3D-printed Net-Structured Porous Capacitive Sensors Based Upon Silver-Coated-Glass Fiber-Filled Polymer Composites

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Abstract. Flexible sensors modified with microstructures possess excellent high sensitivity and ultralow detection limit. In this study, silver-coated-glass fiber-filled silicon rubbers with their net structures were 3D printed and designed. Porous structures were introduced through the multi-layer printing of the net structure. The high conductivity of the printed composites originated from the conductive fillers, which assure the composites applied in circuit connection. Flexible capacitive sensors were further fabricated with the porous composites as electrode layers and the flat polyethylene terephthalate film as the middle dielectric layer. The prepared capacitive sensors owned an excellent sensing property to detect ultralow load with a sensitivity of 0.0666 kPa\textsuperscript{-1}. The evolution of the porous structure was schematically described, when the capacitive sensors were compressed. The net-structured porous capacitive sensors fabricated with 3D process would inspire us a new branch in the printing electronics.

Keywords: Conductive silicon rubber; Flexible sensor; 3D printing; Microstructure

1. Introduction
Flexible sensors have attracted tremendous research interests with their bright potential application in wearable device, human-machine interaction [1-3]. Flexible sensors, with various sensing mechanism, are roughly categorized into piezoresistive, capacitive, piezoelectric, and field effect transistor [4]. Flexible capacitive sensors have attracted ever-increasing attention with their fast dynamic response, excellent stability and low hysteresis compared with other types of sensors.

Microstructures have been introduced into flexible sensors to improve the sensitivity of sensors to small load, with which the pressure sensors can be compressed more readily with smaller pressure [4-5]. The microstructured sensors are usually molded with rough surface like plant leaves, textile, rough molds, etc. [4-6]. However, the uncertainty of some rough surfaces cannot guarantee the repeatability of the microstructure further leading to the uncertain properties of the sensors.

The rapid development of advanced technology enriched the preparation methods of fabricating flexible sensors, the 3D printing technology of conductive rubber have been developed in the design of flexible sensors [1,7]. The more important, repeatable microstructure can be therefore designed with the repeatable preparation method of 3D printing, under constant printing pathway and parameters. The electrical conductivity always affect the stability of sensing property, and the silver-based fillers...
will highly reduce the resistance of the filled composites further improve the sensing stability, the filler of silver-coated-glass fiber is therefore been chosen as filler in this study.

Herein, silver-coated-glass fiber-filled silicon rubbers with their net structures were 3D printed, the printed composites were further fabricated into capacitive sensors with the porous composites as electrode layers and the flat polyethylene terephthalate film as the middle dielectric layer. The capacitance response of the sensors to pressure was characterized, and the microstructure was observed. Finally, the evolution of the porous structure, when compressed was schematically described.

2. Experimental

2.1. Materials

The matrix rubber (methyl vinyl rubber) and vulcanizing agent were obtained from Blue-star Silicone Co. Ltd. Shanghai, China. The filler of 45 wt% silver-coated-glass fiber was filled into the matrix, which was supplied by Potters Industries Inc., America, and the nominal length was 130 μm and diameter was 15 μm.

2.2. Preparation and the Fabrication of the Capacitive Sensor

Conductive silicon rubbers filled with 45 wt% silver-coated-glass fiber were printed with four layers of net structures according to the process in our previous study [1]. The printing pathway and the net structures can be schematically depicted as the figure 1. The printing paths in each layer are parallel and not overlapped with each other, the printing pathway for each layer is perpendicular to the near layer, further resulting the net structure in the top view of the sensors. The void between layers and paths are dedicated as the porous structure of the four-layered sensors.

The printed composites were then pre-cured at 150 °C for 10 min in an oven. Capacitive sensors, in a dimension of 10mm x 10mm, were finally combined with the porous composites as electrode layers and the flat and uncompressed polyethylene terephthalate film as the middle dielectric layer, where the thickness of the electrode layers and dielectric layer is 1mm and 0.05mm, respectively.

![Figure 1. Schematic of the net structure for the printing of multi-layers.](image)

2.3. Characterization

Metallographic microscope (BX51M) and scanning electron microscope (S-3400 N) were used to observe the microstructures. LCR bridge (Tonghui TH-2830) used to measure and record the capacitance response of the microstructure sensors to compressive loads (0–200 kPa). The sensitivity of the capacitive sensors to compressive loads can be estimated with the following equation:

$$S = \frac{d(\Delta C/C_0)}{dF}$$
where $C_0$ is the initial capacitance free of load, $\Delta C$ is the capacitance change, and $F$ denotes the magnitude of the applied compressive stress.

