A Survey of Printable Piezoelectric Sensors

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***Abstract*— Availability of solution-processable piezoelectric sensor and electrode materials enable low-cost and high-throughput fabrication of fully printable piezoelectric sensors. Results obtained with piezoelectric polymer (polyvinylidenefluoride, PVDF), cellulose nanofibril (CNF) and cellulose nanocrystal (CNC) films as sensor materials are presented here. These sensor materials can be processed in solution and used in combination with printed electrodes to obtain full printability of the sensors. A commercial PVDF film and in-house fabricated CNF and CNC film are used as sensor materials. In addition, conducting polymer, graphene and carbon nanotube (CNT) based inks are used as solution-processable electrode materials in the sensors, whereas conventional metallic electrodes are used as reference electrode material. The sensor operation of the fabricated sensors is evaluated through piezoelectric sensitivity measurements. The sensor sensitivity measurements revealed mean sensitivities from 2 pC/N to 42 pC/N in transverse direction, depending on set of the sensor and electrode materials used.**

Keywords—printable sensor, piezoelectric polymer, cellulose nanofibril, cellulose nanocrystal, piezoelectric sensitivity

I. INTRODUCTION

The sensor and electrode materials presented in this study allow fabrication of all-printed sensors. Piezoelectric polymer (polyvinylidenefluoride, PVDF), cellulose nanofibril (CNF) and cellulose nanocrystal (CNC) films are potential printable piezoelectric materials, while conducting polymers, graphene and carbon nanotube (CNT) based inks are potential printable electrode materials. In addition to the piezoelectric sensors, these printable non-metallic materials enable fabrication of stretchable and transparent films, which has plenty of potential applications for example in transparent touch panels [1] and supercapacitors [2, 3].

The PVDF is a piezoelectric plastic material that generates a charge when it is mechanically deformed [4]. Thin and flexible sensors made of PVDF (and its copolymer PVDF-TrFE, a mixed composition of PVDF and trifluoroethylene) have a wide range of applications in the field of mechanical (e.g. pressure, acceleration, vibration and tactile sensors etc.), acoustics and infra-red-radiation sensors [5]. Other possible application areas include energy conversion [6] and medical measurements, e.g., measurement of vital signals such as heart rate and respiration [7-9].

Nanocellulose is an interesting bio-based nanomaterial, which has potential applications for example in electronics, material sciences and biomedical engineering [10, 11]. The cellulose nanofibrils (CNF) are nanoscale cellulose polymers which are either mechanically or chemically produced from e.g. wood-based cellulose. The CNF contains crystalline and amorphous regions and it can be further processed by e.g. chemical hydrolysis to produce cellulose nanocrystals (CNC) [11]. The piezoelectricity of wood has been first reported already in 1955 [12]. Further, since the piezoelectricity is resulting from the crystalline regions of the cellulose, the phenomenon is expected to be remarkably pronounced in the aligned nanocellulose films. However, there are only a few experimental studies of piezoelectric properties of nanocellulose in the literature [13, 14].

There are a few attempts to fabricate printable electrodes on piezoelectric PVDF films. Use of printable electrode materials enables mass manufacturing of the discrete and matrix PVDF sensors in a desired and customized shape and size. Metal electrode fabrication on PVDF material using ink-jet printing has been previously demonstrated by Kärki et al. [15]. The required high-temperature sintering step (150 °C) needed in metal electrode fabrication, however, caused limitations in sensor functionality. Also Seminara et al. used ink-jet printing to deposit patterned metal layers on PVDF material to realize scalable, bendable and low-cost sensing system for large area artificial skin [16].

An alternative way to fabricate the electrodes is to use solution-processable non-metallic electrode materials to overcome the problem concerning the temperature sensitivity of the PVDF material [8]. Lee et al. fabricated flexible organic film speakers with ion-assisted-reaction (IAR) treated PVDF as the active layer and PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) materials with various organic solvents, indium tin oxide (ITO) or copper (Cu) as the electrodes [17]. Schmidt et al. developed both airbrush and inkjet printing methods for applying PEDOT:PSS electrodes to PVDF sheets [18]. Tuukkanen et al. demonstrated the use of various printable inks as electrode materials, e.g. CNT-cellulose nanocomposite ink, PEDOT:PSS ink, carbon ink and silver flake ink [8, 9]. More recently, Rajala et al. studied the sensor characteristics of PVDF sensors with solution-processable electrode materials, i.e. two graphene-based printable inks [19]. Rajala et al. also developed versatile methods for systematic and comprehensive characterization of solution-processed electrodes [20].

