3D printing of polymer composites to fabricate wearable sensors: A comprehensive review

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ABSTRACT

The application of wearable sensors in domains related to healthcare systems, human motion detection, robotics, and human–machine interactions has attracted significant attention. Because these applications require stretchable, flexible, and non-invasive materials, polymer composites are now at the forefront of research aimed at preparing innovative wearable sensors. Three-dimensional (3D) printing techniques can be used to obtain highly customised and scalable polymer composites to fabricate wearable sensors, which is a challenging task for conventional fabrication techniques. This review provides insights into the prospects of commonly used conductive nanomaterials and 3D printing techniques to prepare wearable devices. Subsequently, the research progress, sensing mechanisms, and performance of 3D-printed wearable sensors, such as strain, pressure, temperature, and humidity sensors, are discussed. In addition, novel 3D-printed multifunctional sensors, such as multi-directional, multi-modal, self-healable, self-powered, in situ printed, and ultrasonic sensors, are highlighted. The challenges and future trends for further research development are clarified.

1. Introduction

Wearable sensors are devices that are directly attached to human skin to monitor daily physical, biological, chemical, and environmental activities in a continual and non-intrusive manner [1–9]. Various relevant products, such as smartwatches, smart clothes, and fitness bands, have been developed to enhance the quality of human life and healthcare systems [10–13]. The global market size will continuously grow to reach USD118.16 billion by 2028, which highlights the importance of this ongoing technology in industries [14]. The application of wearable sensors has been expanded to robotics and human–machine interactions as well [15–20]. To accommodate the potential multiscale variations encountered in these applications, a paradigm shift from rigid metals and semiconductors to flexible soft sensors must be promoted. These wearable sensors must be flexible, stretchable, highly sensitive, durable, and biocompatible and able to be manufactured using scalable and economic protocols [21–23].

Stretchable wearable sensors are mainly composed of conductive nanomaterials integrated with soft polymers that have Young’s moduli comparable to those of human skin and biological materials [24–26]. Polymeric materials provide the necessary stability and stretchability, while conductive nanomaterials can impart electrical, functional, and sensing abilities into the entire device. Several approaches, such as photolithography [27,28], screen printing [29,30], spin and dip coating [31,32], electrospinning [33,34], and casting [35,36], have been universally used to synthesise wearable sensors. However, these techniques are typically time-consuming and cumbersome and characterised by material wastage and low scalability. In contrast, three-dimensional (3D) printing, also known as additive manufacturing, has several advantages, such as the ability to provide customised designs, short processing times, reduced waste, and scalability [25,37–39]. 3D printing techniques can be used to build intact 3D structures from inks and raw materials through layer-upon-layer assembly based on the designed models. The associated technologies have been widely applied in the

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fields of aerospace [40,41], biomedicine [42,43], and electronic devices [44,45], and their potential for manufacturing high-performance wearable sensors with well-designed geometries is being investigated [46,47].

To mimic the sensing abilities of human skin, sensors that can provide comprehensive information regarding rigorous and subtle motions, pressure, temperature, and humidity must be developed for applications related to humans and robots [48–50]. By transforming external stimuli into electrical signals, single-modal wearable sensors can be prepared for strain, pressure, temperature, and humidity sensing. Interestingly, human skin possesses multifunctional sensing abilities with regenerative properties and can clearly distinguish between different applied stimuli [51]. Inspired by these intrinsic features, several researchers have developed multifunctional wearable sensors with multi-directionality [52,53], multi-modality [54,55], self-healing [31,56], and self-powering properties [57,58]. Furthermore, artificial intelligence based techniques have been used to directly print wearable sensors on freeform and intricate curvilinear surfaces, which is especially important for patient-customised wearable sensors and biomedical implantations [59–61]. Recently, wearable ultrasonic sensors have been fabricated to provide continuous monitoring with ultrasound images of central organs and tissues in real time, allowing for early detection and precise diagnosis of diseases [62,63].

Notably, most studies have focused on wearable sensors fabricated using conventional techniques and specific materials [64–66], and only a few researchers have reviewed the use of 3D printing techniques to develop sensors, emphasising strain sensors [67,68]. It is necessary to perform a comprehensive investigation of different types of wearable sensors fabricated using 3D printing technologies. Moreover, the potential of using this novel approach to prepare more contemporary multifunctional sensors with multi-directionality, multi-modality, self-healing, self-powering, in situ printing, and ultrasonic imaging has not been discussed. Therefore, as shown in Fig. 1, this review describes the recent state-of-the-art advancements in 3D-printed wearable sensors, focusing on strain, pressure, temperature, humidity, and multifunctional sensors. First, the shift of material candidates for wearable sensors from rigid metals and semiconductors to stretchable polymer nanocomposites is discussed. Subsequently, the properties of various conductive nanomaterials, such as carbon nanomaterials, metallic nanomaterials, liquid metals, MXenes, and conducting polymers, are discussed. The potential of different 3D printing techniques in manufacturing high-performance and customised wearable sensors is explored. Overall, the research progress of 3D-printed wearable sensors based on polymer nanocomposites is reviewed, and corresponding challenges and future outlooks are highlighted.

2. Overview of wearable sensors

Sensors are transducer devices that transfer external loading into electrical signals compliant for postprocessing [69]. Wearable sensors can be placed on the body to obtain detailed information regarding individual physiological and physical conditions for health monitoring, posture detection, and rehabilitation applications [28,37,70–72]. According to the applied stimulus, wearable sensors can be categorised as strain, pressure, temperature, and humidity sensors. The central component of a wearable sensor is the sensing element that converts input signals into electrical signals. Conventional sensors prepared using rigid conductive metals and semiconductor-based sensing elements are not sufficiently flexible and stretchable, which limits their use as wearable sensors for health monitoring and motion detection applications [23,73]. A potential solution to these problems is to incorporate advanced structural designs into traditional conductive materials, such as wavy [74], serpentine [75], spiral [76], or fractal designs [77] over elastic polymer substrates. The strain induced on the conductive component can be efficiently released under applied strain, and the stretchability and reliability of the devices can be enhanced. However, the inherent rigidity of the metals and semiconductors may lead to premature mechanical and electrical failures owing to the generation of microcracks and disconnections of the conductive materials upon loading [78].

Another effective approach is to incorporate electrically conductive materials into stretchable polymeric materials into fabricate polymer nanocomposites with tuneable mechanical performance and electrical conductivity. Stretchable polymers typically include thermosetting elastomers [47,79], thermoplastic elastomers [65,80], hydrogels [81,82], and elastic textiles [83,84], whereas conductive nanomaterials predominantly include carbon nanomaterials, metal nanomaterials, liquid metals, MXenes, and conducting polymers [85–87]. By uniformly dispersing nanomaterials inside the polymer, the synergistic effects from the established conductive networks of the nanofillers within the matrix and the intrinsic stretchability and stability of the elastic polymer can be exploited. In this manner, wearable sensors with tuneable performance can be achieved. Techniques such as photolithography [27], spray coating [88], dip coating [89], vacuum infiltration [34], layer-upon-layer assembly [90], and electrospinning [33] can be applied to attain durable and sensitive composites as wearable sensors.

![Fig. 1. 3D printing techniques for fabricating strain, pressure, temperature, humidity, and multifunctional sensors for healthcare systems.](image-url)
The key metrics for assessing the performance of wearable sensors include sensitivity, stretchability, durability, linearity, hysteresis, and response and recovery times. As the main sensing parameter, sensitivity is described as the ratio of the relative change in the output signal to the applied stimulus, where the latter can be strain, pressure, temperature, or humidity [105]. The applied stimulus is typically presented on the x-axis, and the resulting output change is plotted on the y-axis. The slope of the resulting curve is the sensor sensitivity [106]. Stretchability is essential to ensure that the sensor can adapt to dynamic deformations during daily human activities. In other words, this factor determines the maximum strain under which the fabricated sensor can preserve its sensing characteristics when subjected to frequent loading–unloading cycles [73,107]. Durability is the ability of the wearable sensor to sustain stable response and structural integrity under long-term cycling [108].

Linearity, which reflects how close the sensitivity curve is to a straight line, can be determined through linear regression of the sensitivity curve [23]. Linear sensors are highly recommended as nonlinearities complicate the calibration and data processing of the resulting signals [22]. Hysteresis occurs when the output values during unloading do not match those during the loading cycle. Therefore, hysteresis is referred to as the maximum difference between the values measured at the same input in a specific loading–unloading cycle divided by the full-range output [106,109]. For wearable sensors based on conductive polymeric composites, the polymer–viscoelasticity and interfacial adhesion between the filler and matrix influence the generation of hysteresis [22,110]. Response time indicates the period in which the sensors reach their steady-state response during loading, whereas the recovery time indicates the time required for sensors to return to their initial state during unloading [111].

3. Conductive nanomaterials

The characteristics of conductive nanomaterials help control the electrical conductivity and other properties of the polymeric composites in which they are incorporated. The nanomaterials must be evenly distributed inside the soft matrix for constructing multiple electrically conductive networks. In this scenario, electrons can easily transport through the built-in pathways. The morphology, pristine electrical conductivity, and dispersibility of the nanomaterials influence the minimum required loading to generate the percolated networks inside the polymer matrix. A lower percolation threshold is desirable as minimal filler concentration can help preserve the intrinsic physical and chemical properties of the host polymer and ensure the cost-effectiveness of the final products. Additionally, intrinsically conducting polymers can be used, in which electrical currents are transmitted through their distinctive structures. This section describes the widely used conductive nanomaterials, and their properties are summarised in Table 1.

3.1. Carbon nanomaterials

Carbon is the fundamental building block of several materials. Carbon atoms can bind together in different arrangements to yield diverse carbon allotropes with unique morphologies and properties [133]. Carbon allotropes exhibit a wide range of material characteristics in terms of thermal (thermally conductive to insulative), electrical (electrically conductive to insulative), mechanical (hardest to softest), and optical (opaque to transparent) properties [134]. Therefore, these allotropes have attracted massive attention by academia and the industrial sectors in recent decades [66,135–137]. In terms of electrically conductive allotropes, carbon nanomaterials can be categorised depending on their dimensionality as 0D carbon black (CB), 1D carbon nanotube (CNT) and carbon nanofiber (CNF), and 2D graphene and its derivatives.

CB materials are aggregates of spherical carbon particles (10–100 nm in diameter) fabricated from the thermal decomposition of hydrocarbons. The structure of CB has an amorphous core enveloped by a shell of 2D stacked graphitic layers [138–140]. CB is a filler that has been widely used for leveraging the electrical conductivity of elastomeric composites owing to its abundance, low cost, reasonable electrical conductivity, and outstanding stability [24,141,142]. However, high CB fractions are typically required to attain electrically conductive composites. The resulting composites have been used in various applications, such as supercapacitors [143,144], batteries [145,146], and wearable devices [147,148].

CNTs are 1D nanomaterial that have a tubular structure consisting of carbon atoms in the sp² configuration. Generally, two forms of CNTs are

![Fig. 2. Summary of state-of-the-art studies in which wearable sensors were fabricated using conventional and 3D printing techniques [31,44,47,55,62,72,74,75,77,91–104].](image)
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epoxide groups on the basal plane and edges of the graphite oxide cylinders of wrapped graphene layers with diameters ranging from 2 to – vapour deposition (CVD) [162] , and epitaxial growth [163] . However, graphene and few-layer graphene (1

SWCNTs represent rolled-up mono-graphene layers with a diameter of – carbon atoms organised in a honeycomb-like architecture. High-quality derivatives include graphene oxide (GO), reduced graphene oxide (RGO), graphene nanoplatelet (GNP), and 3D graphene foams and aerogels. GO is obtained by severe oxidation of graphite using acids and oxidising agents that leads to the attachment of hydroxyl, carboxyl, and epoxide groups on the basal plane and edges of the graphite oxide sheets. Several GO sheets are obtained through ultrasonication in a solvent such as water [165] . The presence of these functional groups compromises the unique electronic structure of graphene and subsequently endows GO with chemical and electrical properties that are different from those of graphene [166] . Additional chemical or thermal treatment must be performed to restore the physical properties of graphene [167,168] . The final product after this reduction step is known as RGO. GNPs represent several stacks of graphene layers with a thickness of 1–5 nm [168,169] . This derivative is typically prepared using liquid phase exfoliation methods [170,171] . Unique and stand-alone 3D porous graphene structures such as aerogels and foams are designed to build interconnected conductive networks inside polymer matrices. These structures can be prepared by 3D printing [172] , template-assisted CVD [173] , and self-assembly [174] . The diverse graphene derivatives can be used to prepare customised composites with outstanding characteristics to fabricate wearable sensors [66,175,176] .

3.2. Metallic nanomaterials

Although carbon nanomaterials are chemically and thermally stable, their intrinsic electrical conductivity depends on their size, quality, and morphology. In comparison, metallic nanomaterials, such as silver (Ag), copper (Cu), and gold (Au), with diverse dimensionalities are superior candidates for yielding conductive polymer composites because of their distinctive electrical conductivity. By controlling the concentrations of the metallic nanomaterials inside the host matrix, the resulting composites can be tuned to fabricate a wide range of devices from highly sensitive sensors [97,177] to stretchable conductors with stable electrical conductivity [178,179] . Various wet chemical techniques have been reported to produce metallic nanostructures in the form of particles, wires, sheets, and rods [180–182] . Compared to nanoparticles and nanosheets, metallic nanowires exhibit high aspect ratios, flexibility, and conductivity. Therefore, they can facilitate the construction of robust conductive pathways through polymers with minimum filler-to-filler contact resistance [21] .

The high surface energy of Ag and Cu makes them susceptible to severe oxidation upon exposure to air and water vapour. This oxidation deteriorates the properties of these metals and thus those of the
resulting wearable devices. Furthermore, the leakage of toxic Ag ions from the oxidation of Ag nanomaterials can adversely influence human health [183]. Consequently, a protective coating must be introduced to improve the chemical stability of these materials [184]. In contrast, Au, as a noble material, exhibits chemical inertness, biocompatibility, non-toxicity, and flexibility, rendering it an ideal candidate for developing nanocomposites for wearable sensors and implantable devices [182, 185–187]. The wearable sensors that have been prepared using Au nanomaterials are highly sensitive and durable with fast responses and are thus suitable for healthcare and motion detection applications [32, 177]. Au nanomaterial can also be introduced as a sheath layer over AgNW to form chemically stable, biocompatible, and highly conductive hybrid nanostructures [184]. Nevertheless, the exorbitant cost and low mass production rates of Au nanomaterials limit their industrial application.

