

Recent Developments in Bio-monitoring via Advanced Polymer Nanocomposite-based Wearable Strain Sensors: A Review

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Abstract

The enormous usage of wearable devices has been trending in recent years. There is a massive demand for sensitive and stretchable wearable strain sensors in the field of medical practice, robotics, sports, entertainment, prosthetics, etc. The paper describes polymer nanocomposite based wearable strain sensors for bio-monitoring the motions. With the excellent features of a highly stretchable polymer matrix and nanomaterials conductivity, nanocomposite based strain sensors have become superior in the market.

Keywords: - *bio-monitoring, polymer, nanocomposite, strain.*

INTRODUCTION

The development of polymer nanocomposite based strain wearable sensors in medical diagnosis, robotics, sports, and other fields has risen due to progress in bioelectronics wearable devices and nanotechnology. There is an ease of attaching the device to the human skin with the help of elastic straps, or it can be placed on the garment to monitor the physical biochemical signals and motions. The material and structure should be mechanically flexible to adapt themselves according to the motions of rotating joints of the human body. It should be soft enough so that the user doesn't feel the discomfort of the device on their skin. There are multiple applications of wearable strain sensors, and strain sensing is one of them. But difficulties lie in fabrication, performance, measurement, which has decreased its applicability. The standard strain sensors are more economical, but they are not sufficiently stretchable, and they are considerably bulky too. Due to advancements in science and technology, the requirement for high-performance wearable strain sensors has expanded to emphasise highly sustaining stretchability without affecting the conductive pathways. The standard semiconductors such as silicon and metal oxide film are fragile plus inflexible. Hence their purposes are restricted in numerous ways. They can't be utilised in integration with curvilinear surfaces such as human skin and garments, and

they can't be bent, twisted in a large amount. With the utility of ultra-thin films of silicon and metal oxide semiconductors, stretchability in bending can be achieved. Reducing the thickness didn't affect young's modulus, and stretchability also doesn't improve much; hence semiconductors for strain sensors became impractical to use. To address this issue, the strategy applied was "materials that stretch" and "structure that stretch". The solution found was the polymer nanocomposite based strain sensor. It has two main components: 1. Conductive network 2. Elastomeric polymer. The first component is a sensing element, and the second one ensures the stretchability and guards the conductive network. With the physical change in the strain in clothes or human skin, the appropriate signal is generated. Concerning getting accurate results, the direct meeting of strain sensor with human skin is unnecessary as long as adhesion is firm enough to estimate the same degree of strain. The interruption of resistive and capacitive signals produced by a strain sensor with the outer atmosphere and body fluids can be reduced with the help of encapsulating the sensor using properly biocompatible and stretchable polymer. The paper presents a review of the past and the recent developments done in polymer nanocomposite based wearable strain sensors. It describes the performance metrics and features of the wearable strain sensors. And finally, it discusses the

selection of material, including the elastomeric substrate and conductive nanomaterials and recent development. [1]

SENSING MECHANISM

The purpose of strain sensors is to transform the mechanical deformation into an electrical signal. There are several sensing mechanisms: Piezoelectricity, optical methods, capacitive, resistive. The most familiar and generally used are resistive and capacitive methods. To estimate a strain sensor, the term, Gauge factor (GF) is defined. It is defined as the relative change in resistance or capacitance divided by a mechanical strain.

[2] The sensing mechanism of polymer nanocomposite based sensors is not the same as regular strain sensors owing to their conductive network and designs.

Geometric Effect

A stretchable capacitor is a highly promising element, and it can be used as a stretchable strain capacitive sensor. It can sustain a large strain. If mechanical stimulation is applied, the geometry of the capacitive strain sensor can be modified.