Also, some attempts to manufacture all-printed piezoelectric polymer film sensors have been made. Zirkl et al.

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demonstrated an all-printed matrix sensor array using P(VDF-TrFE) as the sensor ink [21]. The bottom electrodes for the sensor array were screen-printed on top of a PET (polyethylene terephthalate) sheet that was used as a substrate; conductive polymer PEDOT:PSS was used as electrode ink. The PVDF-TrFE sensor ink was screen-printed onto the PEDOT:PSS bottom electrodes and the fabrication was finalized by screen-printing of carbon or PEDOT:PSS top electrodes. Also Rendl et al. have used printable piezoelectric PVDF-TrFE film as an active layer in their sensors and conductive polymer (PEDOT:PSS) and carbon as electrode materials [22]. Besides the PVDF-TrFE, also other piezoelectric sensor materials than the PVDF film have been used as an active layer in the printed sensors. Watanabe et al. reported a printed pressure sensor array based on poly(amino acid)-based piezoelectric elements and silver paste ink as the electrodes, fabricated on a polyimide sheet as a substrate [23]. Almusallam et al. studied the use of PZT-polymer composites for screen-printed piezoelectric shoe-insoles [24].

In this study, PVDF and nanocellulose films are used as piezoelectric sensing materials. Even though the piezoelectricity of wood has been known for decades, to our knowledge, the piezoelectric measurements of nanocellulose films have not been reported in the literature before us. In our previous study piezoelectric sensitivity of CNF film sensors was measured [25]. A new set of measurements made with CNF and CNC sensors with copper electrodes are presented in this paper. The piezoelectric sensitivity measurement results obtained earlier with the PVDF sensors with solution-processed electrodes [19, 20] are collected here and discussed. The PVDF film used in this study can be replaced by a commercially available PVDF-TrFE, which is a printable piezoelectric sensor material. As a combination of these studies, fully printed piezoelectric sensors can be obtained.

II. MATERIALS AND METHODS

A. Piezoelectric polymer PVDF

Polyvinylidenefluoride (PVDF) is a semicrystalline piezoelectric material having a solid and homogenous structure. During the manufacturing process the polymer is stretched uniaxially and exposed to high electric field to generate piezoelectric properties. The manufacturing process of PVDF material is described e.g. in references [4] and [26].

The change in film thickness due to an external force compressing the film generates a charge and thus, a voltage to appear at the electrodes. The piezoelectric coefficient d_{mn} is related to the electric field produced by a mechanical stress; the first suffix m = 1, 2, 3 refers to the electrical axis and the second n = 1, 2, … , 6 to the mechanical axis [4]. The main axes 1, 2 and 3correspond to length, width and thickness and the shear about these axes is represented by 4, 5 and 6 [4]. The d_{mn} is a third-rank tensor conventionally expressed in terms of 3 × 6 matrix, however, crystal symmetry reduces the number of independent piezoelectric coefficients [27]. For the PVDF the matrix can be written as [13]

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

The unmetallized 28 μm thick PVDF film used in this paper was manufactured by Measurement Specialties Inc. (Hampton, VA, USA).

B. Cellulose nanofibrils and cellulose nanocrystals

The aqueous CNF dispersion was obtained by a mechanical homogenizing process using a protocol described in more details in [5]. In this process, the wood based cellulose starting material underwent six passes in microfibrillator equipment. The CNF film was then fabricated from obtained bleached birch cellulose mass. The 70-μm-thick CNF films were prepared by pressure filtering (15-30 min) followed by pressing and drying in hot-press at 100 °C for 2 h. The same CNF films were previously used in [25].

The aqueous CNC dispersion was then fabricated from CNF dispersion by chemical hydrolysis using sulfuric acid. Preparation has been explained in more detail in [14].

C. Electrode materials

The electrodes for CNF and CNC film sensors were made from a tin-plated copper tape. The tape was folded so that the metal side was in contact with the sensor material. The electrode width was 5 mm.