3.3. Liquid metals

Liquid metals are metals or metal alloys that melt near room temperature. The electrical and thermal conductivities of these materials are comparable with those of metals [188]. The most representative groups are gallium-based materials, such as eutectic gallium indium alloy (EGaIn; 75 wt% Ga and 25 wt% In; melting point: 15.5 °C) [188] and gallium–indium–tin alloy (Galinstan; 68.5 wt% Ga, 21.5 wt% In, and 10 wt% Sn; melting point: –19 °C) [128]. Unlike solid and rigid metals, liquid metals can deform and exhibit low viscosity, high stretchability, and self-healing capability [189, 190], which allow them to be directly patterned as circuits [191], electrodes [192], stretchable hermetic seals [193], and wearable sensors [194]. Moreover, liquid metals can be used as additives to improve the properties of polymer composites. For instance, liquid metal droplets were embedded into polydimethylsiloxane (PDMS) polymer using an immersion shear mixer and applied as a thermal interface material in wearable thermoelectric generators [195]. Liquid metals form a nano-thick oxide layer on their surfaces when exposed to air. During printing, this layer helps maintain the stability and integrity of the 3D-printed liquid metal structures and functions as an active site for in situ functionalisation with a variety of polymer brushes [196]. This framework can stabilise the liquid metal droplets and increase their compatibility with polymer matrices even if embedded with concentrations of as high as 50 wt% [197]. By adjusting the printing parameters and droplet size, spherical droplets of liquid metal within elastomeric media can be transformed into highly elongated ellipsoids and increase their compatibility with polymer matrices even if the printing parameters and droplet size, spherical droplets of liquid metal can form chemically stable, biocompatible, and highly conductive hybrid nanostructures [184].

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3.4. MXene

Since the discovery of graphene in 2004, researchers have increasingly focused on other 2D materials. MXenes are a contemporary family of 2D nanomaterials synthesised from ternary MAX ceramics with the general formula $M_{n+1}AX_n$ ($n = 1–4$), where M is an early transition metal, A is an element from group 13 or 14, and X is C or N [103]. The resulting MXene can be expressed as $M_{n+1}X_nT_x$, where $T_x$ represents the decorated functional groups (i.e., $–O_2$, $–OH$, and $–F$ groups). The universal strategy for producing MXene is to selectively etch the middle layer from the MAX gallery using controlled concentrations of hydrofluoric acid (HF). Nanosheets can then be obtained by performing delamination [198]. Other efficacious and safer methods have been established to obviate direct exposure to the toxic HF, such as the use of fluoride-containing salts and benign acids [199, 200], molten salts [201], and electrochemical etching [202]. More than 40 MXene nanomaterials have been synthesised from large precursors of more than 100 MAX phases [203].

When the ternary metal carbides/nitrides are etched with aqueous HF or in situ HF, the produced MXenes possess abundant terminations of functional groups (T$x$), leading to highly hydrophilic products that easily disperse in water without requiring surfactants. The conductivity of MXenes is close to that of metals (e.g., the value for Ti$_2$C$_2$Tx is $2.4 \times 10^4$ S/cm) [126]. Therefore, MXenes are considered ideal candidates for preparing conductive additives [204], sensors [205], supercapacitors [206], and batteries [207]. Moreover, MXenes exhibit a high Young’s modulus (∼330 GPa for Ti$_2$C$_2$Tx) and mechanical strength [125]. These features and straightforward fabrication processes render MXenes suitable for the evolution of polymer composites to fabricate wearable sensors.

3.5. Conducting polymers

Conducting polymers, such as polyaniline (PANI) and poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), exhibit exceptional electrical and optical properties. The structure of insulating polymers consists of covalently bonded sp$^2$ hybridised carbon atoms. In contrast, conducting polymers have a conjugated molecular structure with hybridised carbon atoms in the sp$^3$ arrangement. The electrons are highly mobile in the presence of highly delocalised π-bonds [131, 208]. To enhance the electrical conductivity and stretchability of such polymers, dopants and additives are incorporated using chemical or electrochemical methods [130, 132, 209]. For instance, various ionic additives were added to the PEDOT:PSS polymer to soften the PSS chains and densify the conductive networks between the PEDOT domains. The reported electrical conductivity of this polymer was more than 3100 S/cm with a maximum stretchability of up to 600% strain [210]. Owing to their high electrical conductivity, flexibility, chemical stability, biocompatibility, and mechanical properties, these polymers are primary candidates for preparing flexible electronic devices and strain-insensitive interconnections [44, 211–213]. To impart conducting polymers with shear-thinning characteristics suitable for 3D printing, cryogenic freezing was applied to aqueous PEDOT:PSS solution followed by freeze drying [44]. Printable ink was then obtained by dispersing the lyophilised polymer with controlled concentrations in a mixture of water and dimethyl sulfoxide. The developed ink was used to fabricate a flexible circuit and biocompatible neural probe for signal recording.

4. 3D printing techniques for fabricating wearable sensors

3D printing is a technique that yields products through a layer-by-layer assembly based on designed models [214]. First, computer-aided design software or a 3D scanner is used to create a 3D model, which is then exported to an STL file [215]. Subsequently, slicing software is used to transform the saved STL file into a G-code format. The designed model is sliced into a sequence of 2D layers, allowing the objects to be deposited in a layer-upon-layer style [214]. Various techniques have been used to print polymers and their composites; for example, fused deposition modelling (FDM), direct-ink writing (DIW), stereolithography (SLA), inkjet printing (IJ), binder jetting (BJ), and selective laser sintering (SLS). This section discusses these techniques, and their main characteristics are summarised in Table 2.

4.1. FDM

FDM, also known as fused filament fabrication, is a popular technology for printing 3D objects owing to its user-friendliness, low cost, and simplicity [216]. As shown in Fig. 3a, a filament is fed into the FDM printer, heated to a semi-molten state at the nozzle, and directly extruded onto the printing bed. Subsequently, the platform descends, and another layer is extruded in a similar manner. These steps are repeated until the 3D object is built in a layer-by-layer manner. The layers are fused and solidified at room temperature. The fidelity and integrity of the printed products rely on numerous factors, such as the nozzle diameter, temperature, raster angle, and layer height [217].
Several thermoplastic polymers, such as polycarbonate (PC) [218], polyolactic acid (PLA) [219], acrylonitrile butadiene styrene (ABS) [220], polyamide (PA) [221], poly(etheretherketone) (PEEK) [222], poly(vinyl alcohol) (PVA) [223], polyethylene terephthalate glycol (PETG) [224], and thermoplastic polyurethane (TPU) [225], have been printed using FDM. To fabricate composite filaments, solution mixing or melt compounding are typically performed to premix the nanofiller and matrix. Subsequently, the mixture is extruded through a single- or twin-screw extruder to yield the filaments [226]. The nanofiller dispersion inside the polymer and heating temperature are crucial parameters for attaining a higher homogeneity and minimum voids in the printed products, as void formations can deteriorate the quality, structural integrity, and mechanical properties of the final objects [19].

As shown in Fig. 3b–d, FDM can be used to build complex structures such as soft actuators for robotic applications [227,228], overhanging structures based on sacrificial materials [229], and hierarchical polymeric structures [230]. Multiple nozzles can be integrated into the FDM machine to selectively print different materials through a one-pot process, yielding precisely controlled and intricate multi-material structures [19,223,224,231,232]. For example, a commercial FDM installed with a dual printhead was employed to print a smart tensile structure (Fig. 3e) [223]. This was accomplished by simultaneously printing a sacrificial mold having an internal channel network and struts using PVA and PLA filaments, respectively. Then, an uncured polymeric smart material was injected into the built-in channels, followed by curing and dissolving the mold in water. Furthermore, a microfluidic capillary electrophoresis device was fabricated using two extrusion nozzles (Fig. 3f) [224]. PETG filaments were used to print the main body with the built-in reservoirs and channels, while conductive filaments of PLA reinforced with graphene or CB were employed to generate the electrodes. To fabricate freestanding and shape-customised porous wearable sensors, sacrificial polymeric hollow templates using ABS polymers were constructed using FDM, as depicted in Fig. 3g [233]. Two approaches were used to synthesise flexible porous sensors derived from GNP-based silicone rubber (SR). First, a mixture of SR and hardener were cast into the printed mould. After curing, the ABS mould was dissolved in acetone, leaving behind the porous SR sample. Dip coating was performed to deposit GNP over the sample surface. Second, the porous sensor was obtained by coating GNP over the ABS mould. Subsequently, the SR was cast into the coated mould and cured, resulting in a porous SR sample with GNP embedded in the top surface after washing away the ABS mould. The second method yielded porous sensors with stable conductivity for more than 12 months and high resistance upon exposure to organic solvents. Furthermore, the sensors demonstrated a gauge factor (GF) of as high as 10 at 2–10% compressive strain and a stable response over 400 cycles.

### 4.2. DIW

DIW is an extrusion-based 3D printing technique that enables the deposition of functional materials in the form of viscous inks through a pressurised syringe in a layer-by-layer manner, as shown in Fig. 4a. To obtain a processable ink, the viscosity must be modulated using rheological modifiers and additives [234,235]. Specifically, the ink must exhibit low viscosity during plotting to ensure flowability and high viscosity after printing to maintain the structural integrity of the printed material [236,237]. After final deposition, the printed objects can be post-cured by heat [238] or ultraviolet (UV) induction [239]. Other factors such as the nozzle diameter, printing speed, and applied pressure must be optimised depending on the material to be printed, as they affect the printing resolution, final shape precision, and building time [240]. In contrast to FDM, this technique offers significant flexibility in terms of the starting material. Polymers and polymer composites in the form of pastes can be printed using DIW as long as they fulfil the rheological property requirements. Moreover, the cost-effectiveness, high freedom of material utilisation, and room temperature printing of DIW facilitate the fabrication of highly stretchable and tailorable wearable sensors [57,236].

To enable multi-material printing in a single printing job, multiple extrusion heads can be integrated into the DIW machine [97,234,241–246]. For instance, Kokkinis et al. [243] introduced a magnetically assisted multi-material 3D printing with five degrees of freedom and could thus be used to create heterogenous structures with exceptional microstructural features (Fig. 4b). Lind et al. [244] devised multi-material 3D printing to fabricate fully integrated cardiac micro-physiological devices (Fig. 4c). Six different materials were extruded in a layer-by-layer manner, including biocompatible and soft materials, highly conductive leads, and strain sensors. Such a scenario enabled the integration of sensors composed of CB/TPU ink within engineered micro-architectures, which guided the self-assembly of physio-mimetic laminar cardiac tissues. Therefore, the sensors provided a non-intrusive analysis of tissue contractile stresses. Moreover, free-standing coaxial filaments with multi-materials can be fabricated through core–shell/coaxial DIW printing using nozzles and printheads with sophisticated designs [247–252]. Frutiger et al. [247] fabricated a coaxial aligned capacitive strain sensor consisting of alternating layers of ionically conductive fluid and a silicone polymer (Fig. 4d). What is more, embedded 3D printing has been executed to print functional materials inside uncured elastomer matrices [47,104,253–256]. Muth et al. [47] first introduced this method to directly extrude conductive inks inside elastomeric matrices to prepare extensible strain sensors. As shown in Fig. 4e, this method uses conductive ink (conductive carbon grease), an elastomeric reservoir, and a filler fluid (with the latter two being Ecoflex 00–30). This reservoir exhibited shear-thinning behaviour that facilitated the extrusion of ink and nozzle movement. In contrast, the filler fluid exhibited Newtonian behaviour with low viscosity to concurrently fill the voids appearing from the nozzle translation. Various thinning and thickening agents were used to modulate the viscosity of Ecoflex. The resultant strain sensor exhibited a GF of 3.8 with stretchability of up to 400%, with considerable hysteresis observed.

### Table 2

Main characteristics of 3D printing techniques.

