

Flexible Pressure Sensor Based on Carbon Black/PVDF Nanocomposite

Abstract:

A piezoresistive flexible pressure sensor was fabricated using carbon black and Poly (vinylidene fluoride) (CB/PVDF) composite. The conductive CB/PVDF composite was prepared by a wet-casted method and deposited into a flexible polyethylene (PE) substrate. The surface morphology, crystal structure, and material properties were studied using SEM and X-ray diffraction methods. This flexible pressure sensor was tested in a wide pressure range of about 0-75 kPa and its response time was less than 0.43 s. The sensitivity, response time, and recovery time were studied for different pressures and vibration modes. The repeatability and reproducibility characteristics of the sensor were studied and found that the sensor exhibits excellent characteristics. The sensor was subjected to different loading and unloading pressures and the resistance of the sensor remained stable indicating that the sensor had a high degree of reproducibility. Owing to its flexible properties and the material used, the proposed device can be applied in the next generation of smart sensors for biomedical, robotic, and automotive sensing applications.

Keywords: flexible pressure sensor, carbon black, PVDF, composite, solvent, piezoresistive.

1. Introduction

Sensors with distinct characteristics such as lightweight, high flexibility, and high sensitivity are attracting a wide range of applications. In particular, flexible pressure sensors are increasingly applied in different fields such as electronic skin, health monitoring, robotics, advanced prosthetics, virtual reality entertainment technology, and sports [1-7]. Novel materials such as conductive polymers, carbon nanomaterial, and carbon black are mainly used in these flexible pressure sensors because they possess excellent electrical conductivity, chemical stability, low toxicity and are widely available [8-12]. These novel materials are deposited on polymeric substrates such as polyimide (PI), polydimethylsiloxane (PDMS), polyethylene terephthalate, and PE for flexible pressure sensor applications [3, 13-15]. These

novel materials replace the metal foils and semiconductors which were traditionally used as the sensing platform. The rigidity and high cost of the old materials make them inefficient for current practical applications.

The sensing mechanism of the pressure sensors can be divided into different categories. The four main categories are piezoresistive, piezoelectric, capacitive and transistor [16-18]. Piezoelectric pressure sensors have high sensitivity and stability but have limited applications in pressure measurements because they cannot measure static pressure. The surface charge produced by the applied force in the piezoelectric materials can be neutralized easily by current leakage, charges from the environment, or the resistance from the connected electronics making them require high pass filters. [14, 19-22]. Another disadvantage of these sensors is that they are sensitive to temperature, most piezoelectric materials are pyroelectric, therefore they are temperature sensitive, the temperature may induce crystal deformation, which may in turn produce unwanted forces [22]. The piezoelectric pressure sensors are the most utilized sensors due to their remarkable advantages including simple fabrication, stability, reliability, and they have high pixel density to measure large pressure ranges [23]. The conductive sensing material is an important parameter in evaluating the variation rate of the resistance in these resistive sensors. To improve their sensitivity, porous materials such as the porous elastomers and electrospun nanofiber membrane have been used for increasing the deformation of the piezoresistive sensors. Polymer materials are suitable polymer nanomaterials, including carbon nanotubes, graphene, nanowires, and other metal nanomaterials.

Various publications on piezoresistive materials, using different binders, nanoparticles on different substrates, have been reported in the past on their sensitivity, hysteresis, reproducibility, and resistance performance. For instance, Zhang et al. experimented on carbon black/silver nanoparticles (CB/AgNPs) based strain sensors on polyurethane substrate. They found that the sensitivity improved by 18 times for CB/AgNPs composite compared with bare carbon-based strain sensors [24]. Chang et al. developed a flexible resistive-type pressure sensor using carbonized cotton fabric (CCF). The sensors showed a large measurement range (~ 0.16 kPa), a low detection limit (~ 0.70 Pa), and excellent durability (>4000 cycles) [25]. For fluid pressure sensing on a curved microtube, Yao et al. developed a piezoresistive flexible sensor using micropatterned conductive carbon nanotube as the sensing element. A high sensitivity (0.047 kPa⁻¹ in gas sensing and 5.6×10^{-3} kPa⁻¹ in liquid sensing) and low consumption (<180 μ W) was reported [26]. Kweon et al. fabricated PVDF-HFP/ PEDOT composited-based pressure sensor using 3D electrospinning. These samples indicated higher pressure sensitivity compared with conventional

electrospinning (13.5 kPa⁻¹ for 3D electrospinning whereas 5.1 kPa⁻¹ for conventional). The sensors also showed a minimum detection of 1 Pa and were resilient up to 10,000 compressive cycles [27].

