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ADDITIVE MANUFACTURING OF PHOTOCURABLE PVDF-BASED CAPACITIVE SENSOR

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ABSTRACT

The demand for the capacitive sensor has attracted substantial attention in monitoring pressure due to its distinctive design and passive nature with versatile sensing capability. The effectiveness of the capacitive sensor primarily relies on the variation in thickness of the dielectric layer sandwiched between conductive electrodes. Additive manufacturing (AM), a set of advanced fabrication techniques, enables the production of functional electronic devices in a single-step process. Particularly, the 3D printing approach based on photocuring is a tailorable process in which the resin consists of multiple components that deliver essential mechanical qualities with enhanced sensitivity towards targeted measurements. However, the availability of photocurable resin exhibiting essential flexibility and dielectric properties for the UV-curing production process is limited. The necessity of a highly stable and sensitive capacitive sensor demands a photocurable polymer resin with a higher dielectric constant and conductive electrodes. The primary purpose of this study is to design and fabricate a capacitive device composed of novel photocurable Polyvinylidene fluoride (PVDF) resin utilizing an LCD process exhibiting higher resolution with electrodes embedded inside the substrate. The embedded electrode channels in PVDF substrate are filled with conductive silver paste by an injection process. The additively manufactured sensor provides pressure information by means of a change in capacitance of the dielectric material between the electrodes. X-Ray based micro CT-Scan ex-situ analysis is performed to visualize the capacitance based sensor filled with conductive electrodes. The sensor is tested to measure capacitance response with changes in pressure as a function of time that are utilized for sensitivity analysis. This work represents a significant achievement of AM integration in developing efficient and robust capacitive sensors for pressure monitoring or wearable electronic applications.

Keywords: Capacitance, Additive manufacturing, PVDF, Sensing

1. INTRODUCTION

In the modern Additive manufacturing (AM) era, real-time monitoring of 3D printed components' performance will be highly beneficial when failure or defects are detected at the right time. Integrating a smart sensing device to monitor physical phenomena, such as pressure, temperature, or mechanical strains [1-4], is an efficient way in preventing any possible damage. An innovative method for including such a sensor system is to embed them directly into the printed parts, which not only shields them against external damage but also will measure the phenomena in the area of interest. Especially, the rapid technological development in the fields of health monitoring, robotic e-skin, cognitive manufacturing, and wearable electronics demands a high-performance, embeddable, versatile pressure sensor exhibiting flexibility [5-7]. Pressure for health monitoring applications can commonly be measured using piezoresistive or triboelectric sensors [8,9]; however, high power consumption, signal drift, and lack of continuous feedback make them inefficient sensing options. To overcome these challenges, a flexible capacitive sensor will be an ideal candidate for passive pressure measurement due to its low power consumption, fast response time and simple construction. A capacitive sensor typically consists of two parallel plate electrodes that sandwich a dielectric layer. External pressure or force on the sensor causes a change in thickness of the dielectric layer, resulting in corresponding change in capacitance, as shown in Figure 1. The basic parallel plate equation of capacitance is as follows,

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d} \tag{1}$$

where C is the capacitance (farad), measured from the sensor; ε_0 is the dielectric constant value of free space (8.854×10^{-12} F/m); A is the area of capacitor electrode (m^2); d is the distance between the electrodes (m) and ε_r is the relative permittivity of the dielectric layer.

The recent advancements in the field of AM technology have made it possible to fabricate an array of sensors in a sophisticated manner with minimized material utilization and reduced mass production costs [10-12]. Among different fabrication techniques, the ultraviolet (UV)-based liquid crystal display (LCD) printing method can produce high-quality print, particularly can overcome fabrication challenges with custom-made photocurable resins [13]. Despite these advancements, the range of resins available that exhibit both favorable dielectric property and flexibility remains limited, which underscores the need for developing an optimized photocurable resin.