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<tr>
<th>3D printing technique</th>
<th>3D printing material</th>
<th>Typical neat polymers</th>
<th>Principle</th>
<th>Advantages</th>
<th>Disadvantages</th>
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</thead>
<tbody>
<tr>
<td>FDM</td>
<td>Filament</td>
<td>Thermoplastics</td>
<td>Filament extrusion</td>
<td>Simple, low cost, and multi-material ability</td>
<td>Low resolution, slow, void formation, and nozzle clogging</td>
</tr>
<tr>
<td>DIW</td>
<td>Viscous liquid orpaste</td>
<td>Elastomers and thermoplastics in solutions</td>
<td>Pressurised syringe extrusion</td>
<td>Simple, low cost, multi-material ability, high speed, and high resolution</td>
<td>Nozzle clogging, post-curing, and rheology control</td>
</tr>
<tr>
<td>SLA</td>
<td>Photopolymer</td>
<td>Epoxy and acrylate</td>
<td>Laser scanning and polymerisation</td>
<td>High resolution, multi-material ability, and nozzle-free fabrication</td>
<td>High cost, slow, and material limitations</td>
</tr>
<tr>
<td>LJ</td>
<td>Ink or paste</td>
<td>Conductive inks andhydrogels</td>
<td>Continuous or drop-on-demand</td>
<td>High resolution, multi-material ability, and high speed</td>
<td>Complex ink properties and postprocessing</td>
</tr>
<tr>
<td>BJ</td>
<td>Powder</td>
<td>Polymers in powder</td>
<td>Powder fusion by binder jetting</td>
<td>Low cost, multi-material ability, and self-supporting powder</td>
<td>Low resolution, porosity, binder contamination, and post-curing</td>
</tr>
<tr>
<td>SLS</td>
<td>Polymers in powder</td>
<td>Polymers in powder</td>
<td>Powder fusion by laser</td>
<td>High resolution, multi-material ability, and self-supporting powder</td>
<td>High cost and porosity</td>
</tr>
</tbody>
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**Figure 3**

(Fig. 3f) [224]. PETG filaments were used to print the main body with reinforced with graphene or CB were employed to generate the electrodes. To enable multi-material printing in a single printing job, multiple extrusion heads can be integrated into the DIW machine [97,234,241–246]. For instance, Kokkinis et al. [243] introduced a magnetically assisted multi-material 3D printing with five degrees of freedom and could thus be used to create heterogenous structures with exceptional microstructural features (Fig. 4b). Lind et al. [244] devised multi-material 3D printing to fabricate fully integrated cardiac micro-physiological devices (Fig. 4c). Six different materials were extruded in a layer-by-layer manner, including biocompatible and soft materials, highly conductive leads, and strain sensors. Such a scenario enabled the integration of sensors composed of CB/TPU ink within engineered micro-architectures, which guided the self-assembly of physio-mimetic laminar cardiac tissues. Therefore, the sensors provided a non-intrusive analysis of tissue contractile stresses. Moreover, free-standing coaxial filaments with multi-materials can be fabricated through core–shell/coaxial DIW printing using nozzles and printheads with sophisticated designs [247–252]. Frutiger et al. [247] fabricated a coaxial aligned capacitive strain sensor consisting of alternating layers of ionically conductive fluid and a silicone polymer (Fig. 4d). What is more, embedded 3D printing has been executed to print functional materials inside uncured elastomer matrices [47,104,253–256]. Muth et al. [47] first introduced this method to directly extrude conductive inks inside elastomeric matrices to prepare extensible strain sensors. As shown in Fig. 4e, this method uses conductive ink (conductive carbon grease), an elastomeric reservoir, and a filler fluid (with the latter two being Ecoflex 00–30). This reservoir exhibited shear-thinning behaviour that facilitated the extrusion of ink and nozzle movement. In contrast, the filler fluid exhibited Newtonian behaviour with low viscosity to concurrently fill the voids appearing from the nozzle translation. Various thinning and thickening agents were used to modulate the viscosity of Ecoflex. The resultant strain sensor exhibited a GF of 3.8 with stretchability of up to 400%, with considerable hysteresis observed.
During loading–unloading cycles, Wehner et al. [253] used embedded 3D printing to integrate pneumatic control channels into a moulded octobot body (Fig. 4f).

To upgrade multi-material DIW 3D printing with ultrahigh resolution and short building times, Skylar-Scott et al. [257] developed multi-material multi-nozzle 3D printing to construct highly accurate heterogeneous structures, such as a voxelated matter and a Miura origami pattern, in a voxel-based manner (Fig. 4g). This was achieved by fabricating printheads capable of extruding up to eight different materials simultaneously from a single nozzle with excellent frequency switching through independent dividing channel networks. Recently, Larson et al. [258] have created a rotational multi-material 3D printing to fabricate helically architected filaments with subvoxel control (Fig. 4h). Accordingly, 3D printed artificial muscles consisted of a cylindrical elastomeric matrix embedded with conductive channels in a helical configuration was obtained by vertical printing. When a voltage was applied across the helical filaments, they underwent twisting and axial extension or compression according to the designed rotation rate.
4.3. SLA

SLA represents one of the earliest 3D printing techniques. This method uses a UV laser with a well-defined path to scan and polymerise a light-sensitive polymer resin into a 2D layer. After curing, the platform descends, and an additional layer of the photopolymer is polymerised until the complete part has been printed, as shown in Fig. 5a. At the end of the process, the printed parts are isolated from the uncured resin vat and may be subjected to post-curing in a UV chamber [40,259]. The curing reactions must be well understood to adjust the resolution and mechanical properties of the printed products [260]. The SLA polymer resin typically contains monomers, oligomers, photoinitiators, and fillers. Monomers and oligomers are the essential elements that instantly combine and crosslink upon exposure to UV light to form polymer
Fig. 5. (a) Schematic of SLA. b) DLP 3D-printed structures based on MWCNT-reinforced composites (black) and neat resins (yellow and orange): (i) spring, (ii) hollow structure truss, (iii) capacitor with hollow structure, (iv) wave shape resistor, (v) capacitor array, (vi) capacitor with different heights, (vii), and (viii) structures printed with three types of materials. Scale bar is 10 mm. (c) DLP 3D-printed structure consisting of a rigid material, a hydrogel, and an elastomer. (d) Schematic and photograph of the printed soft pneumatic actuator coupled with conductive hydrogel strain sensor. (e) Application of the hydrogel as a drug delivery stent, where the hydrogel loaded with drugs surrounds a shape memory polymer (SMP) rod. (f) Schematic of the centrifugal multi-material DLP printing and the components of the soft pneumatic actuator seamlessly integrated with temperature, pressure, and bending sensors. (g) Indirect 3D printing of a porous flexible strain sensor (PFSS). (h) Complex structures fabricated using this method: (i) gyroid, (ii) finger cover, (iii) porous lattice, and (iv) octopus. Scale bar is 8.5 mm. (i) Fabricated micro-architected graphene using μ-SLA, including gyroid (top) and cuboctahedron (bottom). (j) Electrical field-assisted μ-SLA of 3D-printed bioinspired nacre-like structures and smart helmet with self-sensing abilities. (k) Selective deposition of conductive materials into 3D-printed multi-materials structures: (i) a conductive circuit deposited into an arbitrary pyramid, (ii) metal-dielectric double gyroid, and (iii) tactile piezoelectric sensor. (b) Reproduced with permission [272]. Copyright 2017, Elsevier. (c-e) Reproduced under terms of the CC-BY license [100]. Copyright 2021, American Association for the Advancement of Science. (f) Reproduced under terms of the CC-BY license [279]. Copyright 2022, Springer Nature. (g-h) Reproduced with permission [285]. Copyright 2020, Wiley-VCH. (i) Reproduced under terms of the CC-BY license [287]. Copyright 2018, Royal Society of Chemistry. (j) Reproduced under terms of the
networks [261]. Photoinitiators are used to initiate polymerisation by producing reactive species under UV light [262]. Finally, fillers are added to enhance the resin performance. Typical polymers such as acrylic and epoxy-based resins are commonly used in SLA [263]. To control the curing duration and printing quality, parameters such as the laser power intensity, exposure time, and scanning speed must be optimised [260]. SLA can print complex structures with high-quality. However, this method is expensive and slow and only a few polymers can be processed. This limited scalability impedes the industrial application of SLA [40,263]. Furthermore, traditional SLA is not practically viable for multi-material printing due to the need for frequent material exchange, which further increases the printing time [264,265]. Instead, two-photon SLA (also known as laser direct writing) integrated with a microfluidic chamber has been performed to fabricate multi-material structures with ultrahigh resolutions [266,267]. While the microfluidic chamber efficiently provides multiple materials, the two-photon SLA enables printing with sub-100 nm resolutions because the laser can concentrate at a minimal volume of the photopolymer. However, the point-by-point nature of the two-photon SLA yields an excessive printing time [268–270].

Other Variants of the SLA technique include digital light processing (DLP) and micro-stereolithography (μ-SLA). DLP is analogous to SLA except that a projected light source is used to concurrently cure the complete layer of the resin [260]. This framework expedites the printing and renders DLP suitable for fabricating wearable strains. Additionally, DLP can fabricate intricate multi-material structures utilising switchable vats [100,271–279], or chemoselective wavelength-control technique to accurately cure various resins in a single vat [280–282]. Mu et al. [272] used a bottom-up DLP technique for developing conductive MWCNT-reinforced photocurable acrylic resin. Several complex structures were generated using single or multi-materials (Fig. 5d). Moreover, the authors fabricated a sensitive strain sensor with a GF of 38 at 2.5% strain. Ge et al. [100] applied multi-material DLP to synthesise hybrid structures composed of acrylamide-based hydrogels. These hydrogels were strongly bonded with different UV curable polymers, such as shape memory polymers, elastomers, Vero rigid polymers, and other (meth) acrylate-based curable polymers (Fig. 5c). The authors demonstrated the potential of soft materials as flexible strain sensors and drug delivery materials (Fig. 5d, e). Most multi-material DLP processes require manual [272,277] or air-jet cleaning [100,273] for residual resin removal during vat switching, which can hamper the quality and building time of the multi-material printed parts. Instead of that, Cheng et al. [279] have recently introduced a centrifugal multi-material 3D printing by installing a rotary motor on the DLP printing platform (Fig. 5f). This strategy provided quick removal of the residual resin during multi-material switching, thus creating heterogenous structures with high resolution. A soft pneumatic actuator with five different materials was fabricated where temperature, pressure, and bending sensors were integrated. DLP can also be used to build complex sacrificial moulds to fabricate structures from materials that are unprintable using DLP [283–285]. For example, Peng et al. [285] devised a DLP technique to fabricate a 3D-printed sacrificial mould composed of 4-acyrylamorpholine (ACMO, monomer) and hindered urea acetate (crosslinker). This mould was then cast with highly conductive MWCNT/PU composite. After curing, the mould was dissolved in hot water to yield a porous sensor, as shown in Fig. 5g, h. The resultant sensor demonstrated high pressure sensitivity (0.111 kPa⁻¹), stretchability (510%), and stability after 100 cycles at a compressive strain of 60%. Additionally, the shape of the porous sensor could be tailored to enable in situ recognition of different human activities.

μ-SLA can be applied for 3D printing detailed and intricate shapes with high resolutions (0.6–30 μm) [286]. Compared with SLA, the scanning system of μ-SLA involves an additional component (i.e., a digital micromirror device). This auxiliary part is used to concentrate the UV laser to precisely adjust the photo-activation of the polymer in a minimal area [263]. Hensleigh et al. [287] optimised and fabricated photocurable acrylic/GO resins that were sequentially 3D printed through μ-SLA to obtain complex hierarchical graphene micro-architectures (Fig. 5i). The sizes of the 3D porous structures ranged from a few to hundreds of microns, highlighting the superior resolution of this technology. The micro-architected graphene exhibited an excellent surface area (130 m²/g) and high electrical conductivity (64 S/m) and could thus be used to obtain high-performance pressure sensors with mesoscale architectures. Electrical field-assisted μ-SLA was used to engineer complex hierarchical structures (i.e., bioinspired nacre-like structures) and a smart helmet with self-sensing abilities, as shown in Fig. 5j [288,289]. The aligned nanosheets acted as bricks inside the polymer matrix, which served as mortar. Hensleigh et al. [290] developed a novel protocol to selectively deposit functional materials into intricate multi-materially printed structures based on localised electrostatic interaction (Fig. 5k). They utilised charged and neutral resins to fabricate lead-zirconate-titanate/photopolymer piezoelectric composites with selectively coated copper electrodes over the pre-programmed charged resin. This led to the fabrication of a tactile sensor that could be applied to the fingertip of a smart prosthesis for acquiring a precise sensation.

### 4.4. IJ

In IJ or polyjet printing, multi-channel jetting heads are used to deposit small droplets of a fluid-like photopolymer onto a platform following the designed model [25,40]. The interactions among nearby droplets yield a continuous pattern (Fig. 6a), which is further cross-linked by exposure to auxiliary UV light [25]. Unlike SLA, IJ requires the use of a supporting material in addition to the building material to prepare complex structures [291]. These supporting materials can be removed through postprocessing. IJ operation involves two main modes: continuous and drop-on-demand inkjet printing [292]. In the continuous mode, ink is continuously ejected from the printing head, and the desired/unwanted droplets are adjusted by applying a potential to the jetting head to charge each formulated droplet. This operation is typically performed for high-speed printing. In the drop-on-demand mode, the droplets are ejected only when an acoustic pulse is generated, either thermally [293] or through piezoelectric effects [294]. The printing speed in this mode is lower than that in the continuous mode, but it achieves precise fabrication involving smaller droplets [25]. The key to successful IJ is to adjust the viscosity, surface tension, and wettability of the ink [292,295]. The ink viscosity must be adequately low to facilitate its propulsion from the nozzle, and surface tension must be maintained to preserve the spherical shape of the printed droplets [292]. Additionally, ink wettability is crucial to confine the droplet spreading likelihood [296]. Conductive materials in aqueous and organic solvents [297–300] and polymers, such as polycaprolactone (PCL) [301] and hydrogels (e.g., PEDOT:PSS [302], PANI [303], and alginate [304]), are typical materials printed using this technology.

Several nozzle heads can be integrated into the IJ machine to rapidly disperse millions of droplets of different polymeric materials or nanoparticle inks, resulting in sophisticated multi-material structures [229,295,305–312]. For example, a bio-inspired Softworm robot (Fig. 5b) was printed using a flexible polymer (Tangoplus™) and hard polymer (VeroClear™) [305]. The lower part of this flexible robot had transverse ribs with channels to insert shape memory alloy actuators to power the robot. A high-resolution voxelated artwork consisting of multiple photopolymer resins is shown in Fig. 6c [229]. To emphasize the
potential capabilities of IJ printing, different sensors and arrays with high precision and customized patterns were introduced. Fu et al. [313] fabricated highly sensitive and durable sensors and arrays that could sense bending and pressure (Fig. 6 d). Additionally, highly conductive traces with high resolution printed over flexible substrates were fabricated using single or multi-material IJ printing, as shown in Fig. 6 e [314, 315]. Lin et al. [307] fabricated a wearable self-powered sensor integrated with supercapacitors, interconnects, and a gas sensor, all printed using IJ (Fig. 6 f). Yu et al. [311] fabricated a multi-modal robotic sensing system consisted of two fully inkjet-printed soft devices, including robot electronic skin (e-skin-R) and human electronic skin (e-skin-H), as displayed in Fig. 6 g. The developed e-skin-R, which coupled with pressure, temperature, and chemical sensors, provided tactile sensing, electrophysiology recording, and robotic sensing of several hazardous chemicals. Additionally, the e-skin-H device was employed as a human-machine interface for robotic control.

