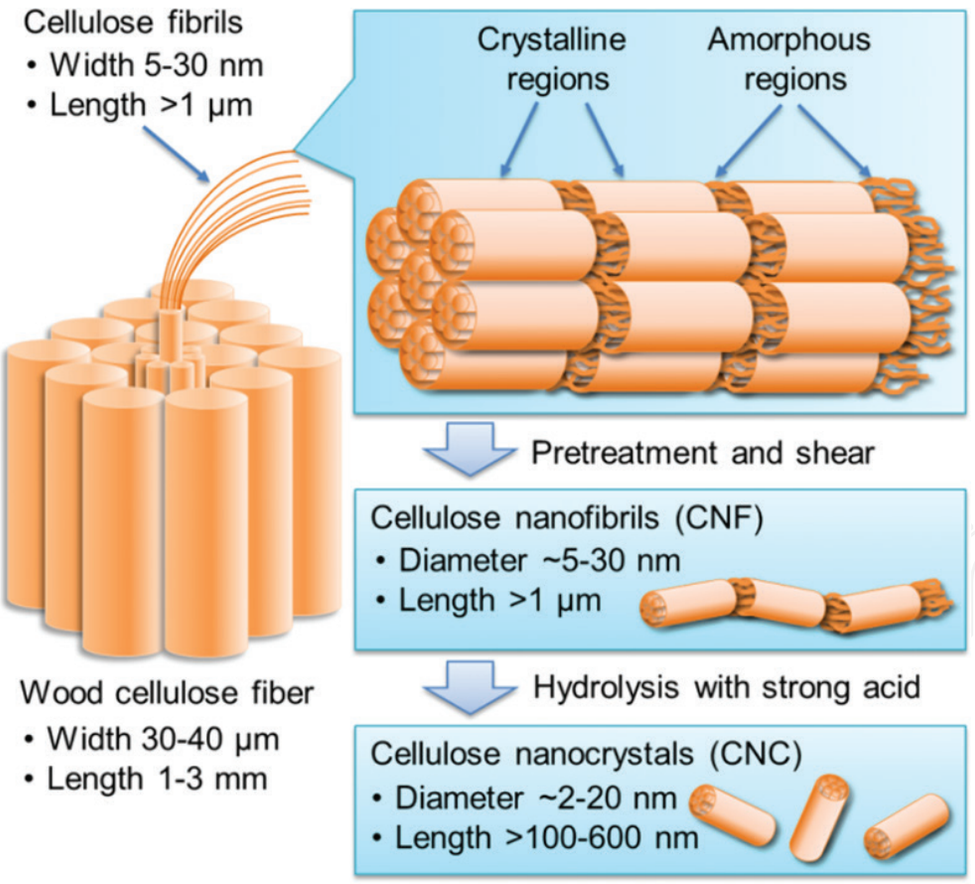

Figure 1. A schematic view of fabrication of nanocelluloses from wood cellulose fibers. The cellulose fibers are first cut up into microfibrils and finally after several processing steps into cellulose nanofibrils (CNF). Cellulose nanocrystals (CNCs) can be then obtained from CNF through acid hydrolysis. Nanocelluloses processing and structures are described in more detail in the literature [1].

In this chapter, we present the basics of nanocellulose as a piezoelectric material. Both the wood-based nanocellulose and bacterial nanocellulose films have been studied, and their sensitivities have been measured with a sophisticated sensitivity measurement setup. Finally, the results are presented, and the possibilities of nanocellulose as piezoelectric material are discussed.

2. Piezoelectricity of nanocellulose

The piezoelectricity of wood, that is, the change of electrical polarization in a material in response to mechanical stress, has been known for decades [12, 13]. The piezoelectric effect is highly enhanced if one considers the isolated crystalline building blocks of wood, CNCs [14, 15]. However, related issues have been covered in the scientific literature to a very limited extent, and only few recent reports discuss the experimental evidence of CNC piezoelectricity [14, 16].