$$C = \epsilon_0 \epsilon_r \frac{A}{d} \tag{1}$$

where, ϵ_0 is the vacuum permittivity

ϵ_r is the relative permittivity of the dielectric layer, A is the area overlapped by the electrode

d is the distance between the two electrodes. Due to externally applied tensile strength, the capacitor can be deformed, area A can be increased, and concurrently, the distance between two electrodes d can be reduced. If uniaxial strain ϵ is applied, the length l is increased to $(1 + \epsilon)l_0$, and the width and distance are reduced by $(1 - \nu \epsilon)$. [3]. Therefore, capacitance is changed by equation 4

$$C = \epsilon_0 \epsilon_r \frac{(1 + \epsilon)l_0(1 - \nu\epsilon)w_0}{(1 - \nu\epsilon)d_0} \tag{2}$$

$$C = \epsilon_0 \epsilon_r \frac{(1 + \epsilon)l_0w_0}{d_0} \tag{3}$$

$$C = (1 + (\epsilon))C_0 \tag{4}$$

When the strain sensor is at maximum stretch, the Poisson ratio is about 0.5 of electrode and dielectrics. [4]. The sensing mechanism of the resistive strain sensor is how the behaviour of the sensor is modified when the microstructure is changed. Hence the conductive path of the resistor changes, and gradually the resistance changes.

From Ohm's law, we know that the resistance of a conductor is given by $R = \rho l/A$ where "ρ" is the electrical resistivity, l is the length, and A is the area of cross-section of the conductor. When a strain is applied on the strain sensor, length l will increase, area A will decrease, and overall there will be an increment in the resistance. The geometric effect plays a more crucial part in capacitive type strain sensors.

$$\frac{\Delta R}{R} = (1 + 2\nu)\epsilon + \frac{\Delta \rho}{\rho} \tag{5}$$

Here, $(1 + 2\nu)$ is the geometric effect and $(\frac{\Delta \rho}{\rho})$ is the fractional change in resistivity of the material undergoing strain.

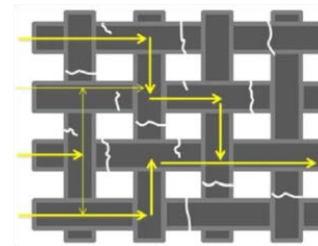


Fig. 1: Current pathway within fractured GWF under stretched state [1]

metals, the change in resistivity is relatively small, in the order of 0.3. On the other hand, for semiconductors, $(\frac{\Delta \rho}{\rho})$ is 50-100 times larger than geometric terms. Heavy semiconductors with high sensitivity could be utilised as a strain sensor, but their purposes are limited due to their inflexible nature. Polymer nanocomposite based wearable strain sensors possess the qualities of conductive nanomaterials and elastomeric materials. Hence there is a mismatch amid these two material's elasticity, and therefore their piezoresistive effect is diminished, which conclusively leads to lower adhesion.

A. Crack Propagation

A thin film covers the soft layer of the polymer. When the thin film undergoes a high strain, the cracks can be formed on the brittle, thin-film propagating around it. In polymers, these cracks can be caused due to static loading. Upon stretching, these cracks can spread and scatter until the material bears a breakage. If the cracks are propagated, the electrical conductivity can suffer in nanomaterials. The original electrical conductivity can be achieved if the cracks are treated and filled, and the thin film is under no strain. This mechanism shows more severe effects in 2-dimensional structures such as polymer thin film, graphene, etc. than 1-dimensional nanowires. [7] demonstrated crack propagation. Ultra-

sensitive graphene on a polymer-based wearable strain sensor with a strain of 8% is demonstrated. By chemical vapour deposition (CVD), graphene woven fabrics (GWFs) are prepared, and it is applied on the surface of elastomeric poly (dimethylsiloxane) (PDMS). When this thin film is subjected to a strain of about 1 to 8%, the cracks are formed and massively scattered on the graphene woven fabric. These cracks significantly caused changes in the resistance. The current path in the fractured GWF is shown in Fig.1

I. Tunneling Effect

Tunneling is the term used when majority carriers cross the non-conductive barrier. Electrons can easily tunnel through tightly packed adjacent nanomaterials. We can estimate the tunneling resistance between two alongside nanomaterials using John Simmon’s theory for electrical tunneling resistance

$$R_{\text{tunnel}} = \frac{V}{AJ} = \frac{h^2 d}{Ae^2 \sqrt{2m\lambda}} \exp\left(\frac{\sqrt{2m\lambda} d}{\hbar}\right) \quad (6)$$

Where J = tunneling current density

V = electrical potential

e = quantum of electricity

m = mass of an electron

h = plank’s constant

d = distance between conductor and elastomer

λ = elastomer’s energy barrier height

A = area of cross-section of the conductor. [8] In a recent study performed by Hu et al.(2008) [9], a carbon nanotube-polymer nanocomposite strain sensor (CNTs) is used to check the tunneling effect. When a section of the volume of the CNT strain sensor was controlled under a small strain, the tunnelling effect was seen to be more dominant than piezoresistivity observed with numerical simulation.

