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An Inkjet-printed, Flexible, Ultra-broadband Nanocomposite Film Sensor for *in-situ* Acquisition of High-frequency Dynamic Strains

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Abstract

We present an ultralight, flexible, nanocomposite film sensor manufactured using a drop-on-demand inkjet printing approach which leverages the integrated inks directly on flexible polyimide substrates. The ink – a hybrid of nanocomposites embracing carbon black nanoparticles and polyvinyl pyrrolidone, is rigorously designed and morphologically optimized to be stable, printable and wettable. The printed film sensor has proven capability of *in situ*, precisely responding to dynamic strains in a broad range from quasi-static strain, through medium-frequency vibration, to ultrasounds up to 500 kHz. This is first ever an inkjet-printed piezoresistive sensor responds to dynamic strains in such a broad band and an ultrasound of such high frequencies. Sensitivity of the sensors can be fine-tuned by adjusting the degree of conductivity via controlling the printed passes, endowing the sensors with capacity of resonating to strains of a particular frequency, authenticating inkjet-printed nanocomposite sensors can be tailor-made to accommodate specific signal acquisition demands.

Keywords: Inkjet printing; Broadband ultrasound signals; Nanocomposite sensor; Structural integrity monitoring (SIM)

1. Introduction

Sensing remains the most elementary yet pivotal constituent in non-invasive or non-intrusive health care for human, as well as in integrity monitoring for engineering structures. In particular, the structural integrity monitoring (SIM) – an emerging technique aimed at enhancing structural safety while in the meantime driving down exorbitant maintenance cost, is a bionic attempt that expands the concept of biological sensing philosophy to engineering structures, and based on sensed structural responses and ambient parameters, assesses the structural health and integrity status in a real-time manner. In SIM, to achieve faithful sensing to enable precise perception of structural responses, a certain number of sensors are networked, in a dense or sparse configuration, and immobilised in the inspected structure, to acquire desired signals. Commercially available sensors are in a diversity of modalities, as typified by metal-foil strain gauges [1], piezoelectric wafers (typically lead zirconate titanate (PZT)) [2], optical fibres [3], electromagnetic acoustic transducers [4], and piezoelectric polymer-type sensors (e.g., polyvinylidene fluoride (PVDF) and its copolymers) [5, 6]. Amid these sensors, the sensitivity of strain gauges or piezoelectric polymer film-type sensors is limited by their intrinsic capacity of only responding to signals in a spectrum of low frequencies [7]; the piezoelectric wafers are usually too rigid to conform onto a curve or complex surface, and the use of a large number of such wafers to form a dense sensor network can introduce remarkable weight and volume penalty to the inspected structure; optical fibre-based sensors are brittle, and embedding optical fibres into structures such as laminated composites may not only complicate fabrication process but degrade local strength of the composites; PVDF enables large area coverage and good adaption to a curved surface, but its piezoelectric coefficients are usually low, which implies inferior sensitivity [8]. In such a backdrop, it is imperative to develop new genres of sensor that are able to strike a compromise among flexibility (adaptability to curved structures), weight (low mass addition

to inspected structures), volume (ignorable degradation in mechanical properties of inspected structures), and very importantly, responsivity and sensitivity (capability of perceiving broad signals up to an ultrasonic frequency regime), whereby to implement *in situ* SIM.

Driven by the recent advances and technological break-throughs in nanomaterials, a great deal of effort has been dedicated to developing functionalized nanocomposites to accommodate specific structural or functional requirements, which has blazed a trail for new generation of human-machine interfaces including sensing devices [9-13]. A variety of carbon nanofillers, represented by graphene and multi-walled carbon nanotubes, are readily available, combing which with polymers leads to nanocomposites with the merits of both the nanofillers and polymers such as low density, good flexibility, environmental and chemical stability, along with improved electrical and mechanical profiles. Central to the interest in using nanocomposites to develop sensing devices is the piezoresistive strain sensors [14]. Representatively, Spinelli et al. [15] fabricated a nanocomposite compound with multi-walled carbon nanotubes and structural thermosetting epoxy resin, and demonstrated its use in SIM. Qin et al. [16] reported a type of nanocomposites with reduced use of graphene oxide/polyimide (PI) that showed enhanced sensitivity to structural deformation under compression, bending, stretching and torsion. Wu et al. [17] designed a piezoresistive strain sensor consisting of vertical graphene nanosheets that were arranged in a maze-like network and sandwiched between two polydimethylsiloxane substrates, and the sensor presented good stretchability, excellent linearity and high sensitivity to dynamic strains when compared with conventional metal-foil strain sensors. Nevertheless, when extended to the acquisition of high-frequency dynamic strains in an ultrasound regime (several kHz or above), majority of the prevailing piezoresistive strain sensors fail to respond.

In the authors' previous endeavours [18-21], a nanocomposite-inspired spray-on sensor, made of carbon black (CB)/PVDF hybrid, has been developed and fabricated, with proven effectiveness in faithfully perceiving dynamic strains with a broad frequency bandwidth (the bandwidth is referred to as the range of strain frequency that the sensor can perceive), from static strain, through medium-frequency vibration, to high-frequency ultrasound signals up to 400 kHz. The sensors can further be networked for implementing acousto-ultrasonic-wave-based passive or active SIM. However, it is envisaged that the fabrication of such sensors using manually manipulated approaches such as screen printing or spraying is yet cost-effective, in particular when a batch of such sensors are needed to form a dense sensor network at a large scale. Moreover, the manual manipulation of screen printing or spraying may introduce discrepancy among individual sensors which is not to be neglectable in some high-precision measurement applications.