The piezoelectricity is a phenomenon, where pressing of a piezoelectric film by an external force causes a change in charge distribution in the film. This change in charge distribution generates a measurable voltage between two electrodes placed on the top and the bottom of the piezoelectric film. The piezoelectric coefficient d_{mn} describes the charge density generated under a certain applied stress. The components of third-rank tensor with piezoelectric coefficients d_{mn} can be expressed using a 3 × 6 matrix, where m = 1, 2, 3 refers to the electrical axis and n = 1, 2, …, 6 to the mechanical axis [17]. The main axes 1, 2 and 3 correspond to length, width and thickness, whereas the shear around these axes is expressed by indexes 4, 5 and 6.

In the case of a single cellulose crystal, piezoelectric tensor d_{mn} can be derived from the symmetry of a cellulose crystal lattice, formed by unit cells of cellulose molecules ($[C_6H_{10}O_5]_n$) [13]. The cellulose possesses a monoclinic symmetry with space group of $C_2 \,||\, x_3$ having a following piezoelectric tensor:

$$d_{mn} = \begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & d_{25} & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & d_{36} \end{pmatrix}. \quad (1)$$

It is important to notice that this tensor is valid only for a single cellulose crystal. However, for an assembly of randomly aligned crystals, such as in a CNF film, the overall piezoelectric response results from the combination of the different coefficients. For example, in the case of wood, the arrangement of fibers and accompanied cellulose crystals have been shown to exhibit significantly reduced effective piezoelectric tensor:

$$d_{mn} = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \quad (2)$$

where $d_{14} = -d_{25}$ [12, 13].

3. Piezoelectric nanocellulose sensors

3.1. Nanocellulose film characterization

The nanocellulose films can be characterized with versatile methods. In our previous approaches, the nanocellulose films are characterized, for instance, by scanning electron microscopy and photometric stereoimaging to obtain information on the structure and surface topography of the films. In addition, dielectric properties such as relative permittivity and loss tangent, and ferroelectric hysteresis have been measured for CNF film [18]. Tensile stress tests have also been performed as well as crystallinity index measured for BC film [19].

The fabricated CNF films had a thickness of 45 ± 3 μm and density of 1.38 g/cm^3 [18]. For the BC films, the thickness of films varied from 4.8 ± 0.8 to 10.3 ± 0.6 μm depending on the film type. Different BC film types were produced in order to improve BC production titer and tailored alterations into the BC films [19]. To do this, we engineered *K. xylinus* to overexpress partial and complete BC synthase operon that encodes BC production activity. The changes in cell growth, end metabolite, and BC production titers obtained from the engineered strains (named pA, pAB and pABCD) were compared with the wild-type *K. xylinus* (named WT).

Figure 2 shows examples of SEM cross-section and surface view images of (a-b) CNF and (c-d) BC films. For the CNF film, the cross-section image reveals a layered a porous structure similar to reported elsewhere [11]. The surface view of the film (**Figure 2b**) shows a random