This paper reports the experimental results of a simple, low-cost and highly sensitive piezoresistive flexible pressure sensor using CB/PVDF composite as the sensing element. The composite was prepared by the wet casting process and deposited on a flexible polyethylene substrate. The pressure vs resistance response was recorded and it resulted in good stability, sensitivity, repeatability. The details of the experimental process and the results obtained will be covered in the subsequent sections.

2. Materials, Methods, and Fabrication of Pressure Sensor

The materials used for the preparation of the sensing element are CB, PVDF, and DMF. The material properties of these materials were taken from the manufacturer's literature. Table 1 gives a summary of the material properties of CB and PVDF. CB was used as the conductive phase, PVDF was used as a binder while DMF was used as the solvent to mix up the composition.

Table 1 Properties of carbon black and PVDF used for the preparation of the sensing element

	Specific surface area (m²/g)	Resistivity (Ω.cm)	Young's Modulus (MPa)	Dielectric constant
Carbon Black	780	0.2	1.5 X10 ⁵	
PVDF	3.76 - 6.61	> 10 ¹⁴	2450	7.5-13.2

The film fabrication process and CB/PVDF nanocomposite preparation are indicated in Fig. 1. A mass ratio of 1:1 between CB and PVDF was deposited onto a glass beaker and average size drops of DMF were added as shown in the schematic in Fig. 1 (a-c). This ratio was chosen in order to have high carbon: binder ratio and to provide clarity on the analysis. The binder also helps in forming a uniform film that is mechanically stable when loading and unloading pressure is applied. The solution was vigorously stirred to ensure homogenous dispersion of conductive nanocomposite. This composition was also ultrasonicated for 1 hour with a constant interruption of 20 mins to avoid the agglomeration of nanocomposites. The PE substrate was then prepared according to standard practice for the preparation of surfaces of plastics to enable adhesive bonding of the CB/PVDF composition. The physical surface preparation of the substrate involved wiping with methanol, sanding, wiping with a clean dry wipe, and then wiping with the methanol wipes again [28].

