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Piezoelectric sensitivity of a layered film of chitosan and cellulose nanocrystals

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Abstract

Free-standing biodegradable films were fabricated by mixing cellulose nanocrystals and nanofibers with a water-based chitosan solution. The piezoelectric sensitivity of the films was measured to find out their suitability in sensing and actuation applications. Also their structure was evaluated with scanning electron microscopy. Our initial results show that a simple solvent casting method can be used to prepare films with varying piezoelectric properties. The composite films of chitosan and cellulose nanocrystals were noticed to have a phase-separated layered structure, resulting in an interesting side-dependent piezoelectric response. Moreover, the sensitivity values of plain chitosan were close to those of a non-degradable commercial sensor material polyvinylidene fluoride. The fabrication process has to be studied further to control and optimize the structure and piezoelectric properties of the films.

Keywords: Nanocellulose; Chitosan; Piezoelectric films

1. Introduction

Bio-based functional materials, such as nanocellulose \cite{1}, have raised a lot of interest lately due to their renewable nature, low cost, and biocompatibility. Wood is known to have piezoelectric properties based on the highly crystalline cellulose chain assemblies \cite{2}, but experimental evidence of the piezoelectricity of cellulose nanocrystals (CNC) was reported only recently \cite{3,4}. Cellulose nanofibrils (CNF), produced by mechanically homogenizing cellulose fibers, contain crystalline and amorphous regions. CNC are made by removing the amorphous regions by hydrolysis \cite{1}. We have earlier reported a significant piezoelectric response of both CNF \cite{5,6} and CNC \cite{7} film based sensors.

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Chitosan has also been studied earlier for its piezoelectric behavior [8]. It is a fibrous polysaccharide that can be produced by deacetylation of chitin, a structural element in the shells of sea crustaceans and insects. As the degree of deacetylation reaches 50%, the resulting polymer is called chitosan which, unlike chitin, is soluble in dilute acids. [9] This allows its mixing with nanocellulose in aqueous media. Along with the molecular weight (MW) of chitosan, also its degree of deacetylation affects chitosan material properties. Our aim was to see if a solvent casting method can be used to prepare chitosan-nanocellulose films with piezoelectric properties suitable for sensor or actuator applications.

2. Materials and methods

2.1. Film preparation

The chitosan solution was prepared by weighing 1.00 g of chitosan (FMC Biopolymer, nowadays FMC Health and Nutrition, Norway) with an MW of 460 000 g/mol and a degree of deacetylation of 91% into 99 ml of distilled water, stirring well and then adding 1 ml of 90% lactic acid (VWR Chemicals, Belgium) to dissolve chitosan. The CNF dispersion was obtained from bleached birch cellulose mass with a mechanical homogenization process (details in [10]). Its chemical hydrolysis in sulphuric acid produced solutions of acidic (pH 2.9) cellulose nanocrystals (CNC1) and neutralized cellulose nanocrystals (CNC2) obtained by a 0.5 M NaOH treatment. Table 1 presents the film recipes.

<table>
<thead>
<tr>
<th>Membrane compositions</th>
<th>Sensors cut from the resulting film</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 ml Chitosan (1.0 wt-%)</td>
<td>S1, S2, S3, S4</td>
</tr>
<tr>
<td>10 ml Chitosan + 10 ml CNC1 (1.39 wt-%)</td>
<td>S5, S6, S7, S8</td>
</tr>
<tr>
<td>10 ml Chitosan + 10 ml CNC2 (0.9 wt-%)</td>
<td>S9, S10, S11, S12</td>
</tr>
<tr>
<td>10 ml Chitosan + 8 ml CNF (1.35 wt-%)</td>
<td>S13, S14, S15, S16</td>
</tr>
</tbody>
</table>

The control film was made from 20 ml of chitosan solution (pH 3.0). For the composite films, 10 ml of CNC1 and CNC2 dispersions, but only 8 ml of the high viscosity CNF gel were used with 10 ml of chitosan. The solutions were mixed well, cast onto Petri dishes and dried at room temperature. Next, the films were neutralized from residual acids with 1 M solution of NaOH after which they were peeled off. The pH was balanced by rinsing the films with distilled water. Finally, the membranes were dried under tension using rubber bands and glasses as seen in the inserts in Fig. 1.