Fig. 6. (a) Schematic of IJ. (b) Schematic of bio-inspired 3D-printed Softworm robot. (c) High-resolution voxelated artwork fabricated by multi-material IJ. (d) Schematic of the preparation of the inkjet-printed bimodal sensor and sensing array. (e) Photographs of inkjet-printed conductive traces with high resolution fabricated from: (i) AuNP ink over a polyethylene naphthalate substrate. (ii) AgNP and carbon inks over a polyimide substrate. (f) Schematic and operational mechanism of the self-powered wearable sensor. (g) Schematic of the multi-modal robotic sensing system, which consisted of fully inkjet-printed soft devices, such as e-skin-R and e-skin-H, for multi-modal sensing and human-robot interactions. (b) Reproduced with permission [305]. Copyright 2016, IOP publishing. (c) Reproduced with permission [229]. Copyright 2016, Springer Nature. (d) Reproduced with permission [313]. Copyright 2019, Wiley-VCH. (e, i) Reproduced with permission [314]. Copyright 2015, Wiley-VCH. (e, ii) Reproduced under terms of the CC-BY license [315]. Copyright 2018, Springer Nature. (f) Reproduced with permission [307]. Copyright 2018, Wiley-VCH. (g) Reproduced with permission [311]. Copyright 2022, American Association for the Advancement of Science.
4.5. BJ

BJ or three-dimensional printing (3DP) is a powder-based technology in which layers of powdered particles adhere together by a liquid binder delivered from an inkjet dispenser, as displayed in Fig. 7a. Before printing, the powder bed is uniformly heated to the desired processing temperature [316]. Subsequently, a thin layer of polymer powders is evenly spread onto the building platform using a roller. The liquid binder is deposited onto the first layer, and it glues the particles together based on the designed model. Next, the stage descends, and another layer of powder is provided and distributed over the building platform. In this manner, the second layer is prepared for binding. This process is repeated until the 3D customised model is built [263]. The unbounded powders can support model building. After printing, the excess powders can be recycled for another printing job, which helps reduce the waste generated from this technique. Additionally, BJ is cost-effective and rapid and can print large-volume parts. However, the printed objects are highly porous and fragile owing to the absence of sintering or melting during this process [317]. Therefore, the finished parts must be post-cured with heat to enhance the binding strength between particles [11]. The composition, morphology, and thermal properties of the powders, binder formulation, polymer/binder interaction, and post-processing characteristics influence the properties of the printed objects [318].

Theoretically, any polymer that can be supplied in powder form can be processed through BJ. However, unlike metals and ceramics, polymers are rarely fabricated as fine powders because of their complicated thermal properties and restricted formulations [319,320]. In addition, the liquid binder is challenging to formulate. Consequently, BJ has rarely been used to obtain polymer composites. Shen et al. [321] prepared an aqueous GO ink with a concentration of 0.5 mg/mL for printing onto polyvinyl alcohol (PVOH) powder to produce highly porous

![Fig. 7. Schematic of powder-based 3D printing techniques: (a) BJ and (b) SLS. (c) Parts with complex geometries printed using SLS with nylon powders: (i) arterial vascular tree, (ii) diamond, and (iii) diagrid structures. Scale bar is 1 cm. (d) Fabrication of pressure sensors of minimal-surface-derived porous structures (Schwarz, gyroid, and diamond macrostructures) by SLS 3D printing using TPU/CNT powders.](image-url)
composites. Chemical reduction of the printed composites by hydroiodic acid increased the electrical conductivity to 0.0925 S/m and enhanced the stability under cyclic tensile loading, rendering the prepared materials suitable for sensor applications.

4.6. SLS

SLS is a powder-based technology similar to BJ, except that a high-energy laser beam is used to accomplish the binding of polymer powders (Fig. 7b). Specifically, the emitted beams sinter and fuse the particles at a temperature below their melting point [322]. Semi-crystalline thermoplastic polymers, such as polyamide (PA; especially PA11 and PA12) [323], PCL [324], and PLA [316], are typically used owing to their clear melting and consolidation behaviours. Examples of SLS-printed parts using PA12 (nylon) powders are shown in Fig. 7c [325]. Amorphous polymers, such as polyurethanes (PUs), have also been printed. However, the lack of definite melting temperatures adversely influences the mechanical properties of the final products [316]. To acquire laser-sintered polymer composites for wearable sensors, feedstock polymer powders can be premixed with nanofillers through mechanical or solution mixing. Subsequently, the composites in powder form can be applied to the SLS system [326]. The quality and properties of the printed parts can be modified by the composition, morphology, and thermal properties of the powders and process conditions, such as the laser power, scanning speed, and printing temperature [322]. Compared with BJ, SLS yields products with higher quality. Additionally, multi-material printing is possible by using vibrating, electrostatic, or pneumatic nozzles that can travel across the building area and deposit several polymer powders [327–330].

Xia’s group [331–333] SLS printed minimal surface-derived 3D porous structures with Schwarz, gyroid, and diamond architectures as flexible pressure sensors using CNT-wrapped TPU powders (Fig. 7d). The SLS machine was equipped with a 60-watt CO$_2$ laser to merge and sinter the powders. Because SLS 3D printing is a nearly shear- and flow-free technique, the CNTs decorated on the surface of the TPU powders were driven into the space between the TPU particles. This phenomenon resulted in the generation of robust electrically conductive segregated networks inside the matrix, which enhanced the sensitivity of the sensors with all 3D configurations. The Schwarz topology outperformed the other structures in terms of the piezoresistive performance owing to the presence of high stress concentration regions that resulted in large variations in the resistance upon loading.

5. 3D-printed wearable sensors

5.1. 3D-printed wearable strain/pressure sensors

Wearable strain/pressure sensors that can transduce mechanical deformations into electrical signals have attracted significant attention for a wide range of applications, such as individual healthcare inspection (i.e., pulse rate, respiratory rate, and swallowing) [70,71], human and robot joint movements [334,335], and human–machine interfaces [17,336]. Wearable strain/pressure sensors can be divided into resistive, capacitive, piezoelectric, and triboelectric sensors according to the transduction principle. The mechanisms, advantages, and disadvantages of these sensors are presented in Fig. 8. Resistive sensors consist of an electrically conductive sensing element designed over flexible substrates. The resistance changes when the sensor is subjected to external strain/pressure [28,109,337]. Capacitive sensors are designed by sandwiching a deformable dielectric layer between two electrodes. Upon stretching/compressing the sensor, the thickness of the deformed dielectric layer varies to induce capacitive changes [338–342]. Piezoelectric sensors generate electric charge at the piezoelectric surface. When an external load is applied, the material polarisation changes to induce current flow [343–345]. In triboelectric sensors, two dielectric materials with different electronegativities are compressed to produce...
triboelectric changes at the interfaces. Upon releasing the applied force, the separation between both layers induces a potential difference [345–347]. Piezoelectric and triboelectric sensors can generate electricity and thus be considered self-powered sensors that are ideal for energy harvesting [348–350]. However, these sensors have limited stability and resolution and involve complex measurements, which limits their use as wearable sensors [31,120]. In contrast, resistive and capacitive sensors have high sensitivity and stretchability and straightforward read-out systems [49,73]. Resistive sensors have a simpler design than those of their capacitive counterparts and outperform the other sensors in terms of sensitivity. Therefore, this section focuses on the mechanisms and state of the art of 3D-printed resistive wearable strain/pressure sensors.

5.1.1. Resistive-type sensitivity mechanisms

The sensitivity of resistive force sensors is defined as the ratio of the relative resistance change (ΔR/Ro) to the applied strain/pressure [105]. Thus, the sensitivity, which is commonly reflected as the GF, can be expressed as follows [351]:

\[ GF = \frac{\Delta R}{R_o \cdot X} \]  

(1)

where \( X \) is the applied strain (ε) for strain sensors or applied pressure (ΔP) for pressure sensors. The change in the resistance of sensors based on metallic or semiconducting elements typically depends on their geometry and resistivity changes:

\[ \frac{\Delta R}{R_o} = (1 + 2\nu)\varepsilon + \frac{\Delta \rho}{\rho_o} \]  

(2)

where \( \nu \) represents the material’s Poisson ratio, and \( \Delta \rho/\rho_o \) reflects the relative resistivity change of the material upon loading. The sensitivity of such bulky sensors can be modulated by varying the electronic conduction in conductive polymer composites is governed by percolation theory, in which electrons move through electrical conduction networks built from the conductive fillers [164]. When these composites are stretched, several conductive fillers disconnect or slip (Fig. 9a). In this case, the overlapping or contacting area between the fillers decreases, thereby raising the electrical resistance of the sensors [354–356]. The slippage occurs owing to the large elastic mismatching between the fillers and stretchable polymer matrix and the weak friction between the overlapping conductive fillers [353]. This principle is known as the disconnection mechanism.

Tunnelling refers to the jumping or hopping of electrons through closely spaced conductive fillers separated with an extremely thin insulating polymer layer, resulting in electrical conduction. In other words, electrons can transfer through the polymer composite through not only direct conductive pathways from connected fillers but also tunnelling junctions between neighbouring fillers [357,358]. Upon stretching/compression, the destruction or densification of the conductive networks causes sharp variations in the tunnelling resistance (Fig. 9b), which help tune the sensitivity [359–361]. The tunnelling resistance (Rt) can be calculated based on Simmons’s theory [22,355,360]:

\[ R_t = \frac{V}{AJ} \exp \left( \frac{4\pi d \sqrt{2m\lambda}}{h} \right) \]  

(3)

where \( V \) is the electrical voltage across the polymer layer, \( A \) is the cross-sectional area of the tunnelling junction, \( J \) is the tunnel current density, \( h \) is Planck’s constant, \( e \) is the electron charge, \( m \) is the electron mass, \( \lambda \) is the energy barrier height of the polymer, and \( d \) is the thickness of the polymer layer or spacing between the neighbouring conductive fillers.

Although cracks are defects that must be eliminated in rigid structural designs, the introduction of cracked structures in conductive polymer composites can enhance the sensor sensitivity and stretchability. This mechanism is inspired by the crack-shaped sensory system of spiders [94]. Microcracks are initiated at stress concentration regions to dissipate the accommodated stresses and propagate upon straining (Fig. 9c), thereby varying the overall resistance [362,363]. Cracking can
be initiated by bending the samples over a controlled curvature [94,364] or prestretching [108,177,365].

5.1.2. 3D-printed wearable strain sensors

Table 3 summarises the main characteristics of 3D-printed strain sensors based on polymer composites. Carbon nanomaterials, particularly CNTs, have been widely used to fabricate wearable strain sensors using 3D printing, owing to their high conductivity, flexibility, and aspect ratio. Christ et al. [225] performed FDM to prepare MWCNT-reinforced TPU composites as strain sensors, as shown in Fig. 10a. Near the percolation threshold (2 v% MWCNT), the nanotubes’ interconnections became highly responsive to deformations and therefore easily disconnected under stretching. Thus, the GF of the sensors was increased to 176 at 65% strain. However, the fabricated sensors suffered from large hysteresis and double-peak incidence in the sensitivity curve (Fig. 10b), attributable to the competition between hydrogen bonds with the elastic polymer. Consequently, the FDM-printed sensors demonstrated reduced hysteresis and high sensitivity of 117,213 at 250% strain. Innovative and conductive 3D-printed CNTs and TPU matrix by forming π–π interactions with the CNTs and hydrogen bonds with the elastic polymer. Consequently, the FDM-printed sensors demonstrated reduced hysteresis and high sensitivity of 117,213 at 250% strain. Innovative and conductive 3D-printed fibres and textiles with intrinsic breathability, wearability, and flexibility are promising material candidates for strain sensors. Cao et al. [366] formulated a hybrid ink by stirring modified cellulose nanofibers (TOCNFs) and 2D Ti3C2Tx MXene nanosheets. A mesh-like strain sensor (derived from the composite fibres) was fabricated by DIW, as shown in Fig. 10d. The GFs of the printed sensors were 87.8 and 399.5 within strain ranges of 4–8% and 8–10%, respectively.

Although it is challenging to directly print strain sensors and arrays and place them with electronic components in a single platform, such frameworks can help eliminate supplementary manual or automated assembly and transfer steps. Valentine et al. [96] reported a hybrid 3D printing technique in which directly printed conductive composites were combined with automatic pick-and-place electronic components. As shown in Fig. 10e, f, conductive inks based on Ag/TPU were patterned as sensor arrays, and electronic components such as LEDs were picked and deposited to their target positions by vacuum using an unloaded nozzle. A serpentine strain sensor integrated with a microcontroller circuit was fabricated using this strategy to provide comprehensive information regarding elbow joint bending angles, as shown in Fig. 10g. The microcontroller device transmitted the resultant strain data into five indicator LEDs, which simultaneously gave different readouts according to the bending angle.