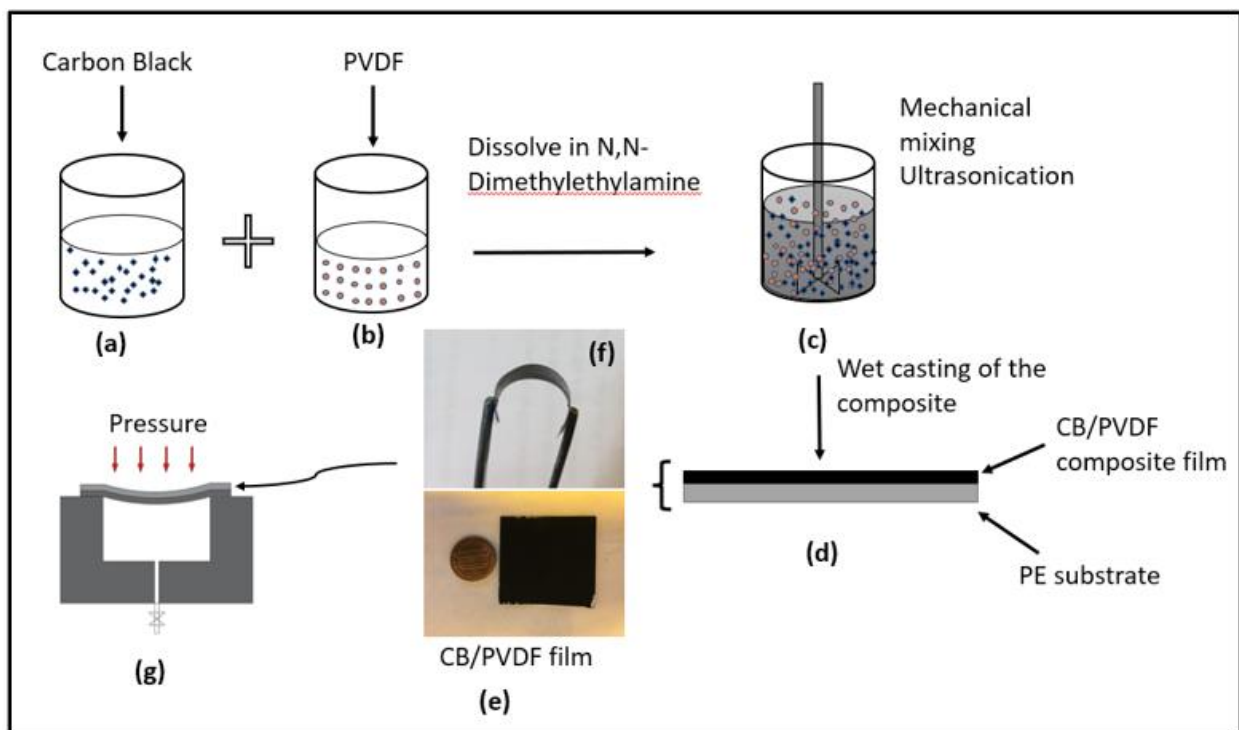


Fig. 1. The schematic illustration for the preparation of CB/PVDF composite film for fabrication of pressure sensor.

The CB/PVDF nanocomposite was wet-casted onto a flexible PE substrate to form a thin CB/PVDF film of about 0.1 mm (Fig. 1. d). The film was then placed on a warm plate at 30 °C for 20 minutes to evaporate the extra DMF solvent, furthermore, the film was set to air dry in the room for 12 hours. A sensitive thin film of CB/PVDF was formed and it had a thickness of about 30 microns, the film was etched to form a thin strip of about 2 mm thick. The film was mounted to a (20 × 20 × 10) mm acrylic PMMA cubic with an opening at the center. The center diameter was measured to be 5 mm with a depth of 5 mm (Fig.1 g). The CB/PVDF conductive film was then mounted to the surface containing the 5 mm hole in the acrylic PMMA cube (Fig. 1. g). A high-pressure compressor was then connected to the acrylic PMMA fixture through the valve attached to the 5 mm hole. The pressure gauges were mounted to regulate the applied pressure on the CB/PVDF film. When the gauge pressure was applied through a valve, the thin CB/PVDF membrane deformed into a dome-shaped structure. The radius of the dome was a function of pressure and hence the strain experienced by the film gave rise to resistance in the material, which changed as a function of applied pressure. The resistance of the film was recorded using a Keithley multimeter connected to a computer through a custom-made LabVIEW interface. The response graphs obtained are a function of resistance and time.

3. Results and Discussion

a. Morphology of Materials/Characterization

The surface morphology of the fabricated film was investigated using scanning electron microscopy (SEM). The SEM image in Fig.2 indicates a good dispersion of CB/PVDF particles. Uniform distribution of the conductive and binder matrix plays a key role in determining the piezoresistive property of the composite film. The uniform dispersion is influenced by the particle size, shape, and orientation of the particles. The XRD pattern has been carried out on CB/PVDF composite in the ratio by mass percentage is shown in Fig. 3. It is clear from the figure that there were peaks of PVDF corresponding to a 2θ angle of 20.160 and 39.840. The presence of a dominant peak at 20.160 confirms the presence of beta-phase in PVDF material. The XRD pattern confirms the semi-crystalline nature of PVDF polymer film [29]. The crystalline size for the PVDF-110 peak was found to be approximately 0.89 nm using the Scherrer equation. The diffused peak of carbon black was observed at an angle of 23.8° (002) plane, this diffused peak may be caused by the lack of crystallinity of the carbon black and polymer mixture at this angle. The PVDF restricts the diffract of the film at this angle due to its polymeric structure, the peaks of PVDF dominated the CB as indicated by the XRD spectra [30-32].