The structure of the films was evaluated using scanning electron microscope (SEM). To obtain cross-sectional SEM images, the films were immersed briefly into liquid nitrogen before cutting, which provides a clean edge.

2.2. Assembly of piezoelectric sensors

The fabricated films were cut into four equal segments. Piezoelectric sensors were assembled by placing the film pieces between two copper electrodes (diameter 15 mm with a circular shape), obtained by evaporating 100 nm of copper on polyethylene terephthalate (PET) substrate using a shadow mask. Crimp connectors (Nicomatic Crimpflex) were used to provide the sensitivity measurement connections.
2.3. Sensitivity measurements

The piezoelectric sensitivity of the sensors was measured using an in-house built setup, described in detail in [11]. Briefly, a shaker (Brüel & Kjær Mini-Shaker Type 4810) provided a dynamic excitation force (1.4 N peak-to-peak; frequency 2 Hz) to the sensor lying on the metal plate. A commercial high sensitivity dynamic force sensor was used as a reference for the excitation force. The measurement was repeated three times per side, resulting in six excitations per sensor. After each measurement, the sensors were re-positioned on the metal plate. The piezoelectric sensitivity (unit pC/N) was obtained by dividing the sensor-generated charge by the force of the dynamic force sensor.

3. Results and discussion

The optical microscopy images in Fig. 1 show the presence of nanocellulose in the composite films. The similarity of the composite films containing CNC1 and CNC2 can also be seen, while the film with CNF seems more uniform. The SEM image in Fig. 2 reveals that the chitosan + CNC1 film is clearly structured in two different phases with nanocellulose crystals forming a layer at the bottom of the film. Both CNC types mix easily with the chitosan solution, but might sediment in the drying phase. We suggest that this layering leads to a side-dependent piezoelectric sensitivity (with potential applications in e.g. bimorph micro-electromechanical systems), observed clearly in chitosan + CNC1 but also in chitosan + CNC2. It might arise from the different piezoelectricity of the materials, but also elasticity differences can affect the sensitivities. The chitosan + CNF forms a structurally uniform film.

![Figure 2: Cross-sectional SEM images of (a) plain chitosan, (b) chitosan + CNC1, (c) chitosan + CNC2 and (d) chitosan + CNF films. The inserts in (a) and (b) show the close-up from the chitosan and CNC areas, respectively. The arrows indicate the surfaces of the films.](image)

The measured sensitivities are shown in Fig. 3 with the sensor structure in the insert. The average sensitivities for each sample type (chitosan, chitosan + CNC1, chitosan + CNC2 and chitosan + CNF), presented as mean sensitivity ± standard deviation for each sensor side, were (21.03 ± 6.80) pC/N, (11.23 ± 6.76) pC/N, (8.74 ± 3.66) pC/N and (5.99 ± 2.91) pC/N, respectively. The results support the uniformity of the chitosan + CNF film. Still, this film type had the lowest piezoelectric sensitivity values. Plain chitosan has a higher sensitivity (even above 25 pC/N) than any
of the composite films. This value is close to that of a commercial sensor material polyvinylidene fluoride (PVDF) which has a sensitivity of about 30 pC/N [11]. Sensors from plain CNF have been reported to have sensitivities of 5-7 pC/N [5,6] while another study reported CNC sensors having 2-4 times larger values compared to CNF [7].

To conclude, the piezoelectric behavior depends strongly on the chosen chitosan-nanocellulose combination. Especially, by mixing chitosan and CNC, films with a highly side-dependent response can be made. This effect was not seen in the chitosan + CNF film, which had the lowest piezoelectric sensitivity values. The highest measured values were obtained with plain chitosan. The piezoelectric properties of different films seem promising for many sensor and actuator applications. However, all the studied films show variability in sensitivity values between individual sensors, indicating a need for optimizing the fabrication parameters like pH, solution concentration and mixture composition. Hence, further studies are needed to optimize the process and thereby the properties of the films.

References