Inkjet printing, among flourishing addictive manufacturing techniques, has gained increased preference for large-scale fabrication of flexible electronics [22, 23]. Being a computer-aided, drop-on-demand, additive manufacturing approach, the inkjet printing features versatility, simplicity, controllability, automaticity with high precision yet low cost. When used for fabricating sensing devices, inkjet printing makes it possible to customize sensor patterns, by precisely regulating the placement of picolitre volumes of ink droplets [24, 25]. The inkjet-printed sensors take advantages of good flexibility, light weight and ease of processability. A broad range of electrical devices have been developed using inkjet printing, showing enhanced sensing performance when compared against those prepared using conventional manufacturing approaches. Amid successful paradigms are transistors [26, 27],

humidity sensors [28, 29], large-area thermo-electrics [30, 31], and solar cells [32, 33], to name a few.

In this study, by extending the authors' continued effort in developing nanocomposite piezoresistive sensors, a new breed of ultralight, flexible, nanocomposite film sensor is manufactured using a drop-on-demand inkjet printing approach which leverages the integrated inks directly on flexible substrates (polyimide films). The rigorously designed ink, made of CB and polyvinylpyrrolidone (PVP), is morphologically optimized towards enhanced stability and printability. The inkjet-printed nanocomposite sensors feature a thickness of only ~1 μm that is remarkably thinner than a hot-pressed CB/PVDF senor (~200 μm) that we developed before. The new sensors show additional merits including remarkably enhanced sensitivity and signal stability when used to acquire broadband ultrasound signals. Notably, conductivity and sensitivity of the sensors can be fine-tuned by precisely controlling the number of printed passes (i.e. printed layers), endowing the sensors with a capacity to resonate to strains of a particular frequency. The inkjet-printed sensors have proven responsivity to dynamic strains in a broad frequency range from quasi-static strain, through medium-frequency vibration, to ultrasounds up to 500 kHz.

2. Experimental

2.1. Ink Preparation and Sensor Fabrication

2.1.1. Selection of Nanofillers and Matrix

To develop the inkjet-printed sensor responsive to broadband dynamic strains, CB is chosen as the nanofiller and PVP as the polymer matrix to prepare a nanocomposite hybrid. Such selection is made based on twofold consideration: (i) CB, the nanofiller with a low-aspect ratio yet high specific surface area can be evenly dispersed in the polymer matrix with

mitigated aggregates and reduced amount of nanoparticle entanglement. Such a trait is beneficial to minimize the blockage and clogging of the inkjet printing nozzle [19, 34, 35]. It is also conducive to the initial formation of a conductive network in the hybrid and the trigger of tunnelling current when the nanofiller contents reach their percolation threshold [21]; and (ii) PVP is soluble in both aqueous and organic solvents, and it can be utilized as a stabilizer for nano-scalar dispersion owing to its amphiphilic groups [30]. PVP presents desirable adhesive, cohesive, and dispersive properties with good wettability, enhancing the stability of the fabricated nanocomposite ink.

2.1.2. Ink Preparation and Substrate Pre-treatment

It is noteworthy that the non-Newtonian rheological properties of the above prepared nanocomposite inks are likely to block and clog the inkjet printing nozzle when the inks are squeezed out from the nozzle orifice [36]. Allowing for this, the creation of ink droplets in the micro-sized capillaries of the nozzle deserves particular attention, and property optimization of the CB/PVP hybrid is a key issue in the printing process (to be detailed in subsequent sections). Bearing that in mind, the nanocomposite ink is formulated by mixing CB powder (CABOT Black Pearl 2000, morphology of which can be referred to [37]); average particle diameter: 30 nm; 0.28 g) with PVP (PVP K-30, Sigma-Aldrich; 0.56 g) in N-methyl-2-pyrrolidone (NMP, J&K Scientific; 40 mL), to which 0.08 g sodium dodecylbenzenesulfonate (SDBS, Sigma-Aldrich) is added as surfactant, to stabilize the dispersions of CB and decrease the surface tension of the ink. The mixture is mechanically stirred at a room temperature (25 ^{o}C) for 2 hours at 400 rpm and sonicated for 1 hour in an ultrasonic bath (Brandson 5800 Ultrasonic Cleaner; 40 kHz), to warrant even dispersion of CB powder in PVP matrix. Before being filled into the cartridge, the as-prepared CB/PVP dispersions are filtered through a 0.45 μm-diameter PVDF micropore sieve to screen larger

CB particle agglomerates. Via such a process, the physical properties and parameters of the ink are regulated to best fit the inkjet printing process. This series of process leads to stable ink droplets, with minimizes possibility of nozzle blockage and clogging.

PI films with a thickness of 25 μm are used as the substrate, on which the nanocomposite hybrid is inkjet-printed, owing to the desirable resistance to high temperature of the PI films and their good flexibility. Printed on the flexible PI films, the sensors can adapt to a curved structural surface. PI films are pre-treated using a plasma cleaner (PDC-002, Harrick Plasma, Inc.), and in the pre-treatment O_2 plasma is generated at a radio frequency power of 30 W and 450 mTorr for 2 minutes, to enlarge the surface energy of the films and consequently improve wettability of the inks printed on the films. The prepared inks are then directly deposited on the surface of a PI film.

2.1.3. Sensor Printing

The inkjet printing is implemented on an inkjet printing platform. The platform consists mainly of a PiXDRO LP50 inkjet printer (OTB Solar-Roth & Rau), **Fig. 1(a)**, equipped with a DMC-11610 cartridge (Dimatix-Fujifilm Inc.) which produces droplets with a volume of 10 pL, through 16 parallel piezoelectric actuated nozzles with a diameter of 21.5 μm for each. The pattern of the sensor is designed to be a rectangle, with a dimension of 10.0 mm in width and 20.0 mm in length.