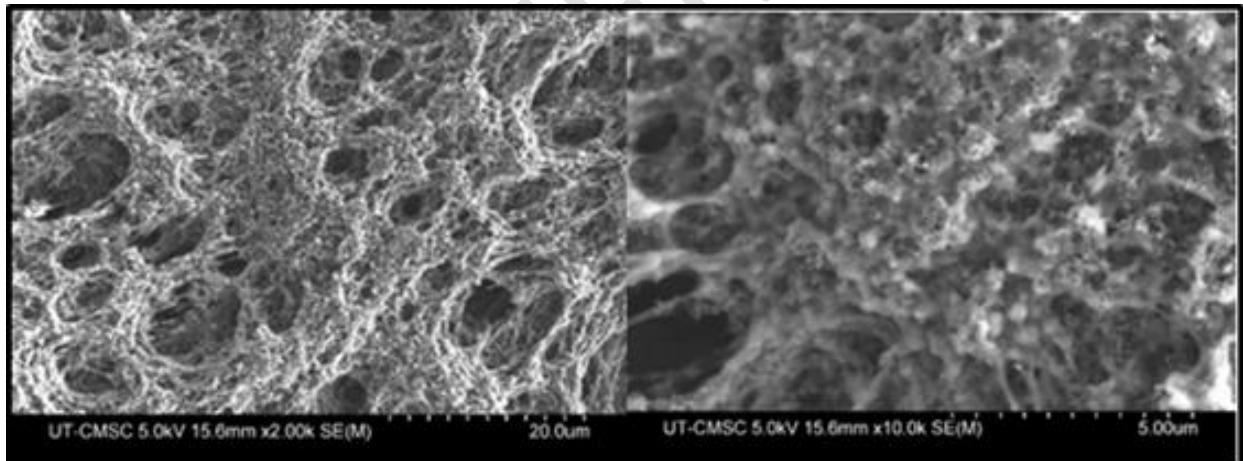


Fig. 2. The surface morphology of the CB/PVDF composite was investigated using a Scanning Electron Microscope (SEM).

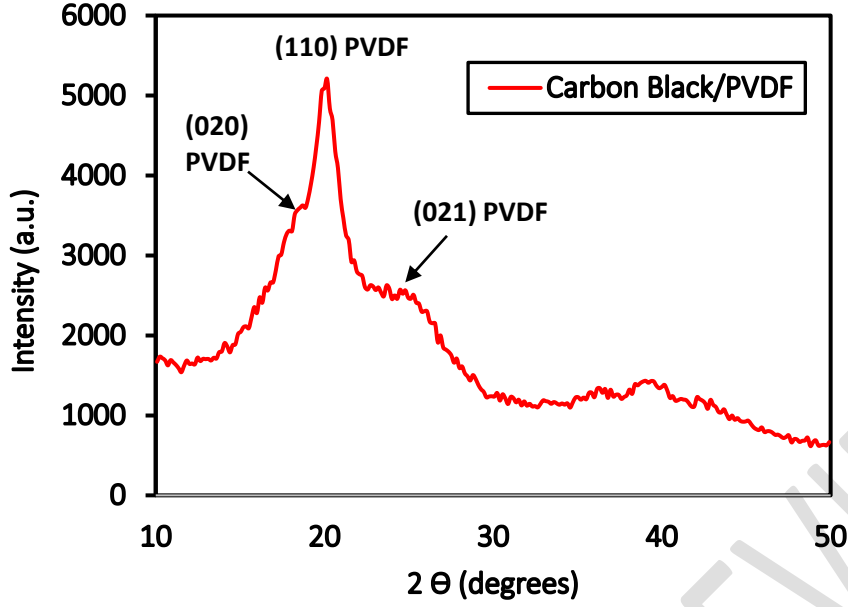


Fig. 3. X-ray diffraction patterns of CB/PVDF.

b. Pressure Sensing Characterization Sensing Mechanism

Fig. 4 shows the time response for CB/PVDF film when vacuum pressure was applied. It was noted that when pressure was applied the film resistance decreases. This decrease in resistance was because the film diaphragm deformed causing compressive stress on the film, the uniaxial pressure causes the gaps between two adjacent conductive particles to be smaller which leads to a decrease in the film's electrical resistance [33]. The PVDF binder helps the active material to mitigate the stresses of contraction and to maintain the adhesion of the CB to the conductive network. The compression destroys the conductive paths of CB by causing the transverse slippage of carbon black particles which contribute to an increase in composite resistance [33]. The electrical resistance of a single conductive path can be described by the equation below [34]:

$$R = \frac{2h^2sL}{3a^2e^2\sqrt{2m\phi}} \exp\left(4\pi\sqrt{2m\phi}\frac{s}{h}\right) \quad (1)$$

Where, R , L , m , e , h , s , ϕ , a^2 are the resistance of the single conductive path, the number of particles forming the conductive path, the electron mass, the electron charge, the Plank's constant, the thickness of insulating film, the height of potential barrier between adjacent particles, and the effective cross-sectional area respectively.

When the pressure was applied on the thin CB/PVDF film, the resistance (response) decreases with time, and when the gauge valve was turned off the response increases abruptly. Eq. 2 can be used to calculate the recovery time on the exponential curve of this pressure response [35]:

$$R = R_0 + A_1 \exp\left(-\frac{t}{t_1}\right) \quad (2)$$

Where, R_0 and A_1 are constants, while t and t_1 are the time response and time constants, respectively. The calculated time constants (t_1) are 0.43 s when the valve was turned off (recovery) and 0.138 s when pressure was initially applied to the film. The time response values were estimated from the linear fit of the exponential curves. The higher recovery time t_1 can be attributed to a slow air intake on the valve but the rapid increase of the air in the chamber resulted in a small t value.