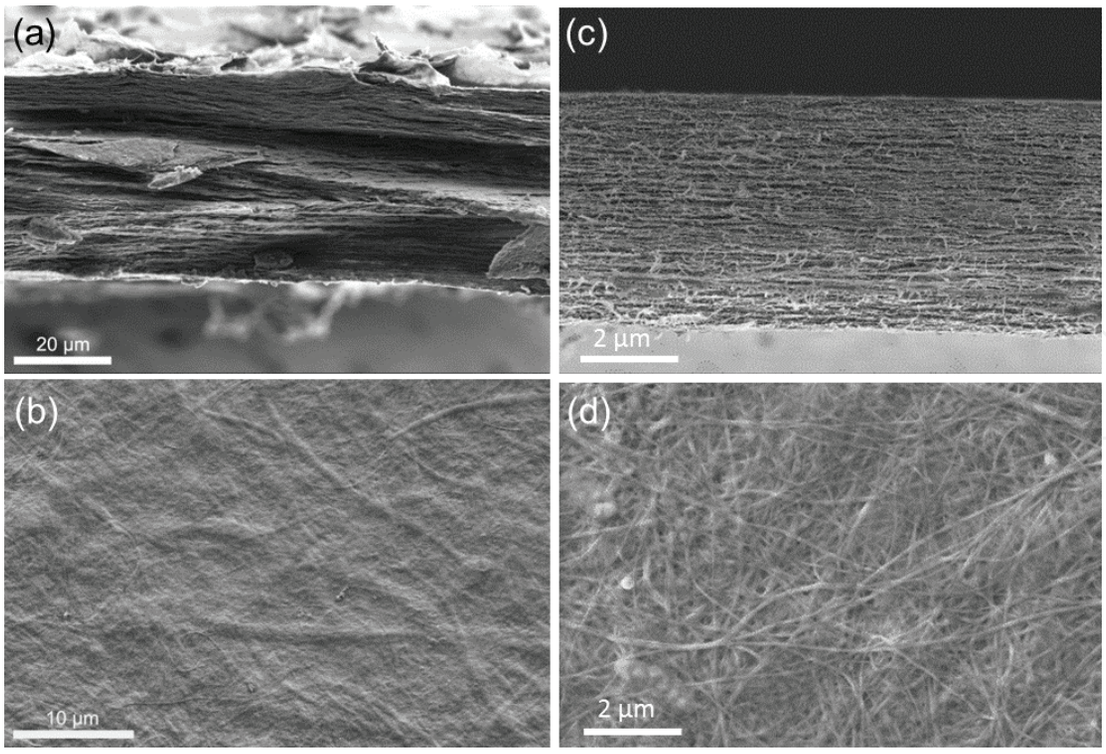

Figure 2. Scanning electron microscope cross-section and surface view images of typical (a, b) CNF [18] and (c, d) BC [19] films.

orientation of the nanofibrils. For the BC film, also a layered structure was found; however, the cross-sectional view of the films reveals that a layered fiber was more distinguished on the top surface of the films when compared with the bottom surface structure.

As the piezoelectricity is closely related to ferroelectricity of a material, the CNF films have been also analyzed by using a ferroelectric tester to measure the ferroelectric hysteresis of the film [18]. The results of ferroelectric hysteresis measurements are shown in **Figure 3**. The capacitance (or linear component in the polarization data) is dominant in the measurements at electric fields from 5 to 15 V/μm (**Figure 3a**). This shows that the CNF film has no significant ferroelectric hysteresis at low or moderate electric fields. However, a nonlinear behavior in polarization is detected at electric fields between 40 and 50 V/μm (**Figure 3b**). This suggests that the CNF film has a certain level of ferroelectric properties at high electric fields. A remanent polarization at 50 V/μm field was as small as 0.15 μC/cm^2.

The ferroelectric hysteresis measurements showed that the CNF film can withstand relatively high electric fields, despite its porous microstructure [18]. Small remanent polarization can be observed with electric fields above 40 V/μm which indicates that nanocellulose acts like an incipient organic ferroelectric material under a very high electric field [20]. The high coercive field in comparison with similar inorganic materials is a commonly known property of organic ferroelectric materials [20]. It should be remarked that at high electric fields, the electrostriction possibly resulting from the using of sandwiched measurements electrodes may also contribute to the polarization, while ferroelectricity is expected to be the dominant effect.

Importantly, our results show that the CNF films investigated in this work need a high electric field for poling and exhibit characteristics of ferroelectricity only above 40 V/μm. In that case, the observed ferroelectric (or piezoelectric) effect of the CNF films is expected to result from the permanent dipole moment of CNCs which possess a certain level of (nonintentional) orientation of dipoles resulting from the film fabrication process. However, the orientation of CNCs is not apparent from SEM images (**Figure 2**) due to limited resolution. There are recent related observations where experimental evidence of giant permanent electric-dipole moment in CNCs is reported [16].