The PVDF micropore sieve-filtered ink (1.5 mL) is filled in the cartridge, and the piezoelectric actuated nozzles, under a driving voltage of 28 V, prints the ink on the pre-treated PI films with a 4 kHz printing frequency. The printing resolution, calibrated by the number of ink drops printed along a line of 25.4 mm (1 inch), is set as 500 dpi in both the

cross-scan and in-scan directions, so that the drop spacing is ~50 μm in both directions. The plasma-treated PI film is fixed on a substrate plate with a substrate vacuum pump, and the film is heated to 45 ^{o}C during the printing process, to gain a solution evaporation rate that is higher than that rate under a room temperature (so as to prevent the lateral flow of the printed ink and create a reduced "coffee-stain" effect [38]). Such printed sensors are displayed in **Figs. 1(b)-(d)**.

2.2. Material Characterization

2.2.1. Inks

The density of the CB/PVP nanocomposite ink, estimated by weighing a certain volume of the filtered ink using a pipette, is 1.12 g·cm^{-3}. A viscosimeter (NDJ-5S, Lichen Technology) is used to measure the viscosity of the ink, and 0 # rotor is chosen with a rotation speed of 6 rpm (for measurement of liquids with viscosity lower than 10 mPa·s). The surface tension measurement of the ink is implemented with a force tensiometer (KRÜSS® K100). The force tensiometer is calibrated by de-ionized water before measurement. A platinum loop is immersed into the liquid and then withdrawn, and the maximum of pull-out force is recorded. To evaluate the effect of plasma treatment on the PI film substrate, as well as the surface matching between the substrate and the inks, 1 μL deionized water with ethylene glycol (EG, Sigma-Aldrich) is dropped through a stainless needle respectively onto the plasma-treated and untreated PI films for comparison, and the contact angles in two cases are measured with an imaging system (ramé-hart, Inc.). The surface energy of the PI films is calculated in terms of the interfacial energy and the measured contact angles of water and EG using DROPimage software (ramé-hart, Inc.). All results are to be presented and discussed in Section 3.1.

2.2.2. Inkjet-printed Sensor

With the same printing approach, a series of sensors are comparatively fabricated, featuring different numbers of printed passes (6, 9, 12 and 15, respectively), whereby to determine the most suitable number of printed passes leading to high sensitivity of the sensor to high-frequency dynamic strains. The thickness of each sensor is measured with a surface profiler (DektakXT Surface Optical Profiler, Bruker). Morphological characterization of the printed sensors that are sputter-coated with a thin layer of gold is performed on a scanning electron microscopy (SEM) platform (TESCAN® Vega 3). The electrical resistance (R) of each sensor is measured using a four-probe method with a dynamic digital multimeter (Keithley® DMM 7510). The measurement is conducted with the "4-wire resistance" mode of the multimeter, and the four probe points are equally arranged in a line on the sensor. The distance between two neighbouring measurement points is 4.0 mm and the voltage-to-current ratio of the inner two probe points is calibrated by the multimeter. R is calculated according to the voltage-to-current ratio with a correction factor of 2.3532 [39]. The conductivity (σ) is calculated via $\sigma = l/(R \cdot A)$, where l and A are the length of the sensor and effective cross-section area of the sensor, respectively. With R, the relationship between σ of a sensor and the number of printed passes can be ascertained. Raman spectra are obtained to show the microstructural properties of the sensors at a room temperature, with a Raman spectrometer (LabRAM HR 800, HORIBA) (a 488 nm excitation laser wavelength and 50 mW laser power in the range of 1100-2000 cm^{-1}). All results are to be presented and discussed in Section 3.2.

3. Results and Discussion

3.1. Inks and Substrates

To warrant good printability of the CB/PVP ink, both the physical properties and fluid mechanics of the ink is worthy of optimization. During the printing process, the viscosity η,

surface tension γ and density ρ of the ink, as well as the nozzle diameter d, are key parameters controlling the quality of liquid drops. With these parameters, dimensionless physical constants, such as the Reynolds (R_e), Weber (W_e) and Ohnesorge (O_h) numbers [40] of the ink, can be ascertained by

$$R_e = \frac{v\rho d}{\eta}, \tag{1}$$

$$W_e = \frac{v^2\rho d}{\gamma}, \tag{2}$$

$$O_h = \frac{\sqrt{W_e}}{R_e} = \frac{\eta}{(\gamma\rho d)^{1/2}}, \tag{3}$$

where v signifies the drop velocity. A figure of merit, Z – the reciprocal of O_h, is used to identify the appropriateness of the ink for printing [31] as

$$Z = \frac{1}{O_h} = \frac{(\gamma\rho d)^{1/2}}{\eta}. \tag{4}$$

It has been demonstrated that the fluid is printable only when $Z > 2$ [41], and a stable droplet can be formed when Z is in a range of (0, 10) [42] or (4, 14) [43], which warrants the single-drop formability, the minimum stand-off distance, position accuracy, and maximum allowable jetting frequency. In the case that $Z < 1$, viscous dissipation prevents drop ejection from the nozzle, while droplets are accompanied by unwanted satellite drops when $Z > 14$.

In this study, η of the CB/PVP ink measured to be 2.42 mPa·s with the viscometer. Knowing γ = 43.9 mN/m and ρ = 1.12 g·cm^{-3}, Z value of the ink is calculated to be 13.5 according to Eq. (4), with a nozzle diameter of 21.5 μm. Such a value of Z falls in the optimal range of [1, 14], indicating that the inks prepared can form stable droplets. This can further be demonstrated in the droplet screenshot, **Fig. 2**, which is captured with a stroboscopic camera

equipped on the inkjet printer. **Figure 2** compares the droplets generated by five successive nozzles of the cartridge, all of which are observed stable without any tail or satellite drop.