3. Result and Discussion

3.1. Microstructures

Microscopic appearances of the printed composites are shown in figure 2. It can be visually observed that the print paths in different layer formed the net structures in the top view of the printed composites, which is in accordance with our design. From the side section of the printed composites, the porous structures regularly distributed around the multi-layered composites, further assure the printed composites more easily-compressible and more sensitive to pressure.

![Schematic of the net structure for the printing of multi-layers.](image)

(a) Top view: net structure. (b) Side section: porous structure.

**Figure 2.** Schematic of the net structure for the printing of multi-layers.

3.2. Conductivity

The inherent conductivity of printed composites was tested by a multimeter according to standard CEPS-0002, the four-layered specimens for test with a dimension of 50 mm $\times$ 10 mm $\times$ 1 mm. Volume resistivity of the printed composites is calculated as $0.36 \pm 0.07 \, \Omega \cdot \text{cm}$, which indicate the printed composites own excellent electrical conductivity with their electrical resistance about $10$–$20 \, \Omega$ of a strip composite. The printed composites are therefore capable to serve as wire to connect into circuit, which is photo demonstrated in figure 3. The lamp bead connected with the printed conductive-composites, can maintain bright under a DC voltage of 4 V.

![Photo demonstration of the printed composites served as circuit connection.](image)

**Figure 3.** Photo demonstration of the printed composites served as circuit connection.
3.3. Capacitance Response to Compressive Load
As shown in figure 4. The capacitive sensors were fabricated with the porous composites as electrode layers and the flat and uncompressed polyethylene terephthalate film (0.5mm) as the middle dielectric layer.

![Figure 4. Picture of a microstructured capacitive sensor.](image)

The initial capacitance value of the capacitive sensors is 5.1 pF. The capacitance response of the microstructured sensors to pressure are described in figure 5. It is clear that the response curve can be roughly divided into two stages around the pressure value of 20 kPa. The capacitance increases sharply in the pressure region of 0~20 kPa, and slowly increases in 20~200 kPa. The corresponding sensitivity in the two stages are therefore various, more sensitive to small load with the sensitivity of 0.0666 kPa\(^{-1}\) and lower sensitivity of 0.0045 kPa\(^{-1}\) in the second stage. The curve is related to the microstructure evolution when compressed. The curve in figure 5a behaves linearly in the 0~7 kPa and the figure 5b are hence derived from the region. What should be highlighted, our microstructured capacitive sensor not only posses a wide working range of 0~20 kPa, but also capable to detect ultralow load 0~1 kPa. The microstructured capacitive sensor even can recognize of the pressure increase from 0.1 kPa to 0.2 kPa.

![Figure 5. Capacitance response of the microstructured sensors to pressure.](image)

(a) 0~180 kPa.  
(b) 0~7kpa

3.4. Evolution of Porous Structure when Compressed
The capacitance response behavior can be attributed to the evolution of the microstructures of the sensor, and it is schematically demonstrated in figure 6. The capacitance (C) of a microstructured sensor is inversely proportional to the distance (D) between the two electrode layers. The porous structures in the electrode layers keep remain when free of load. The more compressible holes were mainly compressed at the pressure of 0~20 kPa, and the matrix only slightly deformed, the capacitance increases sharply in this region, accordingly. When further compressed (> 20 kPa), the porous
Structures are almost completely compressed, and the main deformation is the compression of the matrix, the response curve therefore turn flat.

**Figure 6.** Evolution of the microstructure of the capacitive sensor when compressed.

4. **Conclusion**

In summary, conductive silicon rubbers with net-structure and porous structure were 3D printed, the printed composites were further fabricated into capacitive sensors with the porous composites as electrode layers and the flat polyethylene terephthalate film as the middle dielectric layer. The porous structure guarantees the prepared capacitive sensors with an excellent sensing property, in which the sensors are capable to detect ultralow load with a sensitivity of 0.0666 kPa$^{-1}$. The evolution of the porous structure was schematically responsible for the capacitance response to compress load when the capacitive sensors were compressed. The net-structured porous capacitive sensors fabricated with 3D process would inspire us a new branch in the printing electronics.

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