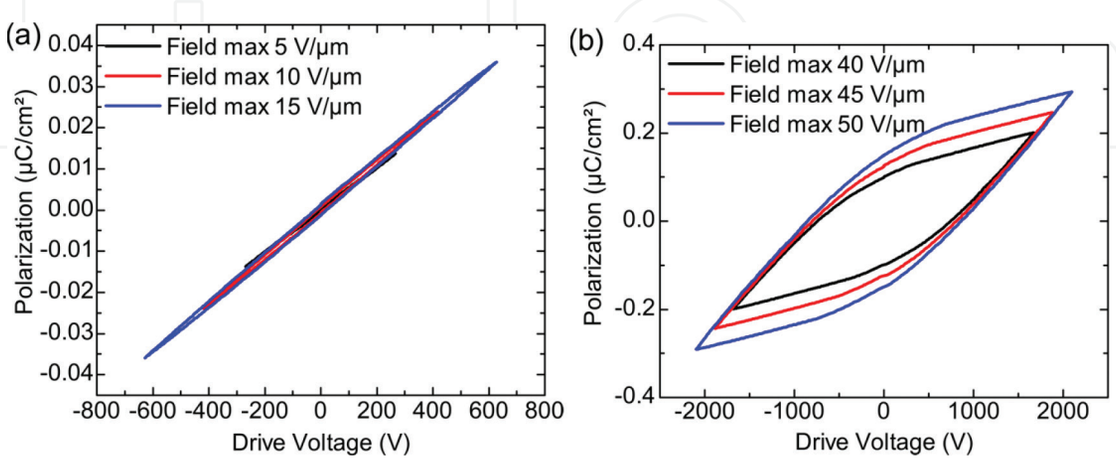

Figure 3. Polarization-voltage hysteresis curves for the CNF film at (a) 5–15 V/μm and (b) 40–50 V/μm electric fields at room temperature.

In addition, the relative permittivity and dielectric loss tangent for the CNF film have been determined [18]. At a 1 kHz frequency, the obtained relative permittivity of the CNF film was about 3.47, whereas the dielectric loss (tan δ) was about 0.011. The capacitance of the CNF film varied from 78 to 73 pF at frequencies from 100 Hz to 1 MHz, respectively. The average values for relative permittivity and dielectric losses were 3.38 and 0.071, respectively.

3.2. Sensor assembly

The sensors are typically assembled by sandwiching the nanocellulose film between two electrodes. In our approaches, the electrodes for the sensors were fabricated on 125-μm-thick polyethylene terephthalate (PET) substrate by e-beam evaporation. Typically, 100 nm thick layer of copper was evaporated through a shadow mask to provide electrode pattern. The nanocellulose film was then sandwiched between two electrodes, as illustrated in **Figure 4**. The connection to the measurement electronics was provided with crimp connectors (Nicomatic Crimpflex).

3.3. Piezoelectric sensitivity

The piezoelectric sensitivity measurement setup presented here has been previously used to evaluate piezoelectric response of a piezoelectric polymer film (polyvinylidene fluoride, PVDF)-based plantar pressure sensor [21, 22], PVDF sensors with solution-processed electrodes [23, 24],