PERFORMANCE AND FEATURES OF STRAIN SENSORS

Several performance metrics are analysed to devise a high-performance strain sensor. There are various metrics which are sensitivity, linearity, stretchability, discussed below.

A. Gauge Factor (Sensitivity)

It defines the relationship between the relative change of electrical resistance or capacitance and applied strain.

$$GF = \frac{\Delta R}{R_0 \epsilon}, GF = \frac{\Delta C}{C_0 \epsilon} \quad (7)$$

Here, (1 + 2ν) is the geometric effect and (Δρ/ρ) is the fractional change in resistivity of the material undergoing strain. For where ΔR or ΔC denotes a change in resistance or capacitance, ε is the applied strain on the sensor, R₀ or C₀ is the initial resistance or capacitance when the sensor is under 0% strain.

GF is the measure of the sensitivity of the sensor. In metals and semiconductors, the value of the gauge factor is normally very high. It ranges from 2 to 5 for metals and from 100 to 1000 for semiconductors. But as we know, their restrictions in stretchability and hence their practical applications are limited. Progressions made in nanotechnology and microelectronics have made the wearable strain sensor achieve excellent gauge factor value, and therefore their applications have increased immensely. For the capacitive type strain sensor, the dominating sensing mechanism is the geometric effect.

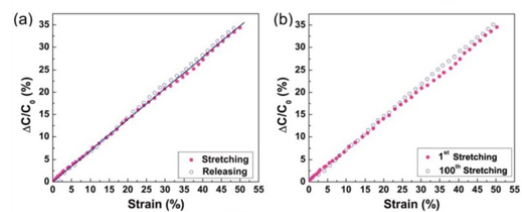


Fig. 2: Strain sensing performance: a) Linear fit of strain

The restrictions of the geometric effect have reduced the GF factor to 1 for the capacitive strain sensor. In the resistive type strain sensor, the solid and robust mechanisms are tunneling effect and crack propagation. Any changes in composition lead to fluctuations in the value of resistance which ultimately leads to the increment in the value of the gauge factor. Cai et al.(2013) [10] demonstrated the multifunctional carbon nanotube (CNT) based capacitive strain sensor. It can measure and detect a strain of about 300 %. The durability of this sensor is excellent because it can measure the strain even after sensing capability of the capacitive sensor up to 50%. b) Relative capacitance change for 1st and 100th stretching of the capacitive sensor. [11] a thousand cycles. It has the highest sensitivity because its gauge factor is reported to be 1. The carbon nanotube-based strain gauge device exhibits the linear capacitive response.

B. Linearity

If the device has a linear gauge factor, then the strain sensor can have a simple calibration and also, the obtained results will be accurate. For most resistive type strain sensors, as it comes under extreme strain, its linearity starts decreasing. One of the main causes of nonlinearity

is when the sensors are subjected to stretch and suffer from nonhomogenous morphology. For the capacitive type strain sensor, the linearity can be compromised when the device is subjected to immense strain due to variations in the Poisson's ratio. Yao et al.(2014) [11] fabricated a highly stretchable and multifunctional strain sensor. It is based on a capacitive sensing mechanism, and the silver nanowires are used as conducting electrodes and for dielectric, Ecoflex has been deployed. Silver nanowire electrodes are screen printed. This strain sensor can detect the strain up to 50%, as shown in figure 2 and pressure up to 1.2MPa. The strain sensor also has an excellent and fast response time of 40ms. [11].

MATERIALS SELECTION FOR STRETCHABLE STRAIN SENSORS

The strain sensors hold the properties of flexibility, stretchability, sensitivity, and broad detecting range. It is very important to select suitable materials so that these properties are obtained. Several different nanomaterials utilised for polymer nanocomposite based strain sensors are Carbon black (CB), Carbon Nanotubes (CNTs), graphenes, Silver nanowire (AgNWs), copper nanowire (CuNWs), Au nanowires (Au NWs). The conductive polymers that can be used are polypyrrole (PPy), polyaniline (PANI), PEDOT: PSS. These conductive materials have excellent electrical conductivity, suitable for sensing mechanisms, but they have poor mechanical properties. By fabricating a composite of electrically conductive fillers, high sensitivity can be accomplished, and by preparing the composite of an elastomeric matrix, the desirable mechanical properties are obtained. In the following section, we have discussed a few composites which have gained both sensitivity and flexibility.