For the polymeric substrates, the low surface energy makes it challenging for a printed droplet to form a uniform layer because the droplet tends to bead up [44]. Good adhesion can be achieved by using a swelling polymer layer, a porous layer or a roughened surface [45], whereby a higher surface energy of the substrate can be obtained. **Figure 3** compares the contact angle of water drops on the PI film substrate before and after plasma pre-treatment, to observe a decrease in the angle from 48^{o} to 7^{o} – suggesting improved wettability of the printed ink on the PI film upon plasma treatment. The surface energy is calculated to increase from 50.62 (before plasma treatment) to 86.93 mJ/m^2 (after plasma treatment). The imide groups in the PI film are modified to secondary amide and carboxylate groups after being exposed to O_2 plasma [46], and the formation of these polar components increases the surface energy.

3.2. Characterization of Inkjet-printed Sensors

No obvious discrepancy in the morphological characteristics can be observed among the inkjet-printed sensors of different printed passes (6, 9, 12 and 15, respectively), and **Fig. 4** shows a typical surface pattern of the sensor of 15 layers. The morphological characteristics of the sensor is observed to be of good homogeneity. As can be seen from the SEM image, the CB/PVP aggregates densely and evenly distribute, creating a highly consolidated nanostructure that is a building block to form a uniform electrical-conductive network in the sensor.

To further examine the geometrical uniformity and consistency of the printed sensors, the sensor thickness against the number of printed passes are presented in **Fig. 5(a)**. It is apparent that the average sensor thickness increases linearly with the number of printed layers (the red line). Exemplarily, the average thickness of the sensor of 6 layers is 410 nm only and that of 15 layers is 1.3 μm, both of which are much thinner than that (~200 μm) of the nanocomposite sensors manufactured using conventional melt-mixing and pressing adopted in the authors' earlier work [19, 21]. The black curve in **Fig. 5(a)** argues an increase in the measured electrical conductivity of the sensor with the number of printed passes. It is noteworthy that from 12 to 15 layers, the electrical conductivity witnesses a remarkable leap from 0.35 S/m to 0.63 S/m, which can be attributable to the decrease of the roughness-to-thickness ratio [47] of the sensor with an increase in the layer number. As the ink for fabricating the nanocomposite sensor is rigorously designed and optimized, and the manufacturing process is precisely controlled, the electrical conductivity of all the printed sensors, regardless of the number of printed passes, is within the regime of the percolation threshold of the nanofiller [48]. At the percolation threshold, the accordingly prepared nanocomposite sensor exhibits the highest sensitivity to external strains (e.g., the strain induced by acousto-ultrasonic waves), as a result of the tunnelling current in the conductive network induced by particulate movement [7].

The primary spherical particles of CB in the nanocomposite ink comprise graphitic and amorphous-like domains, and the graphitic-like domains typically consist of 3-4 turbostratically stacked carbon polyaromatic layers [49]. The obtained Raman spectra of the printed sensors of different passes are shown in **Fig. 5(b)**, in which two peaks are observed, namely, the *D* peak at ~1355 cm^{-1} and *G* peak at ~1586 cm^{-1}. The former peak indicates the structural defects ascribed to the structural edge effect, while the latter asserts the tangential

mode vibration of the *C* atoms in the graphite structure [50]. It is the structural defects in the graphite structure that affects the electrical conductivity of the conductive network formed in the printed sensors. For the nanocomposite sensors, if the intensity ratio of the *D* peak and *G* peak (I_D/I_G) calculated from the Raman spectra is exceptionally high, a large quantity of intrinsic microstructural defects will be present in the sensor, indicating a low local conductivity which is not conducive to electron movement; on the other hand, an exceptionally low I_D/I_G will result in a highly dense and saturated conductive network, and under that circumstance the nanofiller has little tunnelling effect when the sensor is subject to external strains.

Subsequently, I_D/I_G of the printed sensors is calculated from the Raman spectra, and exemplarily it is 1.07 when the sensor has 6 printed passes. I_D/I_G of the printed sensors decreases with the printed passes, and it is 0.83 for the sensors of 15 layers. A lower intensity ratio suggests a weaker *D* peak induced by the defect and thus a better electrical-conductive carbon aromatic structure (this resulting in a more compact conductive network in the sensor), and this speculation agrees with the increasing tendency of the electrical conductivity measured and shown in **Fig. 5(a)**. For the sensors of different printed passes (6, 9, 12 and 15, respectively), I_D/I_G varies from 0.83 to 1.07, while the electrical conductivities are within the regime of percolation threshold, indicating that I_D/I_G of the printed sensor should be kept at around 0.95, and tunnelling effect can be triggered among CB particles in the conductive network when the sensor is subject to dynamic strains.

3.3. Sensor Response to Dynamic Strains

The piezoresistive characteristics of the inkjet-printed sensors is interrogated using electro-mechanical analysis and the responsive capability of the sensors is calibrated in a broad

frequency range from quasi-static strain (uniaxial and mixed (uniaxial + flexural) mode), through medium-frequency vibration, to ultrasounds up to 500 kHz.