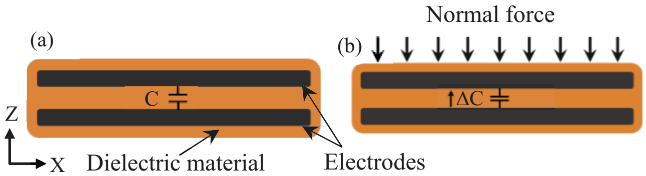

Figure 1: Working principle of capacitive sensor (a) sensor cross-section with parallel plates made of conductive material enclosed inside dielectric material and (b) change in capacitance with applied force

Polyvinylidene fluoride (PVDF), a well-known polymer for its strong chemical resistance and good mechanical properties, is selected as a polymer matrix due to its intrinsic dielectric property and mechanical compliance nature. The main objective of this paper is to 1) develop a photocurable resin for capacitive sensor that can be printed using the LCD process, 2) infill embedded electrodes channel, and 3) validate pressure measurements.

2. MATERIALS AND METHODS

This section describes the selected materials, manufacturing process, and various measured properties of the developed capacitive sensor.

2.1 Materials

The process of 3D printing a capacitive sensor involves mixing the polymer with additives that enable photo curability using UV based process. The resin development primarily consisted of the following materials: PVDF polymer, 1,6-hexanediol diacrylate (HDODA) monomer, diethyl fumarate (DEF) solvent and Bisacylphosphine oxides (BAPOs) photoinitiator (Sigma Aldrich, St. Louis, MO, USA) and are used as is with Sudan 1 UV absorber (Thermo Fisher Scientific, Waltham, MA, USA). The resin composition investigated in this work comprised of 35 wt.% PVDF, 40 wt. % HDODA, 23 wt. % DEF, 1.9 wt. % BAPOs and 0.1 wt.% Sudan 1 and is mixed using a centrifugal planetary THINKY mixer (Laguna Hills, CA, USA) for 16 min at 2000 rpm. Particles are mixed well with the selected combination in rotational and revolutionary axes motion without any air bubbles due to the deaeration capability of the mixer used.

2.2 Printing process

The capacitive sensor is fabricated using Phrozen Sonic Mini 8K LCD based 3D printer exhibiting high XY print resolution up to 22 µm. A sensor design with an empty electrode channel representing a parallel plate capacitor concept is designed and modeled. After the model is sliced using the Chitubox, the sensor array is printed using the developed photocurable piezoelectric resin, as shown in Figure 2.

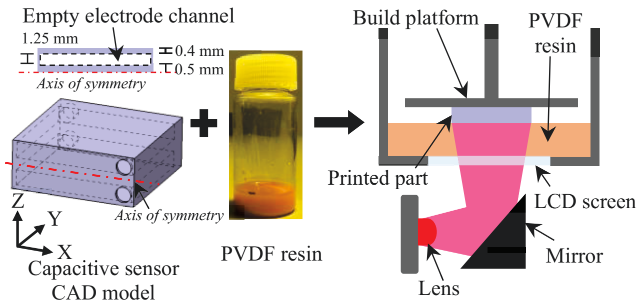

Figure 2: Experimental UV-assisted LCD printing setup for sensor development

As it is a custom-made novel piezoelectric resin, the printing parameters are optimized after multiple trials, which mainly evades factors, such as over polymerization, delamination between layers, and build platform adhesion.

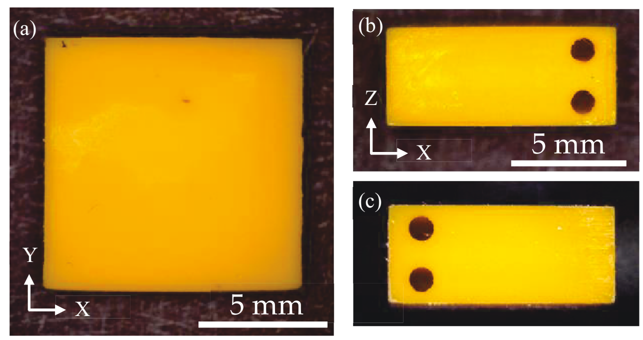

Figure 3: LCD printed PVDF capacitive sensor with hollow embedded electrode channels: (a) top, (b) front and (c) back view

Figure 3 shows the successful sensor print with 1 mm thick dielectric layer and 1.25 mm empty electrode channel by following the optimized printing parameters listed in Table 1. The fabricated sensor with drain holes is rinsed in isopropanol and blow-dried to remove uncured resin from the empty channels.