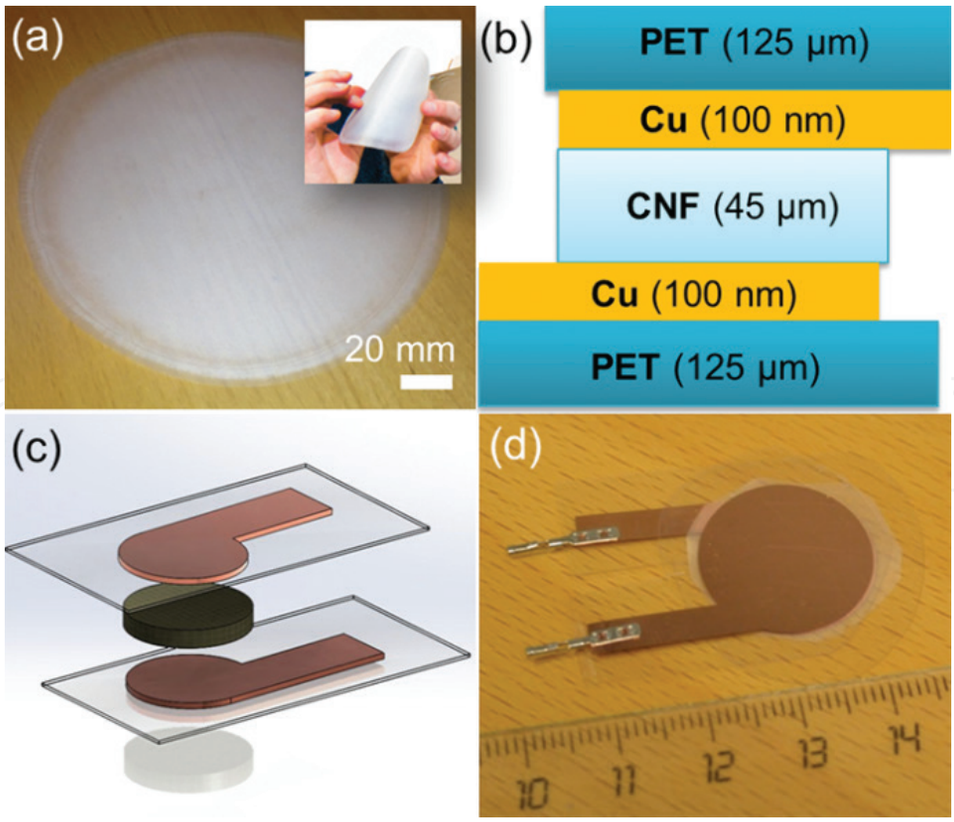

Figure 4. (a) Photographs of a fabricated self-standing CNF film and its bending robustness (an insert). (b, c) Schematic side view and (d) a photograph of assembled sensor.

ferroelectret film-based sensors [25] and nanocellulose sensors [18, 19, 26–28]. This section briefly describes the setup.

The Brüel & Kjaer Mini-Shaker (Type 4810) used in the setup generates a dynamic excitation force. A sinusoidal input signal for the shaker was provided from a function generator (Tektronix AFG3101). A high sensitive dynamic force sensor (PCB Piezotronics, model number 209C02) was used as a reference sensor to measure the dynamic excitation force applied to the piezoelectric sensor sample under test. The dynamic force 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-20 L) was used as a reference sensor to measure the static force applied to the sample by the shaker's piston. A pretension, which is producing static force, is required to hold the sample in place and to prevent the piston jumping off from contact during the measurement. A static force of approximately 3 N is typically used in the measurement setup.

The sensor sensitivity measured with the setup is closely related to the longitudinal piezoelectric coefficient d_{33}. The longitudinal d_{33} coefficient describes the electric polarization generated in the same direction as the stress is applied [29]. Thus, to measure the sensor sensitivity in normal force direction, the sensor was placed horizontally on the metal plate. The charge developed by the sensor was measured with a custom-made combination of a charge amplifier and a 16-bit AD-converter. **Figure 5a** illustrates the sensor sensitivity measurement setup.

A dynamic force of approximately 1.3 N (peak-to-peak), measured with the reference dynamic force sensor, was typically applied on the sample in the sensitivity measurements. This dynamic force was obtained by applying a dynamic, sinusoidal 2 Hz input signal of 1000 mV (peak-to-peak) to the shaker. To increase statistics, the sensitivity was measured from nine different positions on the sample, as shown in **Figure 5b**. The same positions were excited from both sides of the sample, resulting in a total of 18 excitations per sensor. Finally, 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.

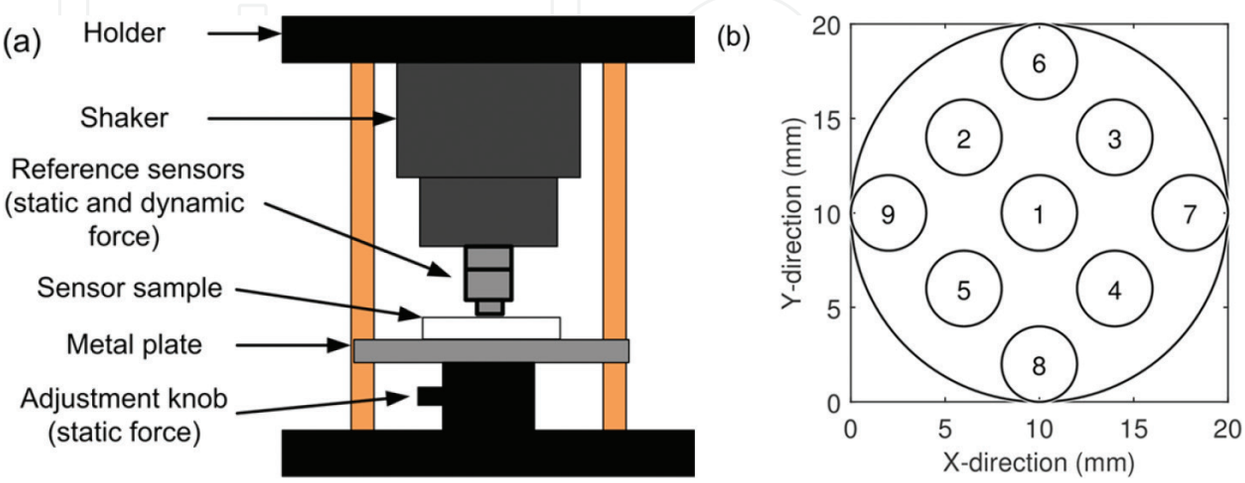

Figure 5. (a) Piezoelectric sensitivity measurement setup and (b) excitation positions for the sensitivity distribution measurements.