3.3.1. Tensile Strain (*quasi-static*)

A series of epoxy dogbone samples (2.0 mm thick each) is prepared for quasi-static electro-mechanical analysis, each of which undergoes a uniaxial tensile test on a tensile machine (MTS Alliance RT/50), as shown in **Fig. 6(a)**. The speed of the crosshead is set to be 1 mm/min, while the tensile stress (σ) and strain (ε) are calculated according to the applied force, crosshead displacement and specimen dimensions. Surface-glued at the midpoint of each sample is a sensor printed on the PI film, respectively featuring 6, 9, 12 or 15 layers. Each sensor is silver-pasted with a pair of electrodes, and the gap (2 mm) between the two electrodes is the effective sensing area. Electrical resistance of the electrodes is neglectable compared with the resistance of the printed sensor which is of an order of several kΩ [51]. The electrodes are connected to a dynamic digital multimeter (Keithley DMM 7510) via shielded cables. Using a two-probe method, the electrical resistance (R) of the sensor under the quasi-static loading is real-time measured, as depicted in **Fig. 6(a)**. For comparison and calibration, a commercial strain gauge with a gauge resistance of 120 Ω is mounted on the opposite side of the sample, to record the load-induced train simultaneously.

Figure 6(b) shows the normalized change in electrical resistance of the printed sensors of different layers against the applied uniaxial quasi-static loads. The results reveal that the electrical resistance of the sensors increases exponentially with loading. To put it into perspective, the gauge factor (K), a key figure of merit to describe the sensitivity of the sensor, can be calculated as

$$K = \frac{\Delta R}{R_0} / \Delta\varepsilon \,, \tag{5}$$

where $\Delta R = R - R_0$, and R_0 is the initial sensor resistance. Using Eq. (5), the gauge factor of the printed sensors is calculated using linear fitting of all the measured strains from 0.8% to 2.0%. Note that the pre-loading of the tensile machine at the beginning of the test up to 0.8% introduces measurement deviation, and data when the strain is below 0.8% are not included into fitting. As indicated by the fitted results (dash lines in **Fig. 6(b)**), the gauge factor of the sensor of 6 layers is 10.7, which is much higher than that of a commercial strain gauge and also higher than those of the rest of the printed sensors. During the tests, it has been observed that a sensor of fewer printed layers has a higher resistance, and thus a higher gauge factor, a higher resistance change rate and a greater sensitivity to dynamic strains (to be detailed in Section 3.4). The total resistance of the conductive network formed in the prepared CB/PVP nanocomposite ink mainly includes (i) the intrinsic resistance of the conductive CB particles ($R_{particle}$) and (ii) the tunnelling resistance (R_{tunnel}) among adjacent nanoparticles induced by microstrains. The change in $R_{particle}$ can be neglected because of the intrinsic good conductivity of CB particles (compared with the insulating PVP matrix), and it therefore postulates that the piezoresistive response of the printed sensor is induced dominantly owing to the change in R_{tunnel}. Under an external strain, the distance between two adjacent nanoparticles alters, leading to the tunneling of charged carriers and a consequent increase in local electrical conductivity, making it possible to generate quantum tunnelling effect and consequently leading to the change of R_{tunnel} [52]. R_{tunnel} is described based on a tunnelling model [53, 54], as:

$$R_{tunnel} = \left(\frac{8\pi hsQ}{3A^2\gamma s^2 N}\right)\exp(\gamma s) \,, \tag{6}$$

$$\gamma = \frac{4\pi(2m\varphi)^{1/2}}{h} \,, \tag{7}$$

where h is the Plank's constant, s the least distance between conductive particles, Q the number of particles forming a single conducting path, A^2 the effective cross-section of a tunnelling current, N the number of conducting paths, m the mass of an electron, and φ the height of potential barrier between two adjacent particles.

When an external strain, ε, is applied on the sample, the electrical resistance measured by the sensor changes from s_0 (the initial particle separation) to s (the particle separation under ε), and the destruction of the tunnel-conducting pathway from N_0 (the initial number of tunnel-conducting path) to N [55, 56], as

$$s = s_0(1 + \varepsilon)\,, \tag{8}$$

$$N = N_0 \exp[-(\alpha\varepsilon + \beta\varepsilon^2 + \delta\varepsilon^3 + \tau\varepsilon^4)]\,, \tag{9}$$

where, α, β, δ and τ are four constants related to the status of conducting path under ε. Considering the variation of both the particle separation and tunnel-conducting path destruction, the resistance of the sensor changes from R_0 to R, and based on Eq. (6), the resistance change ratio can be calculated as

$$\frac{\Delta R}{R_0} = \frac{R - R_0}{R_0} = \frac{R}{R_0} - 1 = \frac{sN}{s_0 N_0}\exp[\gamma(s - s_0)] - 1\,. \tag{10}$$

Substituting Eqs. (8) and (9) into (10) yields

$$\frac{\Delta R}{R_0} = (1 + \varepsilon)\exp\{-[(\alpha - \gamma s_0)\varepsilon + \beta\varepsilon^2 + \delta\varepsilon^3 + \tau\varepsilon^4]\} - 1\,. \tag{11}$$

Equation (11) can be simplified as

$$\frac{\Delta R}{R} = (1 + \varepsilon)\exp(c_1\varepsilon + c_2\varepsilon^2 + c_3\varepsilon^3 + c_4\varepsilon^4) - 1\,, \tag{12}$$

where c_1, c_2, c_3 and c_4 are four constants linked to the resistance change under ε. The linear term c_1 is associated to both particle separation (tunnelling gap) and destruction of conducting network, while the values of high-order coefficients c_2, c_3 and c_4 are correlated to the degree of conducting network destruction. These coefficients can be obtained with an ordinary least squares approach [15], and the calculated results for the printed sensor are shown in **Table 1**. Also included in **Table 1** are the uncertainties of resistance changing ratio (U) which are smaller than 0.1% and the estimate of the coefficients of determination (C^2) which are close to 1, implying good agreement between the theoretical prediction and experimental measurement.