Table 1: LCD printing parameters

Print parameter	Value
Layer height (mm)	0.05
Bottom layer count	6
Exposure time (s)	30
Bottom exposure time (s)	55
Lift distance (mm)	6
Lift speed (mm/min)	60
Retract speed (mm/min)	150

2.3 Chemical, Dielectric, and Mechanical properties

Fourier transform infrared spectroscopy (FTIR) spectra of developed PVDF resin consisting of monomer and polymer provide more information about the crystalline structure, which is related to dictating the dielectric property. An Agilent Cary 630

FTIR spectrometer is operated at 16 scans per spectrum at 4 cm^{-1} resolution to measure absorption spectra of UV-cured PVDF photo resin in a wavenumber range from 650-1850 cm^{-1}, as shown in Figure 4. Absorption peaks at 762 cm^{-1} (CF^2 bending and rocking), 872 cm^{-1} (C-F stretching), and 1062 cm^{-1} (C-C-C bonding) represent non-polar α-phase, while peaks at 840 cm^{-1} (CF^2 stretching and CH^2 rocking), 1179 cm^{-1} (C-C bonding, HDDA's C-O stretching vibration), 1406 cm^{-1} (CH^2 wagging, HDDA's C=C) and 1423 cm^{-1} (CH^2 bending) signifies polar β-phase presence in PVDF polymer [14-17]. Additionally, peaks at 1620 cm^{-1}, 1636 cm^{-1} (C=C bond), 1719 cm^{-1} (C=O stretching vibration), 2864 cm^{-1} (=C-H stretching vibration), and 2938 cm^{-1} (CH^2 symmetrical) indicate the presence of HDDA (monomer) in the developed photo resin [10].

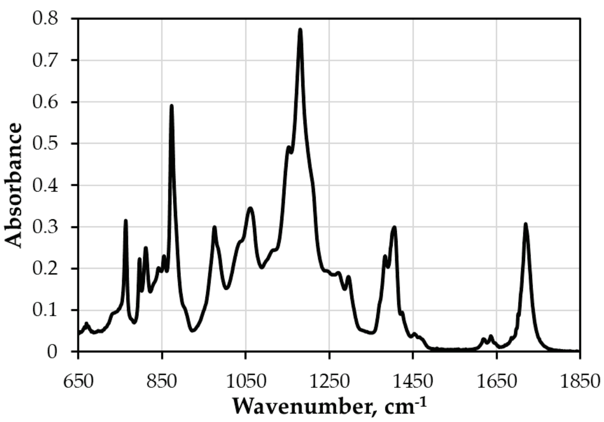

Figure 4: FTIR spectra of developed PVDF photocurable resin

Figure 5 demonstrates the UV-visible absorption spectra of the developed PVDF photo resin. The high absorption peak at 420 nm is caused by the initiator, indicating a UV-curable region.

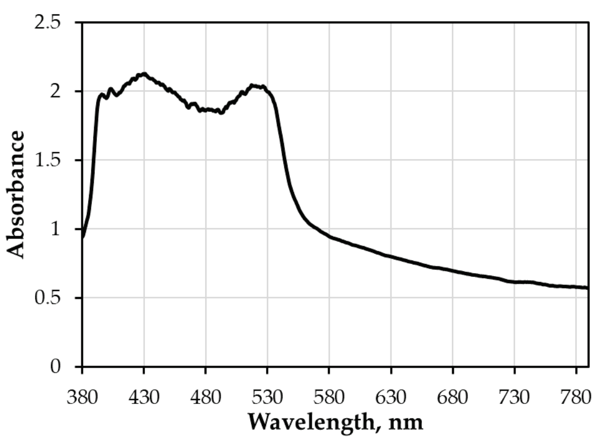

Figure 5: UV-visible spectra of developed PVDF resin

The dielectric constant, an important property of the capacitance sensor, is measured using the parallel plate capacitor theory, as shown in equation (1). The sample is installed in between the metal plates, and a dielectric value of 7.24 ± 0.11 is measured for the printed PVDF sample. The mechanical properties, such as Young's modulus (E) and hardness of developed PVDF piezoelectric resin, are obtained using a Nanoindenter Bruker Hysitron TI-980 with 10 mN load transducer. Figure 6 shows a force-displacement curve obtained through the indentation of PVDF sample. The sample is loaded at 5mN force with 5 sec dwell time to minimize the viscoelastic effect of the measured modulus. A Young's modulus of 1.51 ± 0.04 GPa is derived from the curve's slope, including Poisson's ratio in plane stress condition, and indentation hardness of 118.16 ± 3.49 MPa is measured using the nanoindenter.