The same setup can also be used to measure the nonlinearity and hysteresis of the sensors. The sensor nonlinearity is determined by increasing the amplitude of the dynamic excitation force from approximately 0.1–5 N (peak-to-peak, frequency 2 Hz) and measuring the charge generated by the sensor. The sensor hysteresis error is defined as the deviation of the sensor output charge at a specified point of the excitation force when this point is approached from opposite directions (increasing or decreasing dynamic force) [30]. The excitation force range used was approximately from 0.7 to 2.8 N (peak-to-peak, frequency 2 Hz).

Table 1 summarizes the results of piezoelectric sensitivity measurements, shown as average values, obtained for the nanocellulose sensors and compared with reference PVDF sensors. The nonlinearity is defined as the maximum difference between the measured values and the fitted first degree polynomial, and the hysteresis as the maximum difference between the values measured when the excitation force was increased and decreased. The nonlinearity and hysteresis for CNF and reference PVDF sensors are further illustrated in **Figure 6**. **Figure 7** illustrates the BC and reference PVDF sensor charges as a function of increasing applied force, from which the nonlinearity presented in **Table 1** for BC can be obtained.

	Sensitivity (pC/N)	Nonlinearity (pC/N)	Hysteresis error (pC/N)
CNF [18]	4.7 ± 0.9	0.9 ± 0.5	0.9
CNF [27]	2.2 ± 1.5	—	—
CNC [27]	7.3 ± 2.5	—	—
BC WT [19]	16.8 ± 3.9	0.4 ± 0.1	—
BC pA [19]	7.3 ± 1.6	—	—
BC pAB [19]	5.0 ± 1.9	—	—
BC pABCD [19]	8.2 ± 5.5	—	—
PVDF [18]	27.5 ± 2.6	6.5 ± 3.8	0.9

Table 1. Summary of results for the sensor sensitivity, nonlinearity and hysteresis error measurements [18, 19, 27].

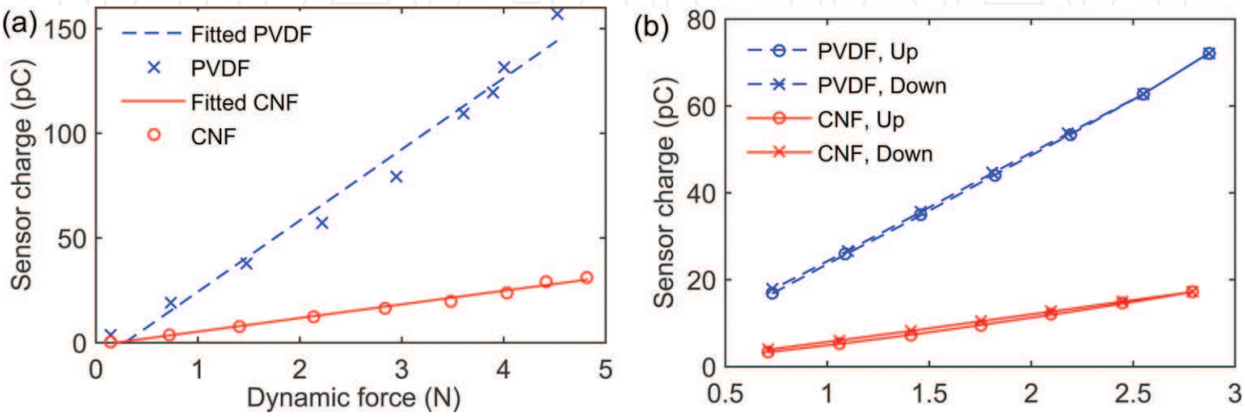

Figure 6. (a) Nonlinearity and (b) hysteresis curves measured for the CNF and reference PVDF sensors.