3.3.2. Mixed (uniaxial + flexural) Strain (quasi-static)

In reality, strains undergone by an engineering structure, either static or dynamic, are usually not uniaxial only and their magnitude could be small (<0.3%). Considering this, the above electro-mechanical test is implemented using a mechanical analysis platform (METTLER TOLEDO Dynamic Mechanical Analysis DMA 1), via which quasi-static three-point bending is applied on samples made of epoxy (1.5 mm thick each), as shown in **Fig. 7(a)**. Knowing the span (l) of the two sample holders on the platform is 30 mm, under the bending, the strain (ε) of the sample can be obtained by [15]

$$\varepsilon = \frac{6Dt}{l^2}, \tag{13}$$

where D and t signify the maximum deflection of the centre of the sample and its thickness, respectively. Identical to the above quasi-static test, response of the sensor of 6, 9, 12 or 15 layers is respectively comparatively examined, and calibrated against commercial strain gauges using a two-probe method.

Figure 7(b) shows the relative change (upon the slopes of linear fitted dash lines) of electrical resistance of the printed sensors of different printed passes when the bending-induced mixed strains vary from 0.10% to 0.30%, to note that the gauge factor of the sensor of 15 printed layers is ~31.0 – that is 15 times higher than that of a commercial strain gauge. Using the same theoretical model defined by Eq. (12), four parameters (c_1, c_2, c_3 and c_4), uncertainties of resistance changing ratio (U) and coefficients of determination (C^2) are ascertained, as listed in **Table 2**. U is only around 0.1% and C^2 approximates 1 in **Table 2**, indicating good agreement between the theoretical prediction and experimental measurement.

3.3.3. Vibration-induced Strain (*medium-frequency*)

The capability of the inkjet-printed sensors for sensing medium-frequency vibration loads is assessed by quantifying their response to dynamic strains using a dynamic vibration test system, in **Fig. 8**. A set of four beams made of glass fibre/epoxy composites (280 mm long, 40 mm wide and 1.5 mm thick) is prepared, and each sample is clamped at one of its ends as a cantilever beam. An inkjet-printed sensor of 6, 9, 12 or 15 layers is adhered on the surface of each beam 70 mm from the clamped end. For comparison, a strain gauge is collocated to the printed sensor on the opposite side of the beam. An arbitrary waveform generator (HIOKI 7075) excites a continuous sinusoidal vibration signal (from 200 to 2000 Hz), which is applied on each beam 40 mm from its free end via an electro-mechanical shaker (B&K 4809). Each sensor is connected to a signal acquisition system comprising a Wheatstone bridge of which the resistor is compatible with the electrical resistance of the printed sensor, a commercial signal amplifier (KYOWA CDV-900A), and an oscilloscope (Agilent DSO 9064A). The electrical resistances of electrical cables and connection in the measurement system are neglected.

The vibration signals captured by the printed sensors along with those acquired by strain gauges, when the excitation frequency is 200 Hz, 800 Hz and 2000 Hz as examples, are shown in **Figs. 9(a)-(c)**, respectively, to observe good stability, reversibility and repeatability of the sensors in responding dynamic strains up to 2000 Hz without phenomenal hysteresis and deviation. **Figure 9(d)**, showing the sensor response magnitude subjected to different degrees of excitation, accentuates that at given excitation frequency and a given printed pass (15 layers as an example for illustration), and argues a linear relationship between the magnitude of excitation and the response intensity of the sensor. Also revealed by **Figs. 9(a)-(c)**, is that a thicker printed sensor with more layers exhibits higher signal-to-noise ratio, the trend of which is the same as the observed in the quasi-static three-point bending test.

The vibration-induced strain at the measurement point can be calculated according to the configuration and specification of the signal amplifier and the Wheatstone bridge [20] by

$$\varepsilon \approx \frac{4V_O}{MV_BK}, \tag{14}$$

where V_O, V_B and M are circuit parameters. V_O represents the output signal voltage and V_B the excitation voltage of Wheatstone bridge (2 V in this study). M denotes the amplification factor of the signal amplifier (×10000 in this study) and K is the gauge factor of the sensor. The sensor of 15 printed layers is chosen for further investigation due to its highest sensitivity to vibration excitation as observed in the test. With known output voltage V_O and gauge factor of the strain gauge ($K = 2$), the strains at the measurement points as well as the gauge factors of the sensor of 15 layers under different vibration frequencies can be ascertained by Eq. (14), as presented in **Table 3**.

As asserted by **Table 3**, the measured strains (±0.0005% ~ ±0.01%) that is induced by vibration are significantly smaller than those (0.1% ~ 0.3%) induced by the quasi-static three-point bending. The strain under the vibration of 800 Hz is the highest because the frequency is close to the resonance frequency of the beam. The gauge factor of the sensor (6.80 ~ 7.65) is smaller than that when used to measure mixed loads (31.0). Apparently, the smaller the strain, the lower the gauge factor of the printed sensor it will be.

3.3.4. Ultrasound-induced Strain (*high-frequency*)

By expanding the above vibration-type excitation from a medium-frequency range to a high-frequency ultrasonic regime, the responsive capability of the inkjet-printed sensors is examined using an ultrasonic measurement system, **Fig. 10**. The ultrasound signal excitation system consists of a waveform generator based on NI® PXIe-1071 platform, and a linear power amplifier (Ciprian US-TXP-3). A glass fibre/epoxy-composite laminate plate (400 mm long and wide, 1.5 mm thick) is prepared, and a PZT wafer (PSN-33, Ø12 mm, 1 mm thick) – used as the ultrasound actuator – is surface-mounted at the centre of the laminate plate, and connected with the excitation system. The sensors printed on PI films are adhered on the surface of the plate, with a distance of 150 mm from the PZT actuator (shown in **Fig. 10**). The sensors are connected to a self-developed amplification module via shielded cables, and the module consists of a resistor-adjustable Wheatstone bridge converting piezoresistive variation to electrical signals, and amplifiers and filters for reducing the contamination from ambient noise and measurement uncertainties. The amplification module is powered by a power supply (GW INSTEK GPC-3030D), and the converted signals are recorded with an oscilloscope (Agilent DSO 9064A). Alongside each printed sensor, a PZT wafer is collocated, functioning as an ultrasound sensor to capture signals simultaneously for signal

calibration and comparison. The electrical resistances of electrical cables and connection in the measurement system are neglected.