A. Stretchable/Flexible Elastomeric Matrix

To provide flexibility and versatility, a flexible matrix is present in a strain sensor. It provides support to the strain sensor. It should possess excellent mechanical, chemical, thermal properties. The adhesion of flexible material with other layers is also satisfactory. Some of the commonly used flexible elastomeric matrices are PU foam, silicon-based elastomers (PDSMs) and rubbers, polyethylene terephthalate (PET), polyimide (PI), cotton, polyvinylidene fluoride (PVdF), Ecoflex and Kevlar fibre. Amongst all these, PDSMs have all the properties expected by a flexible matrix, and hence it is extensively used. Its cost is also low. The young modulus of PDSMs is also less (about 0.4 to 3.5 MPa) [8] than most of the other supporting materials such as PU and

PVdF. The lower value of Young's modulus is a sign of ample flexibility. Liu et al.(2009) [12] has reported that the young modulus rises when the thickness of the membrane decreases. The thickest membrane of about 1.8 mm resulted in the young's modulus of 600kPa, whereas the smallest membrane of 50 m had 1400 kPa with a strain of nearly 125%. With low young's modulus and high stretchability, PDMS can be picked to be used as a matrix for fabricating flexible strain sensors.

B. Electrically Conductive Materials

Carbon-based nanomaterials, graphene, carbon nanotubes have superior mechanical properties, thermal and electrical conductivity. The carbon blacks have achieved dominance in the area of electrical materials due to their polycrystalline nature. The conductive material in the elastomeric matrix should be chemically inert, have low density, and be cheap enough to develop a strain sensor, and CB fulfils these criteria. Shintake et al.(2018) [13] have proposed a stretchable strain sensor with a stretchability of about 500%, fabricated using Carbon blacks filled elastomeric composites. These are fabricated at low cost, and they are batch manufactured. When carbon blacks are employed as fillers for elastomeric composite, they improve light absorption, UV resistance of the composite. The sensors are fabricated using film cast techniques and carbon dioxide laser ablation. This technique allows the manufacturing of both resistive and capacitive based strain sensors. These sensors are manufactured layer by layer. For capacitive strain sensors, the linearity is relatively high, up to 0.995. It faces low hysteresis and gauge factor in the range of 0.83 to 0.98. For the resistive strain sensor, the gauge factor lies in the range of 1.62 to 3.37. These sensors can work for the cycle of about 10000 without facing any failures. The capacitive strain sensor works better as compared to the resistive strain sensor. [13]. It is illustrated in Fig.3

RECENT DEVELOPMENT

In this recent development, Yao et al.(2015) [2] has illustrated Silver Nanowire strain sensors for wearable body motion tracking. The wearable body motion tracking technology is used in the form of a data glove that can read the bending positions of each finger knuckles instantly. The data glove has attached a flexible and stretchable capacitive sensor based on Silver Nanowire (AgNW) and very well adapted to curved surfaces. The sensor can bear large tensile strain up to 60% and has a linear response with less than 5 msec response time. In this recent development, the silver nanowire stretchable wearable strain

sensor detects the state of the finger and instantaneous motion in detail. The AgNW based strain sensor is based on capacitive sensing. In this capacitor, two AgNW forms the electrodes, and eco flex acts as a dielectric.

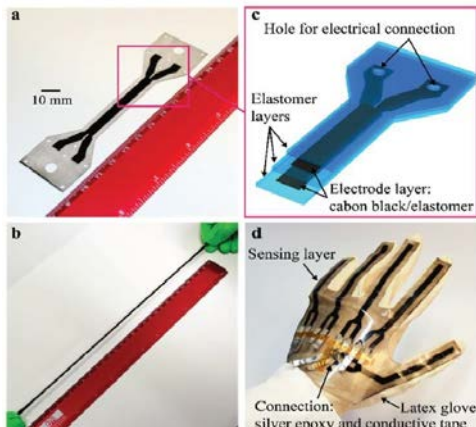


Fig. 3: Highly stretchable sensors with carbon black composite electrodes. a) A fabricated sensor for characterization. b) The sensor stretched up to 500% electrode layers and dielectric layers.

d) An intelligent glove integrating independently operated five sensors, which are fabricated in one single layered structure. [13]

A. Sensor Characterization

The fabricated sensor is characterised in the lab and then fastened to human skin to test motions to obtain the calibration curve. The capacitance value is recorded using an AD7152 evaluation board. The calibration curve shown in Fig.4 is determined by placing a strain sensor under the tensile stage and evaluating the change in capacitance. From the curve, it is observed that there is a linear increase until the sensor is stretched up to 60%. This excellent stretchability makes AgNW based strain sensor a perfect fit for wearables compared to a conventional strain gauge with a stretchability of a mere 5%. The gauge factor is 1.