A manual airbrush (Phene-ink) and manual bar-coating (Vor-ink and CNT-ink) were used for deposition of solution-processed electrodes on PVDF film. The electrode where subsequently deposited on both sides of the PVDF film. The preparation of solution-processed electrodes is described in details in [19] and [20].

D. Sensor assembly

Four sensor types are reported in this study: 1) PVDF film with reference copper electrodes, 2) PVDF film with solution processed electrode materials (two graphene and one CNT -based inks), 3) CNF film with metal electrodes and 4) CNC film with metal electrodes. Fig. 1 shows examples of the photographs of the PVDF sensors with a) Phene-ink, b) Vor-ink and c) CNT-ink sensors. Fig. 2 presents the structure of the CNF and CNC sensors and an example of a NFC sensor with copper electrodes.

The structure of the sensor types 1 and 2, in which the electrodes are deposited directly on PVDF film, is presented in Fig. 2a. The sensor types 3 and 4 were assembled by sandwiching the piezoelectric film between two metal electrodes as shown in Fig. 2b. A two-sided adhesive film was used to keep the assembly together. The connections to the electrodes were made via crimp connectors (Nicomatic Crimpflex) shown in Fig. 2c.

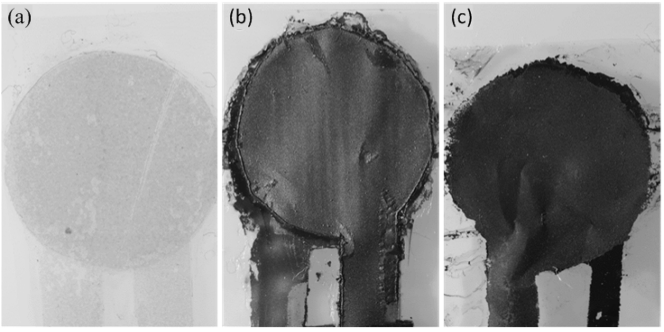

Fig. 1. Examples of the photographs of PVDF sensors with (a) Phene-ink, (b) Vor-ink and (c) CNT-ink electrodes. [20]

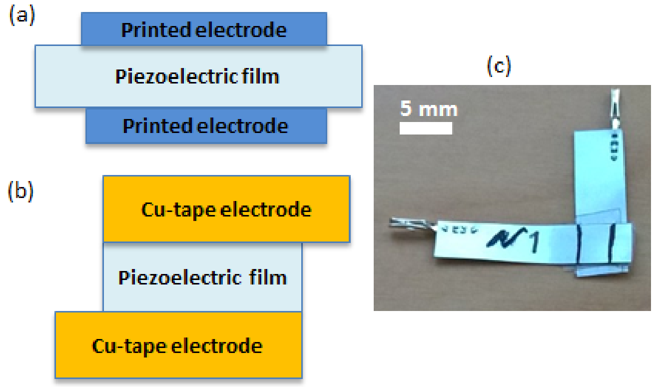

Fig. 2. A schematic side-view of (a) a sensor with solution-processed electrodes and (b) a sandwiched sensor. (c) An example of assembled sensor.

E. *Sensor testing*

The piezoelectric sensitivity measurement setup has been previously reported [19, 28]. Briefly, the Brüel & Kjaer Mini-Shaker Type 4810 was used in the sensor sensitivity measurements. The shaker generates a dynamic excitation force. A commercial high sensitivity dynamic force sensor (PCB Piezotronics, model number 209C02) was used as a reference sensor for the dynamic excitation force. 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 during the measurement. Fig. 3 shows the sensor sensitivity measurement setup in details.