Microscale strain sensors 3D printed at high resolutions are particularly useful for miniaturised applications. To this end, in DIW, the rheology of the printing inks can be tuned to allow them to be extruded from tiny nozzles. A typical shear-thinning ink was extruded from minuscule nozzles with diameters of as small as 50 μm by intermingling

Table 3

<table>
<thead>
<tr>
<th>Method</th>
<th>Strain sensor</th>
<th>GF (at strain%)</th>
<th>Strain range (%)</th>
<th>Linearity</th>
<th>Durability (cycles)</th>
<th>Ref.</th>
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<tr>
<td>FDM</td>
<td>MWCNT/TPU</td>
<td>176 (65%)</td>
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<td>f-CNT/TPU</td>
<td>11.25 (20%)</td>
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<td>AgNP/MWCNT/TPU</td>
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<td>GNP/MWCNT/TPU</td>
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<td>Ti3C2/CNT/TOCNF</td>
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<td>500</td>
<td>[366]</td>
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<td></td>
<td>ROG@TRGO/PDMS</td>
<td>88,433 (350%)</td>
<td>0–350</td>
<td>No</td>
<td>5000</td>
<td>[356]</td>
</tr>
<tr>
<td></td>
<td>GNP/PDMS</td>
<td>67 (20%)</td>
<td>0–20</td>
<td>Yes</td>
<td>100</td>
<td>[378]</td>
</tr>
<tr>
<td></td>
<td>Ag/TPU</td>
<td>13.3 (15%)</td>
<td>0–30</td>
<td>Yes</td>
<td>3000</td>
<td>[96]</td>
</tr>
<tr>
<td></td>
<td>Ca-PAA-SA-CNT hydrogel</td>
<td>6.29 (50%)</td>
<td>&gt; 100</td>
<td>No</td>
<td>200</td>
<td>[101]</td>
</tr>
<tr>
<td></td>
<td>PAAM/PDMS-LiCl hydrogel</td>
<td>0.84 (50%)</td>
<td>0–150</td>
<td>Up to 40%</td>
<td>–</td>
<td>[379]</td>
</tr>
<tr>
<td></td>
<td>x-carrageenan-PAAM hydrogel</td>
<td>0.63 (1000%)</td>
<td>0–1000</td>
<td>No</td>
<td>10</td>
<td>[380]</td>
</tr>
<tr>
<td></td>
<td>PU/PVA/Ti3C2T2 hydrogel</td>
<td>5.7 (66–191%)</td>
<td>0–191</td>
<td>Up to 66%</td>
<td>5000</td>
<td>[102]</td>
</tr>
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<td>Ag/IL/PDMS</td>
<td>9.1 (15%)</td>
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<td>6</td>
<td>[381]</td>
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<td>f-MWCNT/GO/SIS</td>
<td>72 (50%)</td>
<td>0–70</td>
<td>Up to 50%</td>
<td>4</td>
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<td>GNP/AgNP/PU</td>
<td>48.2 (160%)</td>
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<td>[383]</td>
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<td></td>
<td>ACR/MWCNT/PDMS</td>
<td>53 (80%)</td>
<td>0–160</td>
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<td>3000</td>
<td>[384]</td>
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<td>DLP</td>
<td>MWCNT/acrylic</td>
<td>38 (2.5%)</td>
<td>0–25</td>
<td>Yes</td>
<td>10</td>
<td>[272]</td>
</tr>
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<td></td>
<td>MWCNT/elastomer</td>
<td>8.939 (45%)</td>
<td>0.01–60</td>
<td>Up to 45%</td>
<td>10,000</td>
<td>[385]</td>
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<td></td>
<td>RGO/elastomer</td>
<td>6.723 (40%)</td>
<td>0.01–40</td>
<td>Yes</td>
<td>10,000</td>
<td>[386]</td>
</tr>
<tr>
<td></td>
<td>Graphene/photopolymer</td>
<td>2.64</td>
<td>0–67.5</td>
<td>Yes</td>
<td>1000</td>
<td>[387]</td>
</tr>
<tr>
<td></td>
<td>CMC/NVP-PA/PAA hydrogel</td>
<td>1.16 (40%)</td>
<td>0–1000</td>
<td>No</td>
<td>400</td>
<td>[388]</td>
</tr>
<tr>
<td>p-SLA</td>
<td>PEDOT:PSS</td>
<td>0.73</td>
<td>0–6</td>
<td>Yes</td>
<td>10</td>
<td>[389]</td>
</tr>
<tr>
<td></td>
<td>CB-PVP</td>
<td>10.7</td>
<td>0–2</td>
<td>Yes</td>
<td>–</td>
<td>[390]</td>
</tr>
<tr>
<td>SLS</td>
<td>GNP/TPU</td>
<td>668.3 (15%)</td>
<td>0–15</td>
<td>No</td>
<td>10</td>
<td>[391]</td>
</tr>
</tbody>
</table>

as-prepared PDMS submicrobeads with electrochemically derived GO (EGO) in the presence of Polysorbate 20 surfactant and PDMS prepolymer, as shown in Fig. 11a [376]. This appealing strategy was used to fabricate macro-scale strain sensors with a GF of 20.3 over a tensile strain of 40% and a microscale pressure sensor with a broad pressure operating range (0.248–500 kPa). Moreover, liquid metals with modified rheological properties can be used for printing sensors at high resolutions. Centrifugation was performed to concentrate Galinstan microdroplets into PDMS elastomers [377]. Because the composites were not initially conductive owing to the separation of the microdroplets, they were compressed or frozen to aggregate the conductive networks (Fig. 11b). The developed ink could be printed with a resolution of up to 90 µm at a speed of as high as 30 mm/s. The resulting strain sensor exhibited nearly zero hysteresis and excellent stability of up to 500 loading–unloading cycles at 50% strain, highlighting their potential for monitoring human hand movements (Fig. 11c–e).

Nevertheless, the sensitivity and stretchability of physical sensors have scope to be enhanced. To this end, certain researchers developed a self-compensated two-ordered architecture by 3D printing thermally RGO (TRGO)/PDMS open meshes and coating them with chemically RGO (RGO) sheets through a layer-by-layer assembly (Fig. 11f) [356]. The percolation networks of the TRGO inside the PDMS matrix formed a deformable electrically conductive path. Moreover, the RGO-coated layer provided an extra conductive path to compensate for the
conductivity loss resulting from the detachment of the outer conductive path (Fig. 11g). Consequently, the sensitivity of the resultant strain sensors could be tuned from 18.5 to 88,443 along an extensive workable strain range (0–350%). The structural designs of printed sensors can be manipulated through 3D printing to modulate their sensitivity and stretchability. DIW was performed to fabricate graphene/PDMS composites with tuneable sensing performances owing to their ordered porous structures with grid, triangular, and hexagonal macrostructures, as shown in Fig. 11h, i [378].

Composites reinforced with a single nanomaterial without accommodating a special design generally display low sensitivity and high stretchability or high sensitivity with a limited sensing range. Different fillers with various morphologies can be combined to enhance the performance of the 3D-printed strain sensors. The performance improvement is attributable to the enhanced dispersion of the fillers inside the matrix through the prevention of nanofiller agglomeration. In this case,
several electrically conductive networks are easily established inside the matrix, leading to the enhanced sensitivity of the sensors during stretching. For instance, Kim et al. [382] prepared a hybrid filler consisting of amine-functionalised MWCNT and RGO through electrostatic self-assembly and embedded it in a triblock-copolymer elastomer (SIS). The fabricated composite dough was 3D printed using DIW to obtain strain sensors over different porous paper substrates (Fig. 12a). When the weight ratio of the functionalised MWCNT to RGO was 9:1, the sensor exhibited a high GF of 72 and linearity up to a tensile strain of 50%. Kwon et al. [383] performed DIW to synthesise a piezoresistive sensor using GNP/AgNP reinforced PU composite (Fig. 12b). The resulting sensor could respond to external tension and compression forces with a fast response time and high repeatability over 500 cycles.

Xiang et al. [370] used the FDM technique to fabricate highly sensitive and stretchable strain sensors of CNT/AgNP/TPU composites. At a mass ratio of 5:1 (CNT:AgNP), the sensors exhibited a GF of 43,260 at 250% strain, high linearity up to 50%, a short response time (57 ms), and high durability for 1000 cycles. Kwon et al. [383] also designed strain sensors with a higher sensitivity by using CNT/GNP/TPU composites (mass ratio=3:1). These sensors demonstrated a GF of 136,327.4 at 250% strain with excellent durability (3000 cycles).

According to this discussion, 3D printing techniques can facilitate the fabrication of strain sensors with diverse structures and raw materials, and the strain sensor performance can be tuned accordingly. Fig. 13

![Diagram](image-url)

**Fig. 12.** (a) Fabrication of the strain sensors and structural changes of the NH$_2$-MWCNT/RGO conductive networks inside the matrix after stretching. (b) Fabrication of 3D-printed strain sensors based on GNP/AgNP/PU nanocomposites. (c) Electromechanical response of the strain sensor fabricated using MWCNT/AgNP/TPU composites to repeated loading-unloading cycles: (i) finger bending, (ii) mouth opening, and (iii) swallowing.

(a) Reproduced with permission [382]. Copyright 2017, Royal Society of Chemistry. (b) Reproduced with permission [383]. Copyright 2018, Wiley-VCH. (c) Reproduced with permission [370]. Copyright 2020, Elsevier.
shows the relationship between the GF and stretchability of 3D-printed sensors with different geometries. Functionalisation of the nanomaterial surface and use of binary fillers with different dimensionalities can help enhance the sensitivity of the sensors at large strains. Furthermore, both indicators can be modulated by designing 3D cellular and porous structures. Hydrogels can help achieve extremely high stretchability values of more than 1000%. However, the GF is typically low, potentially because of the long-range electron transport through their structure.

5.1.3. 3D-printed wearable pressure sensors

In pressure sensors, the resistance changes owing to variations in the density of the electrically conductive networks within the composites. When pressure is applied, the filler-to-filler contacts become denser

### Table 4

<table>
<thead>
<tr>
<th>Method</th>
<th>Pressure sensor</th>
<th>Sensitivity (at pressure/strain)</th>
<th>Pressure/strain range</th>
<th>Linearity</th>
<th>Durability (cycles)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FDM</td>
<td>GNP/silicone</td>
<td>$10^{-1}$</td>
<td>2–10%</td>
<td>No</td>
<td>400</td>
<td>[233]</td>
</tr>
<tr>
<td></td>
<td>f-CNT/TPU</td>
<td>130.9$^a$ (25–30%)</td>
<td>0–30%</td>
<td>Up to 15%</td>
<td>1500 (at 5%)</td>
<td>[394]</td>
</tr>
<tr>
<td></td>
<td>GNP/TPU</td>
<td>54.58$^a$ (0.3%)</td>
<td>0–30%</td>
<td>Up to 3%</td>
<td>500</td>
<td>[395]</td>
</tr>
<tr>
<td></td>
<td>CNT/SEBS</td>
<td>1.6153 kPa$^{-1}$ (&lt;250 Pa)</td>
<td>0–5 kPa</td>
<td>No</td>
<td>2000</td>
<td>[396]</td>
</tr>
<tr>
<td></td>
<td>CB/TPU</td>
<td>0.7145 kPa$^{-1}$ (0.5 kPa)</td>
<td>0.1–200 kPa</td>
<td>No</td>
<td>10</td>
<td>[232]</td>
</tr>
<tr>
<td>DIW</td>
<td>Ag/silicone</td>
<td>180$^a$</td>
<td>0–500 kPa</td>
<td>No</td>
<td>100</td>
<td>[97]</td>
</tr>
<tr>
<td></td>
<td>CB/TPU</td>
<td>5.54 kPa$^{-1}$ (&lt;10 kPa)</td>
<td>0.01–800 kPa</td>
<td>No</td>
<td>10,000</td>
<td>[98]</td>
</tr>
<tr>
<td></td>
<td>Graphene/PDMS</td>
<td>448$^a$ (at 30%)</td>
<td>0–30%</td>
<td>No</td>
<td>100</td>
<td>[238]</td>
</tr>
<tr>
<td></td>
<td>EGO/PDMS submicrobead/PDMS</td>
<td>0.31 kPa$^{-1}$ (&lt;1.178 kPa)</td>
<td>0.248–500 kPa</td>
<td>Up to 1.178 kPa</td>
<td>1000</td>
<td>[376]</td>
</tr>
<tr>
<td></td>
<td>CNT/SiNP/silicone</td>
<td>0.3 kPa$^{-1}$ (&lt;20 kPa)</td>
<td>0–175 kPa</td>
<td>No</td>
<td>10,000</td>
<td>[392]</td>
</tr>
<tr>
<td></td>
<td>CB/TPU</td>
<td>5.5 kPa$^{-1}$ (&lt;10 kPa)</td>
<td>0–440 kPa</td>
<td>Up to 10 kPa</td>
<td>1000</td>
<td>[397]</td>
</tr>
<tr>
<td></td>
<td>CB/MWCNT/CuNP/PDMS</td>
<td>2.12 kPa$^{-1}$ (163–262 kPa)</td>
<td>0–396 kPa</td>
<td>No</td>
<td>5000</td>
<td>[398]</td>
</tr>
<tr>
<td></td>
<td>CNT/SiNP/PU</td>
<td>0.13 kPa$^{-1}$ (0–10 kPa)</td>
<td>0–40 kPa</td>
<td>Up to 10 kPa</td>
<td>10</td>
<td>[399]</td>
</tr>
<tr>
<td></td>
<td>IL/acylate</td>
<td>2.01 kPa$^{-1}$ (&lt;0.2–2.3 kPa)</td>
<td>0–60 kPa</td>
<td>Up to 2.3 kPa</td>
<td>10</td>
<td>[401]</td>
</tr>
<tr>
<td></td>
<td>SLS SWCNT/TPU</td>
<td>0.111 kPa$^{-1}$ (&lt;0.1 Pa)</td>
<td>0–10 kPa</td>
<td>Yes</td>
<td>100</td>
<td>[285]</td>
</tr>
<tr>
<td></td>
<td>MWCNT/TPU</td>
<td>1.02 kPa$^{-1}$ (&lt;200 Pa)</td>
<td>0.7 Pa–130 kPa</td>
<td>Yes</td>
<td>60,000</td>
<td>[400]</td>
</tr>
<tr>
<td></td>
<td>Ionic hydrogel@ PUA</td>
<td>2.01 kPa$^{-1}$ (0–2.3 kPa)</td>
<td>0–60 kPa</td>
<td>Up to 2.3 kPa</td>
<td>10</td>
<td>[401]</td>
</tr>
<tr>
<td></td>
<td>IL/TPU</td>
<td>0.45 kPa$^{-1}$ (&lt;2.5 kPa)</td>
<td>0–30 kPa</td>
<td>Yes</td>
<td>1000</td>
<td>[331]</td>
</tr>
</tbody>
</table>

resulting in a negative resistance change (negative piezoresistive response) owing to the accompanying rise in the electrical currents. Therefore, most of the existing sensors exhibit the following relationship between the pressure sensitivity or GF of the pressure sensors and the relative current change: $\text{GF} = (\Delta I/I_0)/\Delta P$ [98,392,393]. Table 4 summarises the characteristics of 3D-printed pressure sensors. Guo et al. [97] 3D printed a multi-material pressure sensor integrated with different inks with adjustable conductivity and rheological properties. As shown in Fig. 14a, b, the sensor consisted of a silicone base layer, two electrodes with a 75% Ag/silicone configuration, a helical sensing layer of 68% Ag/silicone, an isolating silicone layer, and a sacrificial layer, fabricated through single-job 3D printing using four independent nozzles. The relative current change in the sensing layer increased with the increase in the applied pressure, leading to a GF of 180 (Fig. 14c). On the other hand, pressure sensors with a positive piezoresistive response ($\text{GF} = (\Delta R/R_0)/\Delta P$) were obtained by blending electrically insulating silica nanoparticles (SiNPs) with electrically conductive CNTs inside the Ecoflex polymer [392]. At low fractions of CNTs and high contents of SiNPs, the 3D-printed porous sensor demonstrated a positive piezoresistive sensitivity of 0.096 kPa$^{-1}$ within a pressure range of 0–175 kPa.