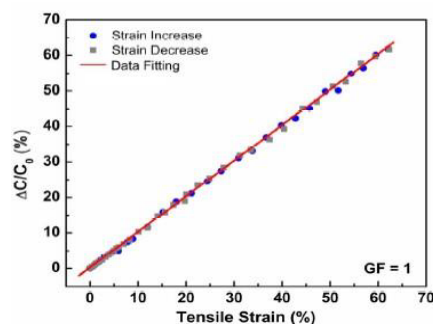


Fig. 4: Strain sensor calibration: relative capacitance change as a function of applied tensile strain during strain increase and strain decrease. The red line shows the fitting to the experimental data. [2]

Before practising the strain sensor in data gloves, it is attached to human skin to examine the illustrations in applications having large deformations such as checking knee motions. The sensor is placed on the knee and the capacitance.

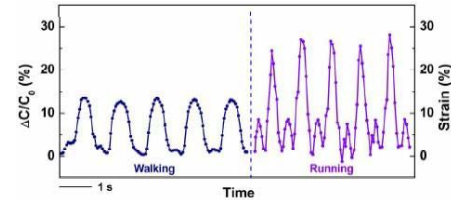


Fig. 5: Demonstration of using strain sensors for knee motion detection: Relative capacitance change and the resulting strain associated with walking and running for five continuous cycles.

of the sensor is monitored while the individual is standing or running. The sensor can experience an increase in strain when there is flex in the knee during the motion. From the results shown in Fig. 5, the amplitude and frequency can be evaluated. Such data is helpful to determine the performance of athletes, give feedback to robots, and monitor motion during rehabilitation.

B. “Glove” user interface prototype

Fig.6 shows the wearable glove with the AgNW strain sensor for the human-machine interface. This glove can detect the entire finger knuckle movement from -30 to 90 degrees. The response time of the strain sensor calculated is 5 msec, and the angular resolution is 5 degrees. This sensor can also monitor the purlicue area motion of the hand depicted in Fig.

7. This motion helps to interpret more complex index finger movements and hand gestures. With the virtue of excellent stretchability, the sensor can be bent for a long time without

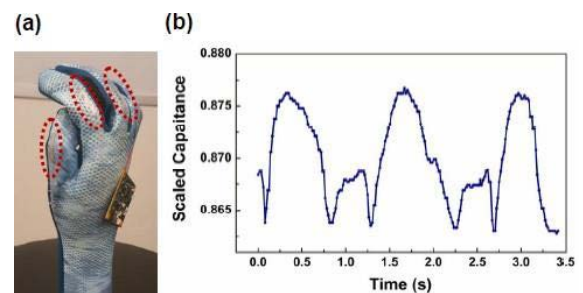


Fig. 6: Strain sensors for wearable glove application. (a) Glove with three sensors (marked by red dashed line) with a data acquisition system. (b) Demonstration of real time tracking of the middle figure knuckle bending by the AgNW stretch sensor glove. Case showing here tracks the knuckle 90 degree bending completed in about 150 msec.



Fig. 7: Strain sensor mounted at pulcrue area to track subtle index finger and palm motion. [2]

suffering the fracture. When the index finger is opened, the sensor experiences the strain, and it helps to increase the capacitance value. [2]

CONCLUSION

Wearable sensor devices are in trend and they are used in great numbers because of its ease of use, easy diagnosis, better user experience, and its durability. It has applications in various applications in medical diagnosis, sports, entertainment, visual realities, prosthetics, and many others. Due to advancements made in the field of microelectronics, nanotechnology, material science, there has been a huge development in the wearable strain sensors. The polymer nanocomposite materials provide much more stretchability and linearity compared to metallic conductors materials used as wearable strain sensors.

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