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}. To measure the sensor sensitivity in transverse direction, the sensor was placed horizontally on the metal plate (see Fig. 3). 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. With the PVDF sensors, the excitation was done by applying the force to nine different positions on the sensor, one at a time [19, 20]. With the CNF and CNC sensors only preliminary sensitivity measurements were done: the force was applied in the middle of the sensors and 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. The same

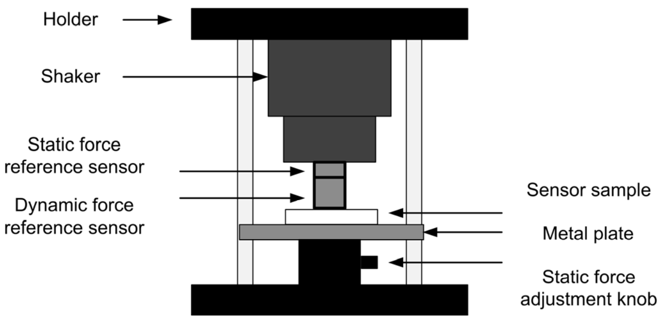

Fig. 3. The sensor sensitivity measurement setup.

measurement principle has been previously used to evaluate the sensor sensitivities of PVDF sensors [8, 9, 15, 19, 20].

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.

III. Results

The operation of two CNF and two CNC sensors were evaluated here with sensitivity measurements. Table 1 presents the results. The values are presented as mean sensitivities ± standard deviations for each sensor side. The average sensitivity values for the CNC sensors was (7.3 ± 2.5) pC/N and for the CNF sensors (2.2 ± 1.5) pC/N.

Rajala et al. have previously measured the sensitivities for PVDF sensors with solution-processable graphene and CNT-based electrodes [19, 20]. Vacuum evaporated copper electrodes were used as in reference sensors. Table 2 collects the results obtained with PVDF sensors.

TABLE I. SENSITIVITY MEASUREMENT RESULTS FOR CNF AND CNC SENSORS.

Sensor name	Sensitivity, side 1 (pC/N)	Sensitivity, side 2 (pC/N)
CNF-1	4.4 ± 0.7	0.8 ± 0.2
CNF-2	2.0 ± 0.5	1.6 ± 1.2
CNC-1	7.7 ± 1.4	4.5 ± 2.0
CNC-2	7.9 ± 2.5	9.3 ± 1.7

TABLE II. SENSITIVITY MEASUREMENT RESULTS FOR PVDF SENSORS WITH DIFFERENT ELECTRODE MATERIALS [19, 20].

Sensor name	Sensitivity(pC/N)
PVDF + Cu ref.	31.1 ± 1.4
PVDF + Phene-ink	26.2 ± 2.2
PVDF + Vor-ink	30.2 ± 1.6
PVDF + CNT-ink	42.2 ± 6.0

IV. DISUCUSSION AND CONCLUSION

The average sensitivities of the PVDF sensors (26-42 pC/N) were remarkably larger than the average sensitivity of the CNF and CNC sensors (2-7 pC/N), depending on the electrode material used. Very recently, Rajala et al. reported sensitivity values from (5.2 ± 1.0) pC/N to (7.0 ± 3.7) pC/N for CNF sensors having 15 mm diameter circular shape evaporated Cu-electrodes on PET [25]. The difference of CNF sensor sensitivity observed in this and in the previous study can be explained by the different area of the sensor film and different electrode material used. Here, the CNC sensors showed 2-4 times larger sensitivities than the CNF sensors.

The CNF and CNC films used here were in their native state, as fabricated, and not polarized, which can explain relatively low piezoelectric sensitivities due to randomly oriented crystalline regions in the films. The piezoelectric sensitivity of the CNF and CNC films is expected to remarkably increase after polarization of the films. Polarization in this case results in orientation of the crystalline nanocellulose regions inside the film. Our first experiment performed with the drop-casted CNF showed that the polarization enhances the piezoelectric sensitivity of the film. About 50-µm-thick CNF film was first drop-casted on Cu-PET bottom electrode and then Cu-PET top electrode was assembled on top with adhesive glue. The CNF film sensor showed no noticeable piezoelectric sensitivity after the assembly. Next, the polarization of the CNF film was performed by applying 8 V/µm electric field for 50 min over the film. After the polarization the sensor showed a piezoelectric sensitivity as high as about 11 pC/N.

These results suggest that PVDF and nanocellulose as sensor materials and nanocarbon based solution-processable electrode materials are suitable for piezoelectric sensors. Since the PVDF material used in this study can be replaced by PVDF-TrFE, which is a printable piezoelectric sensor material, the full printability of the sensors can be obtained. The use of the solution-processable sensor and electrode materials enables low-cost and high throughput mass manufacturing of sensors that can be used in various fields of applications in material science, electronics and biomedical diagnostics.

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