Compared with those of solid structures, sensors with porous structures exhibit higher sensitivity and elasticity values. Notably, 3D printing is a simple and high fidelity technique for building tuneable 3D porous structures for high-performance pressure sensors. The sensitivity of these complex structures can be tailored by tweaking the main parameters of 3D scaffolds, such as the lattice type, filament diameter, interlayer spacing, and interaxial angle. As shown in Fig. 14d, graphene/PDMS 3D structures were fabricated using the DIW method under different design parameters [238]. The GF of sensors with the largest filament diameter (0.5 mm), interlayer spacing of 0.4 mm, and 90° interaxial angle was 448 at 30% compressive strain. Furthermore, the
sensors exhibited high stability after 100 repetitive compression–release cycles. Additionally, the DLP method was used to fabricate pressure sensors with tuneable lattice structures, using a CNT-embedded TPU active layer coupled with a conductive fabric electrode (Fig. 14e) [400]. Among different types of lattices, the sensor with an ‘E’ morphology exhibited the maximum sensitivity (1.02 kPa⁻¹) in the pressure range of 0–130 kPa (Fig. 14f) owing to its lowest elastic modulus that enables the highest deformations against a given applied force. More conductive networks were achieved, resulting in higher sensitivities. Moreover, the filament diameter and active layer thickness considerably influenced the sensitivity of the pressure sensors, as shown in Fig. 14g, h. The prepared sensors were used for real-time pulse monitoring (Fig. 14i–k). In addition, a 4 × 4 sensor array was synthesised for monitoring spatial pressure allocation and an insole was fabricated to measure the foot pressure.

The porosity of 3D-printed open structures can be increased using sacrificial agents to introduce nano- and micro-pores inside the hierarchical structures. Furthermore, the sensitivity and workable sensing range can be extended. Wang et al. [98] developed a multi-modulus and

![Figure 15](image-url)

Fig. 15. (a) Schematic and (b) optical image of the multi-material sensor. c) Optical image of the sensor subjected to twisting. (d–f) Customisation of fabricated sensor arrays for (d) monitoring robot hand holding and releasing a cup, (e) mapping chess pieces, and (f) simulating a stretchable gamepad. (g) Sensitivity response of the cubic porous lattice of CB/TPU composites versus applied pressure. (h) Schematic of the reprocessing cycle for the CB/TPU ink. (a–f) Reproduced with permission [98]. Copyright 2018, Wiley-VCH. (g–h) Reproduced with permission [397]. Copyright 2019, American Chemical Society.
multi-layered stretchable sensor composed of a PDMS elastomer substrate, Ag/TPU electrode layer, and CB/TPU sensing layer, as shown in Fig. 15a-c. The authors incorporated a sacrificial sodium chloride (NaCl) template into the sensing layer to induce microscale pores (20–100 μm) and nanoscale pores (100–500 nm). This unique design endowed the sensor with high sensitivity (5.54 kPa$^{-1}$) and a wide workable range (10 Pa to 800 kPa). Therefore, the sensor could accurately grasp and map when integrated into a variety of devices, as shown in Fig. 15d-f. Wei et al. [397] prepared highly compressible and electrically conductive CB/TPU foams via DIW. The formulated ink contained a mixture of TPU, CB, and nanoclay (Cloisite Na+) dispersed in an N,N-dimethylformamide (DMF) solvent. After printing, the solvent and nanoclay were gradually removed to yield inherently porous TPU/CB structures. As depicted in Fig. 15g, the designed sensor displayed three characteristic regimes corresponding to different sensitivities. The maximum pressure sensitivity of 5.5 kPa$^{-1}$ was captured in the low-pressure range (<10 kPa). The printed parts could be recycled and reproduced to fabricate sensors with similar piezoresistive performances (Fig. 15 h).

Overall, most studies have used 3D printing to devise 3D porous [396,397] and well-designed architectures, such as overhanging [232], helical [97], tip array [398], and cellular structures [400], to tailor the sensitivity of pressure sensors and extend their working range. Fig. 16 shows the performance values for these pressure sensors. Porous structures outperform their solid counterparts in terms of their sensitivity and working range because the pores within 3D structures provide adequate space for bending and buckling, which helps improve sensor compressibility. The improved compressibility enables more particle-to-particle contact from the nanomaterials during loading, causing sensor resistance to decrease. Pore size and shape influence the performance of pressure sensors. Notably, the introduction of complex structures is challenging as it limits the printability and adjustment of the structural parameters.

5.2. 3D-printed wearable temperature sensors

Body temperature must be accurately measured in healthcare settings as it is a key vital sign that reflects patients’ health conditions and can serve as an initial warning for disease [49,403]. Temperature sensing is also important for reflecting the tactile-sensing mechanisms of objects contacting soft robots [404]. Different transduction mechanisms have been introduced to fabricate wearable temperature sensors, such as thermistors [405], resistive-type detectors [406], and pyroelectric detectors [407]. Among these sensors, thermistors are most widely used owing to their high sensitivity, short response time, simplicity, and high accuracy [49,408]. Therefore, the use of 3D-printed polymer composites as thermistors is reviewed in this section. Table 5 summarises the sensing features of 3D-printed thermistors. Thermistors have a simple sensing mechanism: The applied temperatures are transformed into electrical resistance changes within the sensing element. The key indicator of thermistors is the sensitivity or the temperature coefficient of resistance (α), which is equivalent to the GF of strain sensors, except that the applied stimulant is temperature change. Thermistor resistance ($R_T$) typically varies exponentially with temperature ($T$), which can be represented as follows [66,405]:

$$R_T = R_o \exp\left(\frac{E_o}{kT}\right) = R_o \exp\left(\frac{B}{T}\right)$$

where $R_o$ is the initial resistance, $E_o$ is the activation energy for conduction, $k$ is Boltzmann’s constant, and $B$ is the thermistor index. The linear relationship between $R_T$ and $T$ can be reflected by taking the natural logarithm of both sides. The slope of the resultant linear curve indicates the value of index $B$, which typically depends on the thermistor’s material [408]. Specifically, the resistance of thermistors increases or decreases with the temperature (thermistors with positive and negative temperature coefficients, respectively) [49,408]. Compared with rigid active metals and semiconductors [409,410], thermistors based on stretchable polymer composites are preferable for preparing advanced electronics and wearable devices [411,412].

For positive-type thermistors, the increase in the resistance is attributable to the thermal expansion of the polymer matrix upon heating that destroys the built-in conductive networks [422,423]. The temperature rise may be accompanied by scattering of the charge carriers on the conductive nanofiller, which shortens the average electron transfer path [424]. For instance, Wang et al. [417] 3D printed graphene/PDMS composites as temperature sensors with different cellular structures (i.e., grid, triangular, and hexagonal structures). The temperature sensitivities of the solid and cellular structures were identical with a linear response, with values of 0.008 °C$^{-1}$ within a temperature range of 10–1000 kPa.
range of 25–75 °C (Fig. 17a). The grid sensor was integrated into a preheated tube to monitor the changes in the temperature during cooling. The resulting performance was comparable to that of a commercial temperature sensor (Fig. 17b). Moreover, the grid sensor could be mounted on a human wrist to detect the skin temperature. As shown in Fig. 17c, unlike the solid sensor, the grid sensor stably measured the temperature and exhibited a strain-insensitive response under wrist joint bending. Ota et al. [425] embedded various flexible devices, such as a temperature sensor, a heater, and other necessary electronic components, into a 3D-printed glove for thermotherapeutic treatment. As shown in Fig. 17d, conductive microchannels and slots were designed within the FDM-printed form-fitting glove to accommodate the temperature sensor and other electronic devices. Subsequently, the microchannels were injected with Galinstan to establish liquid-derived interconnects and active components. The patient could wear the flexible glove for thermotherapy. The delivery of heat at the location of injury improved the blood flow and minimised pain (Fig. 17e). The temperature sensor was used to monitor the heater temperature, which could be tailored by changing the input power, as depicted in Fig. 17f. In general, the thermal sensitivity of negative-type thermistors depends on the thermal activation of the charge carriers of the conducting material, corresponding to semiconducting behaviour [405,416,426]. Increasing the temperature imparts electrons with sufficient energy to promote transitions to the conduction band and boost electron tunneling effects between the closely spaced conductive fillers [424]. Therefore, the conductivity of the sensing element increases upon heating, concomitant with the decrease in the resistance. Liu et al. [102] 3D printed PU/PVA hydrogels bounded with MXene nanosheets (Ti3C2Tx) through hydrogel binding with the addition of glyceral as a non-electrolyte humectant (Fig. 17g). The obtained composites with a triangular porous structure were used as strain and temperature sensors. The temperature sensor displayed a negative resistance response with increasing temperature, with temperature sensitivities of ~5.27%/°C and ~1.11%/°C in the ranges of 0–30 °C and 30–80 °C, as depicted in Fig. 17h. Although the hydrogel-based sensors were expected to undergo dehydration with the increase in temperature, recharging with glyceral solution could help enhance the stability. The thermistor sensor was used to effectively monitor the temperature changes of a cup being sequentially filled with hot water (Fig. 17i). Furthermore, the printed sensor was used to monitor the change in the temperature of an SMP solar array hinge during Joule heating for aeronautics applications (Fig. 17j, k).

Fig. 18 shows that the temperature sensing mechanisms depend on the material choice instead of the sensor structure. Most researchers have printed temperature sensors with serpentine structures, with the sensing responses varying across the selected conductive materials and polymer matrices, as outlined in Table 5. Therefore, the temperature sensing performance can be enhanced by appropriately selecting conductive materials that are sensitive to the temperature and understanding the thermal expansion likelihood of the matrix. Furthermore, hydrogels with anti-freezing characteristics can respond to temperatures lower than room temperature and can thus be used in extreme and harsh weather conditions.

5.3. 3D-printed wearable humidity sensors

Humidity sensors have attracted widespread attention in not only domestic, agricultural, and food storage applications [427–430], but also in health monitoring and electronic-skin (e-skin) evolution [431, 432]. These sensory devices can be used to continuously monitor the human body dehydration levels and exhaled breath to timely diagnose probable dermatological or pulmonary diseases [433,434]. Additionally, humidity sensors can be used to monitor the healing speed of human skin wounds in dry and wet healing environments [435]. Transduction mechanisms, such as resistive [436–438], capacitive [439–441], optical [442,443], and impedance mechanisms [444–447], have been applied to develop humidity sensors. Humidity sensors convert the changes in the water vapour in air (relative humidity) into electrical signals [448,449]. The sensitivity mechanism depends on the hydrophilicity of the sensing element. When the humidity levels are increased, excessive water molecules are adsorbed onto the surface of the sensing material through the establishment of chemical bonds with the functional groups or surface vacancies [450]. This adsorption facilitates electron transfer among the conductive channels within the polymer matrix, allowing the electrical signal outputs to be tuned. Unlike humidity sensors derived from rigid and bulky inorganic materials [451,452], flexible, stretchable, and highly sensitive humidity sensors are in critical demand for health monitoring and skin-inspired devices [453,454]. 3D printing techniques can be used to fabricate such sensors with customised models. Table 6 summarises the humidity sensors recently fabricated through 3D printing. Ali et al. [437] 3D printed a humidity sensor derived from silver inter-digital electrodes and graphene/methyl-red sensing layer, as displayed in Fig. 19a. When water vapour was absorbed onto the composite layer, the methyl-red helped connect the remote graphene sheets, thereby decreasing the overall electrical resistance. The proposed sensor exhibited a high sensitivity of 1.07%/RH% against a 5–95% increase in relative humidity.

Kalosom et al. [438] performed FDM to obtain a humidity sensor composed of ABC composites reinforced with boron-doped diamond (BDD) microparticles and lithium chloride (LiCl), as shown in Fig. 19b. The BDD particles served as the electrode material, and LiCl served as the electrolyte. With the increase in moisture, LiCl rapidly dehydrated into Li⁺ and Cl⁻ conductive ions that behaved as mobile charge carriers

Table 5

<table>
<thead>
<tr>
<th>Method</th>
<th>Temperature sensor</th>
<th>Sensitivity (% C⁻¹)</th>
<th>Temperature range (°C)</th>
<th>Linearity</th>
<th>Durability (cycles)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FDM</td>
<td>CB/PP</td>
<td>-0.36</td>
<td>25–125</td>
<td></td>
<td></td>
<td>[413]</td>
</tr>
<tr>
<td></td>
<td>GNR/PLA</td>
<td>0.36</td>
<td>10–70</td>
<td>Yes</td>
<td>2</td>
<td>[414]</td>
</tr>
<tr>
<td></td>
<td>CB/PP</td>
<td>-0.5</td>
<td>25–55</td>
<td></td>
<td></td>
<td>[415]</td>
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<tr>
<td>DIW</td>
<td>PU/PVA/Ti3C2Tx hydrogel</td>
<td>-3.27</td>
<td>0–80</td>
<td>Yes</td>
<td>3</td>
<td>[102]</td>
</tr>
<tr>
<td></td>
<td>RGO/SWCNT-V2O5/SWCNT-VN fibre</td>
<td>1.95</td>
<td>30–80</td>
<td>No</td>
<td></td>
<td>[416]</td>
</tr>
<tr>
<td></td>
<td>Graphene/PDMS</td>
<td>0.8</td>
<td>25–75</td>
<td>Yes</td>
<td>100</td>
<td>[417]</td>
</tr>
<tr>
<td></td>
<td>CNT/P5/PANI hydrogel</td>
<td>-1.76</td>
<td>-20–68</td>
<td>No</td>
<td>9</td>
<td>[418]</td>
</tr>
<tr>
<td></td>
<td>Ag/PI</td>
<td>0.223</td>
<td>20–60</td>
<td>Yes</td>
<td></td>
<td>[419]</td>
</tr>
<tr>
<td></td>
<td>Graphene/PEDOT:PSS</td>
<td>0.06</td>
<td>35–45</td>
<td>No</td>
<td>5</td>
<td>[420]</td>
</tr>
<tr>
<td></td>
<td>PEDOT:PSS</td>
<td>-0.77</td>
<td>25–50</td>
<td>No</td>
<td>10</td>
<td>[421]</td>
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</table>

and increased the electrical conductivity of the composites. The connections of these entities with the BDD framework led to the generation of continuous and compact electrically conductive networks inside the matrix. The prepared sensor exhibited a negative resistance response with a sensitivity of 1.827 when the humidity levels increased from 11% to 97%. As shown in Fig. 19c, the developed sensor was placed between two plastic tubes to detect humidity in human breath for 12 sequential cycles by mouth blowing before being dried by compressed air. Additionally, the sensor was used to monitor the humidity of nitrogen gas supply (Fig. 19d).