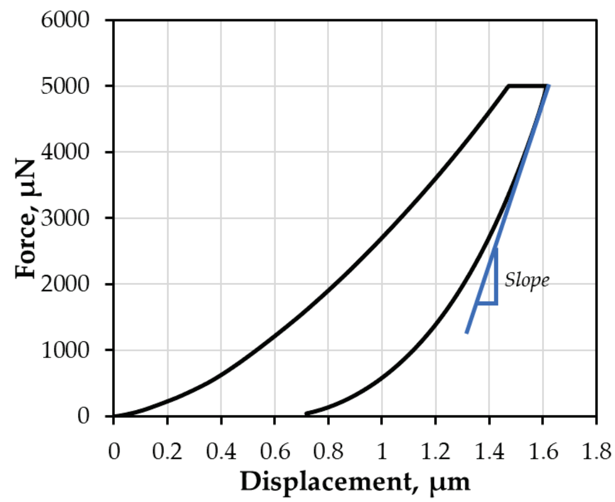

Figure 6: Force vs. displacement curve of PVDF sample tested with a nanoindenter

3. EMBEDDED ELECTRODE FILLING

3.1 Injection printing

Electrode filling through an injection process is a common approach to produce embedded electrodes due to its simplicity and ability to replicate the pre-defined channel using a 3D printing process exhibiting better resolution and smoother sidewalls inside the encapsulated substrate. The electrodes are filled using HYREL 30M (HYREL 3D, Norcross, GA, USA) printer equipped with dispensing gauge needle, where commercially available conductive PE 873 silver ink (Dupont, Wilmington, DE, USA) is manually loaded into the 10 ml syringe.

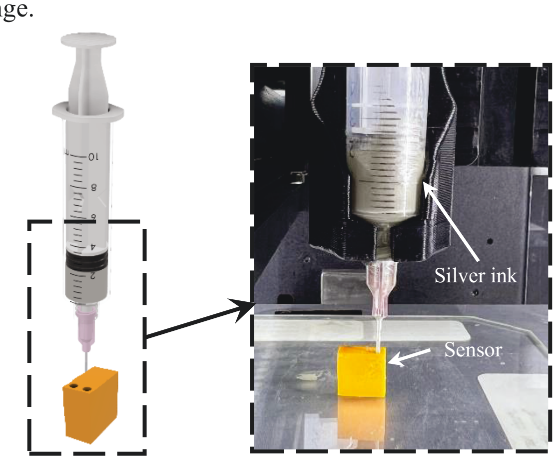

Figure 7: Electrode filling using injection-based 3D printing technique

In this process, the needle injects the conductive ink into the inlet holes of the printed capacitive sensor at a rate of 0.02 mL/min and is cured at room temperature, as shown in Figure 7.

3.2 CT Scan examination

As the printed PVDF resin is not transparent, the sensor substrate is examined using Skyscan 1275 Desktop X-ray micro CT-scanner from Bruker after it is filled with the electrode material. 40 kV X-ray energy is used to scan the sample at different angles.

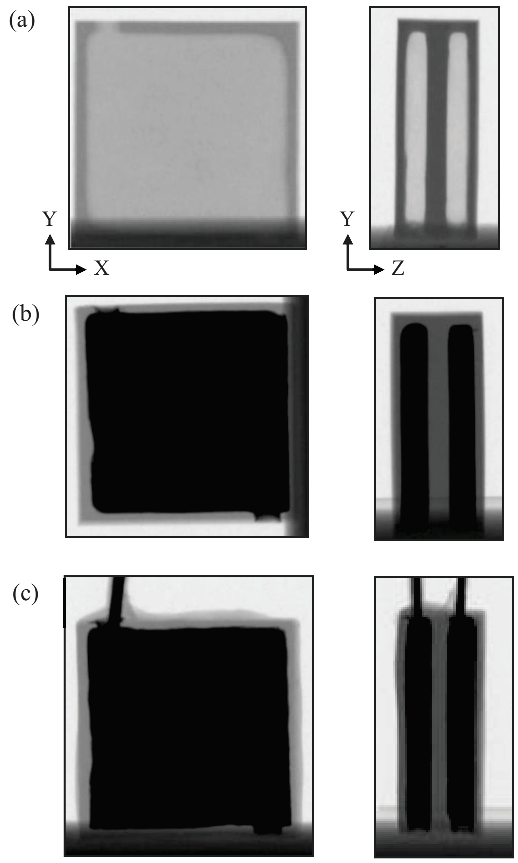

Figure 8: CT Scan inspection of electrode channels: (a) before, (b) after filling using injection process in front and side view, and (c) with wire installed after capacitance measurement