A series of five-cycle Hanning-function-modulated sinusoidal tonebursts with the central frequency varying from 50 kHz to 500 kHz (with a stepping of 25 kHz) is generated by the waveform generator, and applied on the PZT wafer (wave generator) via the power amplifier to emit ultrasound into the laminate plate. The generated ultrasound propagating in the laminate plate is captured by the printed sensors as well as the collocated PZT sensors. **Figure 11** compares representative signals, at 175 kHz, captured by the inkjet-printed sensors of 6, 9, 12 or 15 layers, respectively, as well as the PZT sensor, to observe that the moments at which the first wave component (viz., the zeroth-order symmetric Lamb wave mode guided by the laminate, denoted by S_0 hereinafter) arrives are of the same in the signals acquired by the printed sensors and by the PZT sensors. Not only the S_0 mode, the but other wave modes (e.g. the zeroth-order anti-symmetric Lamb wave mode, A_0) are also faithfully captured by the printed sensors, consistent with those by the PZT sensors in terms of the arrival moment and waveform. To scrutinize the sensor performance at higher frequencies, **Fig. 12** comparatively displays the signals captured by the printed sensor of 12 layers and by the PZT sensor at 500 kHz, as an example for illustration. The signals captured by the printed sensor is filtered by a first-order Butterworth filter to mitigate noise, and good agreement between signals acquired by the printed sensor and PZT sensor is confirmed. Note that the crosstalk included in the signals at the zero moment, as highlighted in **Fig. 12**, originates from the high-voltage power amplifier of the signal acquisition system.

To put the comparison into perspective, **Fig. 13** depicts the sweep frequency responses over the time-frequency domain (from 50 kHz to 500 kHz), obtained using the printed sensor of

12 layers and the PZT sensor, respectively, to observe no remarkable discrepancy in sensing performance between two types of sensors over a broad frequency regime. The results argue that the inkjet-printed sensors are of the capability to perceive dynamic strains in a broad frequency regime with a high signal-to-noise ratio up to 500 kHz, with precision similar to that of a commercial PZT sensor. It is also noteworthy that the magnitudes of the signals from two types of sensors are different – a finding attributed to the different sensing mechanisms: the printed sensor is a sort of piezoresistive sensor, while PZT sensor is based on piezoelectric measurement.

3.4. Comparison of Different Sensors of Printed Passes

As commented earlier (in Section 3.3), the absolute values of high-order coefficients c_2, c_3 and c_4 in Eq. (12) represent the degree of destruction in the nanofiller-formed conducting network of a sensor. In the tensile test when the sensor is used to measure a uniaxial strain – a relatively greater strain that is higher than 0.8%, there is no remarkable discrepancy and tendency in respective coefficient as noted in **Table 1**, regardless of the number of printed passes; while in the three-point bending test when the sensor is used to capture a mixed (uniaxial + flexural) strain – a relatively smaller strain that is lower than 0.3%, the respective absolute values of all three coefficients tend to augment as an increase in the number of printed passes, in **Table 2**. That is because for a printed sensor, a larger strain (>0.8%) suffices to introduce adequate destruction in tunnel-conductive paths, when the sensor is of different printed layers; on the other hand, under a greater strain, it is the original tunnelling gap (i.e., particle separation) [57] rather than the tunnel-conductive path destruction that leads to the resistance change manifested by the sensor, and therefore a thinner printed sensor with fewer layers can achieve a higher gauge factor because of its higher degree of particle separation.

It is interesting to notice in **Table 2** that the absolute values of coefficients c_2, c_3 and c_4 are correlated with the number of printed layers, highlighting that the conductive network of a thicker sensor (with higher electrical conductivity) is more sensitive to a smaller strain. This has also been proven in **Fig. 7(b)**, in which under the lower stains, a sensor with more printed passes shows higher sensitivity, which is in contrast with the case that a greater strain is measured. This also echoes the conclusion drawn elsewhere [56]: a thicker film sensor usually induces more microcracks and larger crack openings in the sensor, especially under a smaller strain, so a thicker printed sensor has more conductive network destruction, exhibiting higher sensitivity to smaller strain.

The comparison between the quasi-static three-point bending test and the dynamic vibration test further verifies that a printed sensor with more layers tends to have higher sensitivity to small deformation due to a larger degree of tunnel-conductive path destruction. However, when the strain is smaller than tens of microstrain, the degree of tunnel-conductive path destruction shows a decreasing trend, and this results in the reduction of the gauge factor for the printed sensors. For ultrasound test, the findings from **Fig. 11** highlight that the inkjet-printed sensors are of high sensitivity to ultrasound signals with high fidelity. It is noteworthy that under ultrasound excitation, the sensor of 12 layers rather than the sensor of 15 layers (in vibration test) shows the strongest response and thus the best sensitivity to the ultrasound. The reason is that the load of ultrasound with ultra-high frequency is much smaller than that of a medium-frequency vibration signal; when the strain is sufficiently small, the degree of tunnel-conductive path destruction shows a downward trend, and for a thicker sensor with a denser structure, it would be more difficult for the small strain induced by the ultrasound to destruct the tunnel-conducting path. As a result, under the ultrasound-

induced load of ultra-low magnitude, the tunnelling gap determined by the particle separation and the tunnel-conductive path destruction strike a balance when the sensor is of 12 printed layers.