5.4. 3D-printed wearable multifunctional sensors

5.4.1. Multi-directional strain sensors

Multi-directional strain sensors that can identify intricate movements in different directions are valuable for applications that require responses in multiple degrees of freedom. For instance, soft robots can move, bend, and flex in different directions. The integrated strain...
sensors must respond to such motions and detect unexpected deformations during operation. Most of the existing strain sensors react in only a single direction, and thus, it is necessary to design a strain sensor with multi-dimensional capability. A common approach is to combine several 3D-printed strain sensors in a rosette-type configuration to identify complex strain conditions, as shown in Fig. 20 a [52]. Another effective strategy is to engineer the anisotropic structures of a single strain sensor capable of detecting multiaxial strains. For example, a double-nozzle FDM 3D printing technique was used to construct a 3D cubic cross-shape force sensor to estimate the forces from three main dimensions (x, y, and z), as displayed in Fig. 20 b [457]. This architecture contained a sensing element made of a CNT/TPU composite and a structural part made of TPU to support the sensors. Furthermore, a highly sensitive and multi-directional strain sensor was 3D printed using a CNT/PLA composite (X-sensor) in a cross-sensor manner (Fig. 20 c) [368]. The sensor, which consisted of two cross-stacked X-sensors separated by a thin TPU layer could detect motion in different directional angles of applied tensile strain. When the cross-sensor was integrated into 3D-printed actuators, it could identify whether the actuator was rolling up or down by collecting the resultant resistance change signals (Fig. 20 d). Additionally, the cross-sensor could inspect the bending of a two-armed pneumatic actuator gripper (Fig. 20 e).

### 5.4.2. Multi-modal sensors

Human skin is a complicated sensory system that can concurrently sense and distinguish a variety of external stimuli, such as strain, pressure, temperature, and humidity. Integrating multiple sensing capabilities in one wearable device is important for collating comprehensive vital signs of health conditions and developing e-skin for robots and prosthetics [51]. Most of the existing wearable sensors have single-modal abilities and thus cannot be applied to the abovementioned domains. Although these sensors have been used to separately detect different stimuli [102,233], they cannot clearly identify each target without interfering with the operation of other sensors. A few successful multi-modal sensor arrays have been reported, including strain/temperature sensor arrays [54,458] and laminated strain/temperature e-whisker arrays [459] developed through screen printing; laminated pressure/humidity/temperature graphene sensors based on photolithography, ion etching, and spin coating methods [460]; and strain/pressure/humidity/temperature/optical sensors based on photolithography [55]. To realise simultaneous sensing, it is necessary to prevent any overlap or contact between the sensors and introduce appropriate insulating layers within each sensory layer. Furthermore, electrically conductive electrodes must be integrated within each layer to collect the electrical signal variations from the sensors during load.

<table>
<thead>
<tr>
<th>Method</th>
<th>Humidity sensor</th>
<th>Mechanism</th>
<th>Sensitivity (%/RH%)</th>
<th>Humidity range (RH%)</th>
<th>Linearity</th>
<th>Durability (cycles)</th>
<th>Ref</th>
</tr>
</thead>
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<tr>
<td>FDM</td>
<td>BDD/LiCl/ABS</td>
<td>Resistive</td>
<td>1.827</td>
<td>11–97</td>
<td>No</td>
<td>14 days</td>
<td>[438]</td>
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<td></td>
<td></td>
<td></td>
<td>(11–67%)</td>
<td></td>
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</tr>
<tr>
<td>DIW</td>
<td>CNT/Chitosan</td>
<td>Resistive</td>
<td>0.334</td>
<td>35–85</td>
<td>Up to 70%</td>
<td>–</td>
<td>[373]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(35–70%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CNT/PS/PANI hydrogel</td>
<td>Resistive</td>
<td>0.27</td>
<td>45–85</td>
<td>No</td>
<td>–</td>
<td>[418]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(45.6–70.2%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DLP</td>
<td>MWCNT/elastomer</td>
<td>Impedance</td>
<td>1.23</td>
<td>10–90</td>
<td>Yes</td>
<td>4</td>
<td>[447]</td>
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<tr>
<td>LJ</td>
<td>Graphene/methyl-red/PET</td>
<td>Resistive</td>
<td>0.401</td>
<td>52–89</td>
<td>Yes</td>
<td>4</td>
<td>[385]</td>
</tr>
<tr>
<td></td>
<td>Ag/PI</td>
<td>Capacitive</td>
<td>1.07</td>
<td>5–95</td>
<td>No</td>
<td>4</td>
<td>[437]</td>
</tr>
<tr>
<td></td>
<td>PEDOT/RGO/AuNP/PEI</td>
<td>Resistive</td>
<td>0.501</td>
<td>40–90</td>
<td>No</td>
<td>–</td>
<td>[455]</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>11–98</td>
<td></td>
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<td>5</td>
<td></td>
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</tbody>
</table>
application. To this end, it is necessary to select appropriate materials and structures that can respond to only the relevant stimulant without being influenced by others. As a proof of concept, Harada et al. [458] fabricated a $3 \times 3$ sensor array consisting of triaxial force sensors and temperature sensors screen printed over a flexible polyester substrate, as shown in Fig. 21 a–c. Based on the strain distribution concept, the fingerprint-like structure enabled real-time monitoring of triaxial forces for tactile and slip detection. The performance varied with the polyester film thickness (Fig. 21 d). The temperature sensor could detect temperature variations with high precision (Fig. 21 e). Consequently, the complete device could concurrently detect strain and temperature stimuli when a human finger touched the device (Fig. 21 f).

Most of the existing multi-modal sensors were fabricated using conventional methods, which are complex and time-consuming and involve multiple steps. In contrast, 3D printing can be performed to fabricate multi-material and multi-modal sensors in a rapid manner with reduced waste. Kim et al. [461] designed a multiaxial pressure sensor coupled with a temperature sensor in a bumper-like structure, all of which were 3D printed using the FDM method (Fig. 21 g). The sensing layers and device body were made of MWCNT/PLA and TPU filaments, respectively. Both sensors could respond to temperature rise (Fig. 21 h).

Under load application, the relative resistance changes of the triaxial pressure sensor (Fig. 21 i, j) depended on the magnitude and direction of the applied load. In contrast, the temperature sensor demonstrated negligible resistance variations. In other words, the responses of both sensors could be differentiated under force application.

5.4.3. Self-healing sensors

Wearable sensors may be damaged under prolonged mechanical and thermal deformations, which may limit their service life. It is desirable to endow sensors with a self-healing capacity resembling the intrinsic healing capability of human skin. Extrinsic self-healing can be realised by embedding microcapsules into the host matrix. In comparison, intrinsic self-healing based on dynamic and reversible covalent or non-covalent interactions is more effective for wearable sensors [462–464]. These molecular interactions, such as hydrogen bonding [465], hydrophobic associations [466], π–π stacking [467], and ionic interactions [468], can yield materials with structures that can rapidly recover. Hydrogels are representative pristine self-healable materials [100]. The crosslinking structures and healing capabilities can be modified, and 3D printing can be performed to create self-healable and customised sensors from ionically conductive hydrogels [380,388].

![Fig. 19. (a) Schematic of the sensing mechanism of graphene/methyl-red humidity sensor. (b) Schematic and photograph of the 3D-printed BDD/LiCl/ABS humidity sensor. (c) Resistance variations of the sensor placed between two plastic tubes during mouth blowing and compressed-air drying for 12 cycles. (d) Response of the humidity sensor with N$_2$ gas supply. (a) Reproduced with permission [437]. Copyright 2016, Elsevier. (b-d) Reproduced with permission [438]. Copyright 2020, American Chemical Society.](image-url)
attain highly conductive hydrogels with enhanced sensitivities, conductive nanomaterials can be embedded into the hydrogel system to yield hydrogel-based composites. As shown in Fig. 22a, b, water-vapour-triggered self-healable and conductive chitosan/CNT composites were prepared by blending chitosan and CNT in a dispersing aqueous solution containing a mixture of citric acid, acetic acid, and lactic acid [373]. Nanocomposite inks were used to obtain various 3D-printed structures. By manipulating the ratio between the printing speed and material speed, micro-structured fibres with sacrificial bonds and hidden length were created, as shown in Fig. 22c–e. The designed strain sensor with a coiled layout exhibited a GF of 4 under 10% strain. The self-healing mechanism could be explained as follows (Fig. 22f): When the broken chitosan/CNT fibres were exposed to water vapour, they swelled, motivating citrate ions (CA–) to retain electrostatic interactions with the ammonium ions (NH₃⁺) on the chitosan. This resulted in complete healing within ~10 s, and the mechanical properties were restored. Nevertheless, the restrictions on the chitosan swelling and chain mobility impeded the healing ability when the spacing between the two cut materials was greater than 100 µm.

Hydrogels with double networks exhibit mechanical properties superior to those with a single network [469,470]. In the double-network structure, the first network is densely crosslinked with non-reversibility,
whereas the second network is loosely and reversibly crosslinked. As demonstrated in Fig. 22 g, partial in situ polymerisation was performed for precuring a mixture of GO, calcium chloride (CaCl$_2$), and acrylic acid monomer in the presence of a N,N'-methylenebisacrylamide (MBA) crosslinker and an ammonium persulfate photoinitiator to provide a shear-thinning ink suitable for 3D printing [470]. After printing the grid-like structure of the hydrogel, hydroiodic acid (HI) vapour was used to reduce GO to RGO, thereby increasing the conductivity of the printed product. Finally, the 3D-printed hydrogel was fully cured to realise the double network and encapsulated within two thin PDMS layers. The high self-healing efficacy was attributable to the dynamic ionic interaction between Ca$^{2+}$ ions and the carboxylic groups in the GO surface and polyacrylic acid (PAA). The 3D-printed sensor could effectively detect human motion and ammonia gas.
5.4.4. Self-powered sensors

Most wearable sensors operate with an external power supply or a battery, with inherent deficiencies of high rigidity, short service life-span, large power consumption, and limited wearability [471, 472]. Therefore, it is imperative to develop wearable sensors with fully integrated self-powered systems to keep pace with the progress in wearable electronics. Here, the power source must have high stretchability with stable performance to accommodate the dynamic motions of the human body. 3D-printed energy storage and harvesting devices, such as supercapacitors [416, 473], batteries [58, 474], nanogenerators [57, 475], and flexible solar cells/supercapacitors combinations [307, 476] have recently been integrated with sensors in a single device. For instance, Zhao et al. [416] coupled a 3D-printed fibre-shaped temperature sensor (FTS) with a 3D-printed fibre-shaped asymmetric supercapacitor (FASC) in a twisted configuration, as displayed in Fig. 23a. The RGO fibre, which served as the FTS, was wrapped on the FASC device consisted of an SWCNT/vanadium pentoxide (V_2O_5) positive electrode and an SWCNT/vanadium nitride (VN) negative electrode. The FASC device provided stable power supply to FTS with a maximum operating voltage of 1.6 V. Furthermore, the temperature sensitivity of the entire device was 1.95% °C⁻¹. Nevertheless, the electrodes in the twisted-shape FASC are prone to separate during long-time bending cycles and lose their mechanical robustness, resulting in deterioration of the electrochemical performance. Accordingly, Zhao et al. [473] fabricated an all-in-one 3D-printed coaxial FASC using a multi-ink DIW equipped with a sophisticated design of the coaxial needles, as shown in Fig. 23b. A pressure sensor based on polypyrrole/PDMS stamps was wrapped around the coaxial device to form a self-powered pressure
sensor (Fig. 23c). The pressure sensor demonstrated a high sensitivity of 70 kPa$^{-1}$ (< 500 Pa) and excellent durability after 600 repetitive cycles.

Costa et al. [474] performed a multi-ink DIW to fabricate a stretchable silver–gallium (Ag–Ga) battery consisting of four printable composites (Fig. 23d). First, they printed an Ag/EGaIn/poly(styrene–polyisoprene–polystyrene (SIS) composite as the main current collector. Second, CB/SIS composite was printed to shield the first layer against chemical corrosion. Third, silver oxide (Ag$_2$O)/SIS and EGaIn/CB/SIS composites were printed as the cathode and anode of the battery, respectively. Last, a hydrogel-based electrolyte was applied. Multiple batteries connected in a 3 × 2 configuration were coupled with 3D-printed electrodes and sensors over a wearable textile belt, as shown in Fig. 23e, f. The electrodes and sensors were fabricated using the same composite as the first layer of the battery, allowing them...
to be printed in a single run. The whole self-powered device was able to
continuously record the heart rate, respiration rate, and body
temperature.

Because batteries and other energy storage devices require frequent
charging or replacement, developing other devices with a sustainable
self-powering feature is of importance [471,477]. 3D printing of
energy-harvesting devices, predominately including triboelectric nanogenerators (TENGs) [45,57,478,479] and piezoelectric nanogenerators (PENGs) [475,480–482], have been investigated as self-powered sen-
sors. These devices can harvest mechanical energy from human motions
and the environment and convert it into electrical energy. For example,
Chen et al. [45] 3D printed TENGs with a hierarchical porous structure
(Fig. 23 g). The device was composed of CNT and poly(glycerol sebacate)
as electrification components. When an external force was applied to the
TENG, positive and negative charges accumulated on the surfaces of
CNT and polymer matrix, respectively, in each deformed pore. After
releasing the force, electrons flowed from the ground electrode to the
CNT network to balance the electrostatic system. A cumulative electrical
current was generated after repetitive compression-release cycles. The
ability of TENGs to harvest biomechanical energy was demonstrated by
obtaining a self-powered lighting shoe integrated with a 3D-printed
TENG insole (Fig. 23 h). Furthermore, a ring-shaped TENG was printed
to monitor the finger motions at different bending angles (Fig. 23 i).