Figure 8 (a and b) shows the CT-scan images of the capacitive sensor without and with highly conductive electrode material after curing, confirming that the channel is filled evenly using the injection approach. Wires are installed for direct capacitance measurement, and the inlet ports are sealed by applying a droplet of PVDF resin and cured for 30 sec under UV light exposure, as shown in Figure 8 (c).

4. PRESSURE DETECTION VALIDATION

The sensor response to change in pressure is analyzed with different applied mass conditions to validate the pressure detection capability of the developed sensor. The change in capacitance with different applied masses is measured using a high precision LCR 6020 meter with a 128-sample average at 1 kHz. Figure 9 illustrates the measured change in capacitance as a function of applied pressure at room temperature.

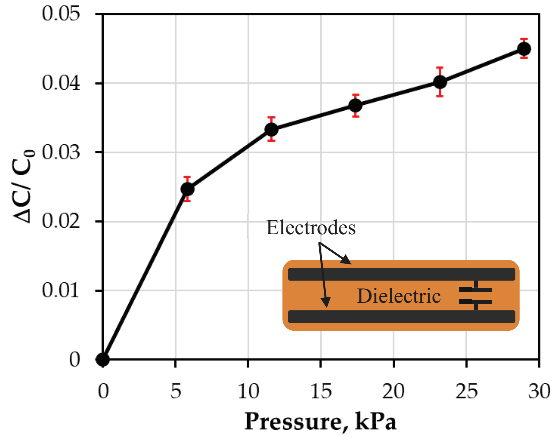

Figure 9: Response curve of developed sensor showcasing change in capacitance with applied pressure

Moreover, a real-time sensing capability is also tested with increased mass applied to the sensor over time, as shown in Figure 10. Overall, the result reveals that the change in capacitance is increased with a decrease in distance between the electrodes, confirming the general capacitance equation. It is also noticed that the developed sensor reacts immediately to the change in applied pressure with a slight relaxation time to settle into a constant value at each step.

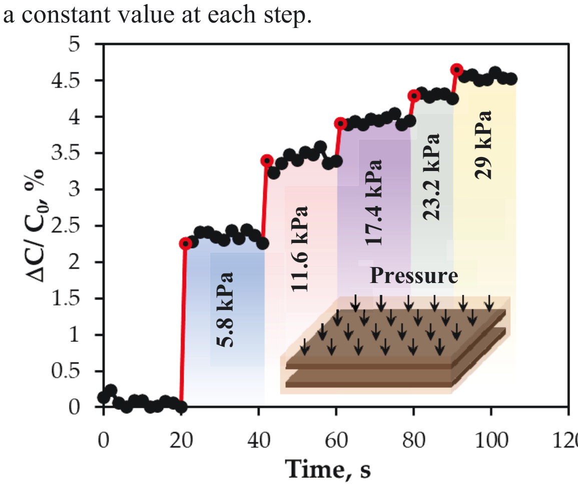

Figure 10: Real-time capacitance change response with applied pressure steps at room temperature

5. CONCLUSION

This paper presents a novel fabrication method of a capacitive pressure sensor developed using a 3D printing process. A photocurable resin with a dielectric constant of 7.24 ± 0.11 is achieved. Electrode filling technique with effective ex-situ CT-Scan analysis is executed showcasing even embedded electrodes. The capacitive sensor response is validated as a function of applied pressure and time. Results show an increase in capacitance with applied pressure that correlates with the constitutive capacitance equation. Future work will be dedicated towards enhancing dielectric properties by adding piezoelectric fillers, optimizing the sensor size to embed them inside the 3D printed host structure, and validating their performance in dynamic environments.

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