In conclusion, the inkjet-printed sensor can be tailor-made towards specific signal acquisition demands by controlling the printed passes. To acquire uniaxial strains, especially when the strains are higher than 0.8%, the inkjet-printed sensors of 6 layers are suggested; to capture quasi-static mixed (uniaxial + flexural) strains or medium-frequency vibration signals, the sensors of 15 layers are preferred; to perceive high-frequency ultrasound signal, a sensor of 12 printed passes shows the highest signal-to-noise ratio.

3.5. Comparison of Different Manufacturing Approaches: Inkjet-printed *vs.* Spray-coated *vs.* Hot-pressed

In the authors' earlier research [19, 21, 58], the nanocomposite-based sensors were fabricated using either the hot-pressing- or spray-coating-based approaches. During the hot pressing, the ingredients were pressed under a high temperature of 190 ºC, and it took 24 h for full curing of the hot-pressed film, after which the cured film was manually cut for preparing the sensors. Compared with the hot-pressing-based approach, the spray coating is conducive for rapid prototyping and scalable fabrication of sensors. However, the spray coating is a manual process, in which it is a challenging issue to precisely control the thickness and conductivity of the sensor. On the other hand, for the inkjet printing, a highly specific pattern of the sensor can be designed accurately, and the rigorously fabricated ink can be directly deposited with desired patterns onto substrates through an automatic printing process. The thickness and conductivity of the sensor that is thus produced can also be tailor-made by controlling the number of printed passes, making it possible to customize the sensor

for a specific application yet without a need to modify the ingredients of the ink. Compared with the hot-pressing- or spray-coating-based manufacturing approaches, the inkjet printing is of high degree of versatility, simplicity, controllability, automaticity with high precision yet material-saving, low-cost and environmental-friendly.

To gain insight into the effect of different manufacturing approaches for sensor preparation on dynamic strain acquisition, the sensing performance of CB nanocomposite-based sensors that are prepared using hot press, spray coating and inkjet printing, respectively, is compared, in terms of their respective sensitivity to broadband dynamic strains and measurement stability. The same type of nanoparticle – CB, is selected and compounded with PVDF (for hot press) or PVP (for spray coating or inkjet printing) to produce CB nanocomposite-based sensors. In particular, without the loss of generality, 12 layers are printed for the inkjet-printed sensors. As some typical results, **Fig. 14(a)** shows the signals respectively captured by three types of sensors at the excitation frequency of 175 kHz, to observe that the inkjet-printed sensor exhibits the highest sensitivity, as reflected by the largest magnitude and therefore the highest signal-to-noise ratio. To evaluate the stability of signal acquisition, for each type of sensor, under every single excitation frequency, 100 signals are extracted randomly from a large pool of acquired signals, when the excitation frequency varies from 50 kHz to 300 kHz with an interval of 50 kHz, on which basis the coefficients of variation (i.e., the relative standard deviations) of signal magnitude are calculated, in **Fig. 14(b)** which confirms that throughout the whole frequency range of interrogation, the coefficients of variation of inkjet-printed CB/PVP sensors are the lowest amongst three types of sensors and at higher frequencies in particular. Within 50 kHz-200 kHz, the relative standard deviation of the inkjet-printed sensors is ~0.1 only. The signal stability and reliability are of great significance for practical real-time SIM applications, and the much-lowered

coefficients of variation of the inkjet-printed CB/PVP sensors under high frequency indicate great application potentials of the inkjet-printed sensor for *in-situ* SIM. These findings indicate that the inkjet-printed sensors, with its even and uniform structure, are conducive to maintain good stability, fidelity and sensitivity in dynamic strain acquisition, when compared with its peers that are fabricated using other manufacturing approaches such as hot press or spray coating.

4. Concluding Remarks

Ultralight and flexible, a new breed of nanocomposite-based film sensor is developed using a drop-on-demand additive manufacturing approach which directly prints CB/PVP inks on flexible substrates. The ink is rigorously designed and morphologically optimized, warranting good stability, printability and wettability of the ink. The great flexibility of the film sensor makes itself conform with non-planar structural surfaces. With a uniform, even and stable nanofiller conductive network, the printed sensor shows a much higher gauge factor than that of a conventional metal foil strain gauge (when used for quasi-static strain or medium-frequency vibration measurement) or a piezoelectric ceramic wafer (when used for high-frequency ultrasound signal acquisition). The sensor has proven responsivity and precision in responding to quasi-static strain, medium-frequency vibration, and ultrasound up to 500 kHz. An additional merit that the printed sensor possesses is that the responsive sensitivity can be fine-tuned by adjusting the degree of conductivity via controlling the printed passes, allowing the sensor to perceive strains of different frequencies precisely and also making it possible to customize the sensor towards a specific application yet without a need to modify the ingredients of the ink. The environmental effects on the inkjet-printed nanocomposite sensor is under the authors' investigation.

With a high degree of automation, good controllability and great precision that the inkjet printing renders, the sensors can be produced in a great quantity for deploying a large-scale, dense sensor network through a simplified fabrication process in a cost-effective manner. A dense sensor network, using ultralight and flexible nanocomposite sensors, in lieu of conventional ceramic-based piezoelectric sensors with high density and rigidity, well corroborates the concept of "quasi-dispersed sensing network", whereby to strike a balance between "sensing cost" and "sensing effectiveness" in a broad spectrum of applications such as *in-situ* SIM, and wearable devices among others.

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