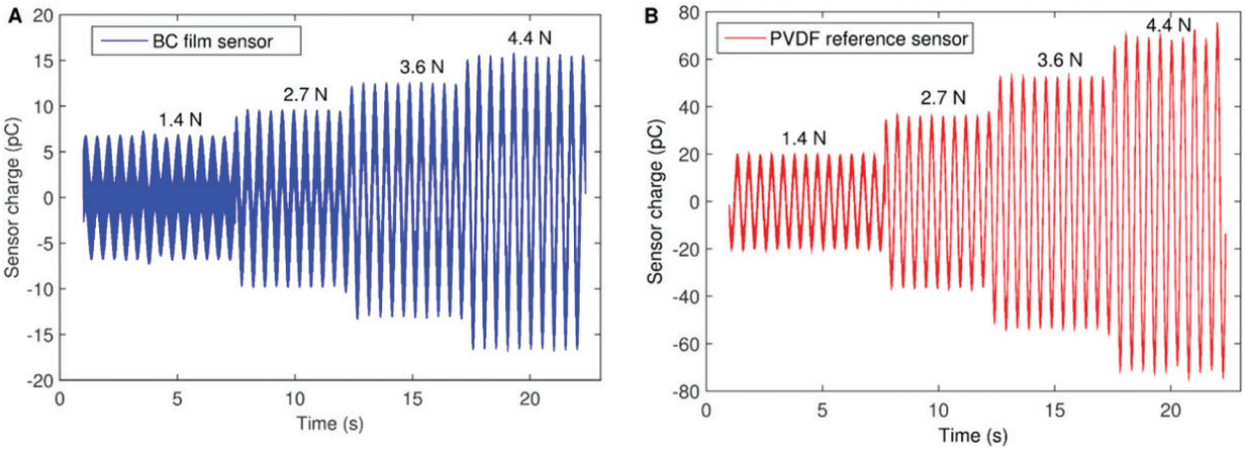

Figure 7. Piezoelectric responses of (a) BC film (produced by WT *K. xylinus*) and (b) commercial PVDF (fabricated using sandwiched PET-Cu electrodes as contacts) sensors under increased mechanical load.

4. Discussion

The SEM images of CNF and BC films revealed a layered structure, resembling that of a ferroelectret material, ElectroMechanical Film (EMFi), widely used in sensor applications [25]. As shown in **Figure 2**, both nanocellulose films have rather smooth surface having a randomly oriented fibrous structure. The density of CNF film (1.38 g/cm^3) is similar to other polymer films, 178 g/cm^3 for PVDF [31] and 0.33 g/cm^3 for EMFi [25].

The sensitivity of wood-based CNF film is around 2–5 pC/N [18, 27]. The sensitivity values measured for CNF sensors slightly vary, but the difference can be mainly explained by the different areas of the sensor films and different electrode materials used. The sensor structure was obtained by sandwiching the CNF film between the copper electrodes (deposited PET film), which may also affect the measured sensitivity values. This is related to the fact that a contact between the sensing material (CNF film) and the electrodes is not as good as in the case of electrodes fabricated directly on the sensing film surface. In comparison, less variation in sensitivity values was observed when electrodes were either screen printed or evaporated directly on PVDF film [23] when compared to PVDF sensors sandwiched between the PET-Cu electrodes.

The CNC sensors showed 2–4 times larger sensitivities than the CNF sensors ((7.3 ± 2.5) pC/N versus ((2.2 ± 1.5) pC/N) [27]. This result was expected since the CNC film consists of solely crystalline cellulose building blocks, whereas CNF contains both crystalline CNCs (cellulose II) domains and amorphous cellulose domains. However, the higher aspect ratio and the stronger ability for entanglement in the case of CNF in comparison with CNC whiskers may offer more versatile options over bare CNC as long as the synthesis of self-standing films and nanopapers is profitable. Despite the intuitively expected purely random alignment of CNCs inside the CNF films, the CNF films may exhibit piezoelectric nature due to the film fabrication process driven non-intentional alignment of CNCs [18].