5.4.5. In situ printed sensors

Wearable sensors are typically fabricated through ex situ printing,
which means direct printing of the material over a flat substrate, fol-
lowed by its transfer to the target location (e.g., a human hand) through
adhesives or medical tapes [61,96]. Notably, this approach may lead to
significant interfacial mismatching between the printed sensors and
target surfaces, especially in the case of surfaces with arbitrary and
complex geometries. Additionally, the transfer of soft sensors containing
biocompatible hydrogels involves risks of damage and contaminations
during handling and implantation [61]. In contrast, in situ printing
enables the use of artificial intelligence to autonomously scan the actual
target surface and reflect kinematic conditions. The sensors can then be

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**Fig. 24.** (a–c) Schematic of in situ 3D printing process: (a) 3D scanning of the target non-planar surface, (b) real-time tracking of the free-moving surface of the human hand, and (c) in situ 3D printing of the designed conductive ink. (d) Photograph of the printed device on a human hand that can freely and randomly move without affecting the printing process. (e) Impedance responses of the humidity sensor under dry and wet moisture levels of human hands. (f) Images of the mice with an artificial wound and trackers before printing the cell-loaded hydrogel. (g) In situ 3D printing system. (h) In situ 3D-printed ionic hydrogel strain sensor on a porcine lung. (i) UV curing of the strain sensor with embedded copper electrodes in a silicone ring.

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accurately printed over non-planar surfaces to obtain perfectly matching interfaces [99,483,484]. For instance, Zhu et al. [484] integrated a DIW 3D printer with a closed-loop feedback control system to print devices on freeform and dynamic surfaces (Fig. 24a–c). The authors successfully printed conductive Ag/poly(ethylene oxide) inks to turn on pick-and-placed LEDs over a free-moving human hand surface (Fig. 24d). Additionally, a 3D-printed coil was used as a humidity sensor that yielded different impedance responses to variations in the moisture state on the human hand (Fig. 24e). The authors used this approach to print cell-loaded hydrogels onto live mice, confirming their potential for wound healing (Fig. 24 f). The same group [99] also directly printed an ionic hydrogel strain sensor on a porcine lung for in situ mapping of its random and time-varying deformations, as displayed in Fig. 24g–l. The outstanding mechanical compliance, sensing resolution, and adhesion of the in situ printed sensor to the breathing lung surface represented ground-breaking achievements in wearable and implantable devices.

5.4.6. Ultrasonic sensors

Existing wearable single/multi-modal sensors have successfully monitored various physical signals from the skin, thus generating electrical signals through changes in resistance, capacitance, or impedance of the sensing elements [55,102,485]. However, continuous imaging of main organs (i.e., heart, stomach, and lung) and tissues during daily life remains a spot challenge in the evolution of non-invasive wearable biomedical devices [63,486,487]. This can provide salient information on human health status and disease diagnoses, particularly for diseases with transient symptoms (i.e., coronary artery disease) [62,488–490]. Conventional ultrasonic images are obtained by correctly positioning a rigid ultrasonic probe on the region of interest by skilled technicians. These probes count on piezoelectric elements to transmit ultrasound waves through the skin/tissue, and then collect the reflected acoustic signals [491,492]. The received signals are further processed and used to construct the ultrasonic images. Due to the limitation of examination sessions and the bulkiness of the ultrasound probes, it is pivotal to develop stretchable ultrasonic sensors with prolonged monitoring capacity and improved wearability [63,493]. Additionally, the ultrasound patches must have strong adhesion to the skin to attain good acoustic transmission and stable performance for continuous imaging [492].

Wang et al. [63] fabricated a bioadhesive ultrasound (BAUS) device composed of rigid ultrasonic probes firmly attached to the skin via a novel hydrogel-elastomer hybrid coated with a bioadhesive layer (Fig. 25a, b). The BAUS probe (Fig. 25c) contained an array of rigid piezoelectric components (400 transducers per square centimeter). Each transducer was governed by upper and lower circuits, which could be fabricated using DIW, laser etching, and photolithography with resolutions of 100, 10, and 1 µm, respectively. The BAUS device enabled 48 h continuous imaging of various human organs under dynamic motions, as shown in Fig. 25d–f.

Continuous monitoring of the heart is critical for predicting many cardiovascular diseases. Therefore, Hu et al. [62] fabricated a wearable ultrasonic device that could provide continuous heart imaging during intensive exercise. The wearable imager (Fig. 25 g) consisted of piezoelectric arrays with a cross configuration to comprehensively provide cardiac images in two orthogonal directions without further realignment. Each transducer element was composed of 1–3 piezoelectric composite bonded with a thin backing layer to alleviate the resonance effect. Multi-layered stretchable electrodes based on liquid metal/SEBS composite were fabricated to control each element. As shown in Fig. 25 h, several standard views of the heart were captured by placing the device in the parasternal and apical positions comparable to those obtained using a commercial ultrasonic imager. The imager was then applied to monitor the heart activities before, during, and after physical exercise (Fig. 25). Therefore, the variations of the left ventricular internal diameter end-diastole (LVIDd) and end-systole (LVIDs) during the whole process were precisely captured. Several key cardiac metrics were automatically obtained from the continuous images using a deep learning model (Fig. 25j).

Although this new technology still relies on conventional methods for fabricating wearable ultrasonic devices, it is believed that additive manufacturing will be a cornerstone of newly developed devices. This is attributed to their potential to build complex structures with high precision and dimensions control. Additionally, the multi-material capabilities of most 3D printing techniques can enable the integration of diverse layers. In general, several components are required to assemble an ultrasonic device. These involve transducers, a backing layer, a matching layer, and circuits. Piezoelectric transducers are often prepared from ceramic and composite materials, where excellent electro-mechanical coupling coefficients and low dielectric losses are demanded [343,486,492]. Several piezoelectric materials with different structures and arrays suitable for ultrasonic sensing have recently been fabricated using SLA [494–499]. Additionally, conductive circuits and other layers can be fabricated from polymer composites or conductive inks, which are reachable using DIW [44,63,96,104,377] or LI [500–504]. Manual/automated assembly is required to build complex multi-layered ultrasonic devices. Multi-ink printing might be possible if the materials and structures are properly designed.

6. Conclusions and future outlooks

Smart wearable sensors have attracted increasing research attention as they can proactively and continuously interact with humans/robots and the surrounding environment. The use of these sensors can revolutionise healthcare systems, inspection of daily activities, and human–machine interactions. 3D printing processes can be implemented with a broad choice of flexible and conductive materials to obtain on-demand, low cost, scalable, and customised wearable devices. This comprehensive review summarises the advancements in the domain of wearable sensors, such as strain, pressure, temperature, humidity, and multi-functional sensors, prepared using 3D printing techniques. Because wearable applications demand highly sensitive, stretchable, and conformable materials, it is necessary to replace metallic and semiconductor sensory components by stretchable polymer composites. The commonly used conductive nanomaterials and their diverse morphologies and properties are discussed. The characteristics of 3D printing techniques (i.e., FDM, DIW, SLA, LI, BJ, and SLA) are described, along with the printing principle and potential for fabricating polymer composites and wearable sensors. Finally, the research progress and perspectives of 3D-printed wearable sensors based on polymer composites are discussed. Despite the notable progress in this field, several aspects remain to be explored to exploit the full potential of 3D-printed wearable sensors:

- In the context of 3D printing, the multi-material feature has an incredible impact on fabricating on-demand wearable sensors and arrays through a one-pot process instead of combining 3D printing with auxiliary methods such as casting or coating. Multi-material sensors typically include flexible substrates, sensory components, electrodes, and packaging. The long processing time and limited availability of raw material may hamper the replacement of conventional techniques for mass producing wearable sensors. The FDM, DIW, LI, and SLA methods are predominately used for 3D printing with multi-material capabilities. Although FDM is a low-cost and easy-to-implement approach, only thermoplastic materials can be processed, which are incompatible with human skin. To fabricate soft devices and e-skin, soft materials, such as thermosetting elastomers and hydrogels, that have elastic moduli comparable to those of delicate human skin must be used. SLA can be performed to print soft materials with ultrahigh fidelity; however, the problems of high cost, processing time, and material constraints must be addressed. LI is suitable for printing multi-layered circuits and wearable sensors with microscale resolutions. Adjustment of the viscosity, surface tension, and wettability of the ink is the key to avoiding the
Fig. 25. (a) Schematic of the BAUS device composed of a rigid ultrasonic probe firmly attached to the skin via a bioadhesive hydrogel-elastomer couplant. (b) Photograph of the BAUS device when a large pulling force was used, revealing the robust adhesion with the skin. (c) Optical image of the BAUS probe with 3D-printed upper and lower circuits. Scale bar is 0.5 mm. (d) Real-time BAUS imaging of blood vessels during different dynamic motions: (i) schematic of the device adhered to the neck to continuously monitor the carotid artery (CA) and jugular vein (JV), (ii) images under sitting and supine positions, indicating the variations of the JV diameter, and (iii) images under neck rotations with angles up to \( \pm 30^\circ \). (e) BAUS imaging of the heart showing the four chambers. The size of the left ventricle (LV) was substantially increased after 30 min of exercise. (f) BAUS imaging of the stomach showing a gradual decrease in the cross-sectional area of the gastric antral after drinking 450 mL of juice. (g) Schematic of the wearable imager indicating its main components. (h) Schematic and ultrasonic images of the heart from the wearable and commercial imagers placed in the parasternal and apical positions. (i) Continuous monitoring of the heart during rest (4 min in supine position), physical exercise (15 min of stationary bike exercise), and recovery (10 min in supine position). The displayed motion mode images were captured from the parasternal long-axis view bright mode images. The variations in the LVIDd and LVIDs were extracted from the zoomed-in images of Sections 1 (rest), 2 (exercise), and 3 (recovery) of the continuous waveforms. (j) Automatic imaging processing using a deep learning model: (i) analysis of the average LV volume versus the differences between the developed model results and the manual labelling for the wearable and commercial imagers; the dates points indicated a 95% confidence interval confirming the high integrity of the model, (ii) the model-extracted key cardiac metrics, such as stroke volume, end-systolic volume (ESV), end-diastolic volume (EDV), and ejection fraction, and (iii) results of heart rate and cardiac output waveforms.

(a-f) Reproduced with permission [63]. Copyright 2022, American Association for the Advancement of Science. (g-j) Reproduced under terms of the CC-BY license [62]. Copyright 2023, Springer Nature.
formation of satellite droplets that can cause short circuits between the conductive traces. Therefore, high-quality multi-material smart devices can be achieved. DIW embraces the merits of using diverse starting materials in the form of inks with multi-material abilities and can thus promote the scalable production of wearable sensors. Moreover, the resolution of DIW can be enhanced by designing multi-channel nozzles that can produce structures on the voxel or subvoxel scale.

• In the context of the sensor performance, it is challenging to fabricate cost-effective 3D-printed sensors with high sensitivity, stretchability, durability, reliability, and linearity and fast response/recovery times. In general, a trade-off exists between sensitivity and stretchability. Additionally, it is pivotal to endow sensors with stable and reliable electrical signals under long cycles (typically more than $10^3$ cycles). Designing novel porous/cellular structures or combining multiple sensing mechanisms may be the key to achieving the desired performance. Additionally, the nanomaterial’s interactions within the polymer matrix can be enhanced to obtain superior interfacial bonding and mechanical properties. Future studies must investigate the effect of filler functionalisation with covalent or non-covalent couplers on the sensor responses. These strategies can be combined with adopting sophisticated designs to obtain wearable sensors with ideal behaviours, as shown in Fig. 26.

• In the context of multi-functionality, multi-modal sensors that can simultaneously detect strain, pressure, temperature, and humidity without signal interference are important for health monitoring and wearable applications. Existing multi-modal sensors are fabricated through conventional processes that involve multiple steps. The use of 3D printing technologies for producing such innovative sensors must be further explored. For self-powered sensors, energy harvesting devices (i.e., TENGs or PENGs) can be used by harvesting surrounding biomechanical energy. However, the power outputs of such devices are far less than required for wearable sensors. Although integrating these devices with printed batteries or supercapacitors is an interesting option, it is rather difficult to tailor the wearability, stretchability, and size of the resulting devices. Instead, combining resistive or capacitive sensors with stretchable energy storage devices in a fully printed smart device is desirable for yielding stand-alone wearable sensors. The storage devices typically consist of electrodes, electrolytes, current collectors, and separators fabricated in fibrous [473,505], in-plane [506,507], or sandwiched configurations [508,509]. 3D printing techniques with multi-ink capability are deemed an appealing option for such integration. Multi-material LJ (for low-viscosity inks) or DIW (for high-viscosity inks) can be performed. Herein, the selection of raw materials is of paramount importance to reach the desired printability as well as the electrochemical and electromechanical performance of the entire device. In situ printed sensors over dynamic and non-planar surfaces are promising alternatives for implantable and biomedical applications. However, the problems of high complexity and limited interactive interfaces between the target surfaces and 3D printer must be addressed. Recently, wearable ultrasonic sensors have been introduced to simultaneously provide continuous monitoring and imaging of central organs and tissues. However, using 3D printing techniques to fabricate such innovated devices has yet to be considered. Other functionalities such as breathability must also be sought. Wearable sensors must be breathable to ensure the comfort of human skin and prevent sweat accumulation that may lead to severe irritations and allergies during long-term use. Sensors derived from elastic textiles or micro/nano-mesh structures are recommended.

• From the industry perspective, to fabricate wearables in the form of wristbands, smartwatches, and fitness trackers, fully integrated devices such as those involving single/multi-modal sensors, power units, interconnects, pick-and-place electronic components, and signal transmission, data processing, and feedback units must be
fabricated. Such comprehensive devices can transfer the input data into the target measurement in a self-confined environment. Details regarding the functions of each unit can be found in recent review articles [10,510]. Stretachable conductors must be prepared to retain high electrical conductivity under large strains for highly conductive components. In general, the integration of these parts in a single device with a stable response is challenging and can likely be realised by fully understanding the materials, structures, electronics, and target performances for each element.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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