The sensitivity of BC film varied from (5.0 ± 1.9) pC/N to (16.8 ± 3.9) pC/N, depending on the film type (see **Table 1**) [19]. Overall, the sensitivity values obtained in our approaches for

wood-based and bacterial nanocellulose are comparable with values reported by others. For instance, Mahadeva *et al*. reported successful fabrication of hybrid paper from barium titanate nanoparticles and wood cellulose fiber and demonstrated piezoelectric coefficient values of d_{33} = 4.8 pC/N [32]. When compared to commercial piezoelectric materials, quartz has rather low but stable piezoelectricity (d_{33} coefficient of around 2 pC/N) and among the poled polymers PVDF exhibits the highest piezoelectricity (d_{33} coefficient of around 25 pC/N) [33]. However, by improving the nanocellulose film fabrication process, also higher sensitivities for nanocellulose may be obtained. For instance, it has been suggested that regenerated CNC (cellulose II) has the apparent piezoelectric coefficient in the range 35–60 pC/N [15].

The level of crystallinity in cellulose films is considered to have a significant effect on the apparent level of piezoelectricity. Thus, we have measured the crystallinity indices (CI) of BC films using X-ray diffractometer (XRD) [19]. The CI of BC films varied depending on the used bacterial strains (film type) from 88.6 to 97.5%. Similar crystallinity indices were recently reported for wood-based cellulose [32]. The similarity in the XRD profiles reflects the presence of native cellulose I type nanocrystals in bacterial cellulose [34] as well as in plant-based cellulose from wood [32, 35] cotton. The alterations that we observed in piezoelectric sensitivities of CNF films and different BC film types cannot be understood solely based on XRD analysis and there are other factors involved, such as film thickness, film surface roughness, as well as elastic modulus and deformations in the films under applied force.

It should be noted that the nanocellulose films presented in this chapter were not optimized as a piezoelectric material and were not polarized or oriented. However, it cannot be ruled out that the film fabrication processes, including filtering and hot-pressing for CNF and fermentation process for BC, may have caused some alignment of the cellulose nanofibrils inside the thick film. The piezoelectric sensitivities shown here are expected to significantly increase after polarization of the films. In the poling process, an electric field is applied over the processed film for a certain period of time in order to generate piezoelectric properties. The poling (or another type of orientation) of the nanocellulose film is expected to lead into alignment of the crystalline regions inside the film, further leading to a remarkable increase in the piezoelectric effect due to the large dipole momentum of the crystalline components [14, 16]. The initial results of orientation of water processed CNF films, using DC voltage, suggest the potential of remarkably higher sensitivity values [18]. In addition, initial tests with BC films showed that polarization using DC voltage can enhance the piezoelectric sensitivity of the BC sensors. 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 piezoelectric sensitivity of nanocellulose films.

Even though both nanocellulose materials, both wood-based and bacterial nanocellulose, exhibit evident piezoelectric properties, also fundamental differences between these materials exist. First, the fabrication processes of the films are fundamentally different: the wood-based nanocellulose is fabricated from wood cellulose by cutting the fibers into nanoscale units, which can be considered as 'top-down approach', whereas the bacterial cellulose is grown through the oxidative fermentation by bacteria which can be considered as 'bottom-up approach'. Wood-based cellulose has certain limitations, such as multistep mechanical

processing to small dimensional constituents resulting in relatively low tensile strength and low flexibility of cellulose films. The most significant restriction in bacterial cellulose production is the slow and relatively expensive fabrication process.

5. Conclusions

In this chapter, we have summarized the recent results obtained with nanocellulose films and compared them with reference piezoelectric polymer film. Both wood-based CNF and CNC films and BC films were discussed here, and the main focus was in the piezoelectricity of these materials. In addition, the results related to microstructure, and dielectric and mechanical properties were discussed.

To conclude, the nanocellulose is an interesting renewable bio-based nanomaterial with potential applications in different fields, such as cell culturing medium, bio-plastic films, high surface-area membranes, or reinforcement material in composites. The more recent application for nanocellulose is its use as bio-based piezoelectric active material. Even though promising results related to the piezoelectricity of the nanocellulose have already been demonstrated, further work to improve the piezoelectric performance of the nanocellulose films is still needed. There are different ways to improve the piezoelectric performance of nanocellulose films by controlled orientation of crystalline areas of nanocellulose films, which will make it suitable for sensors, actuators and energy harvesting applications.

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