UNDER PEER REVIEW

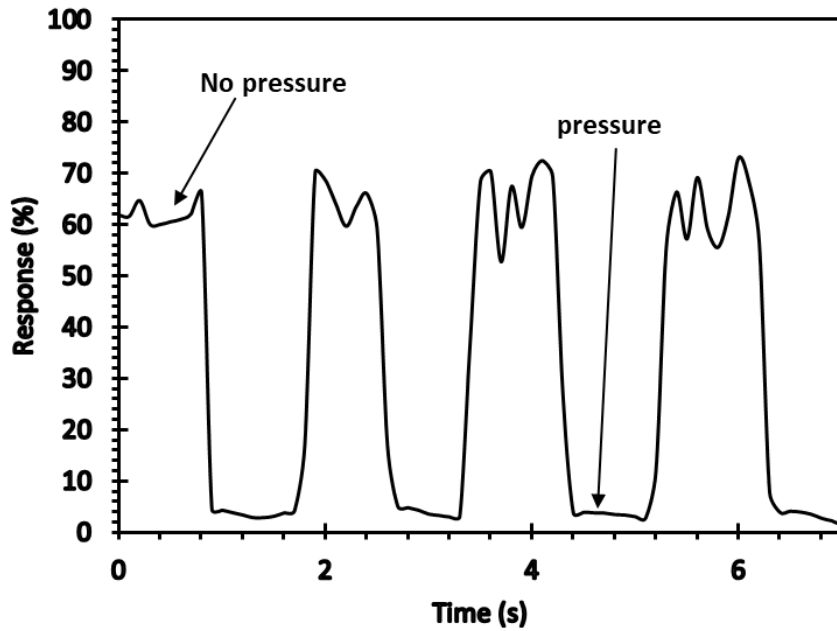


Fig. 4. Sensing performances of the pressure sensor with a thin CB/PVDF membrane under a pressure of 76 kPa.

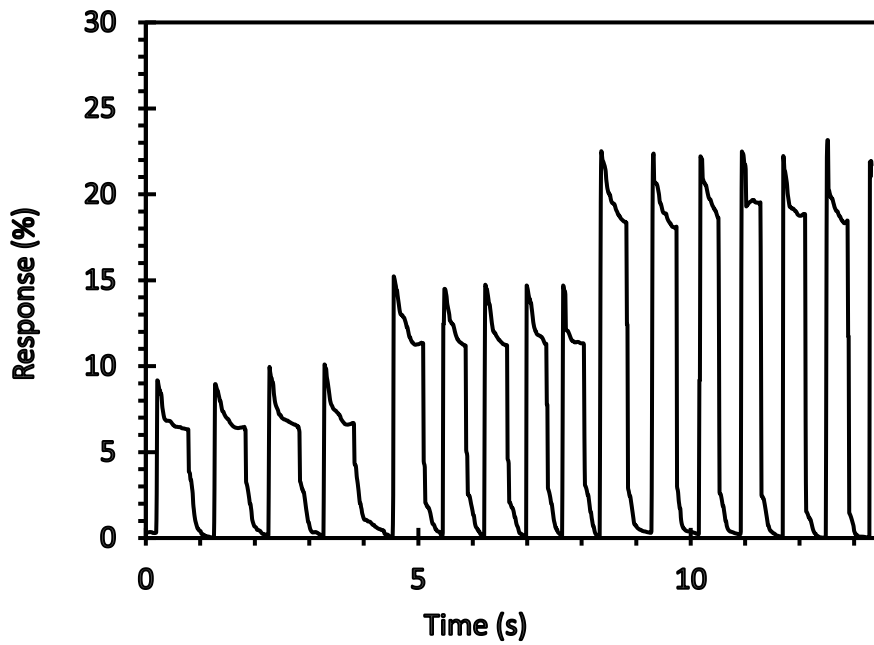


Fig. 5. Time response for CB/PVDF composite with different vacuum pressures applied.

The sensor was then subjected to different pressures as shown in Fig. 5, this test was used to study the repeatability and reproducibility of the sensor. The sensing element was subjected to loading and unloading for several cycles and the response at different pressures was recorded. The mean response at different pressures was recorded and marked as shown in Fig. 6.

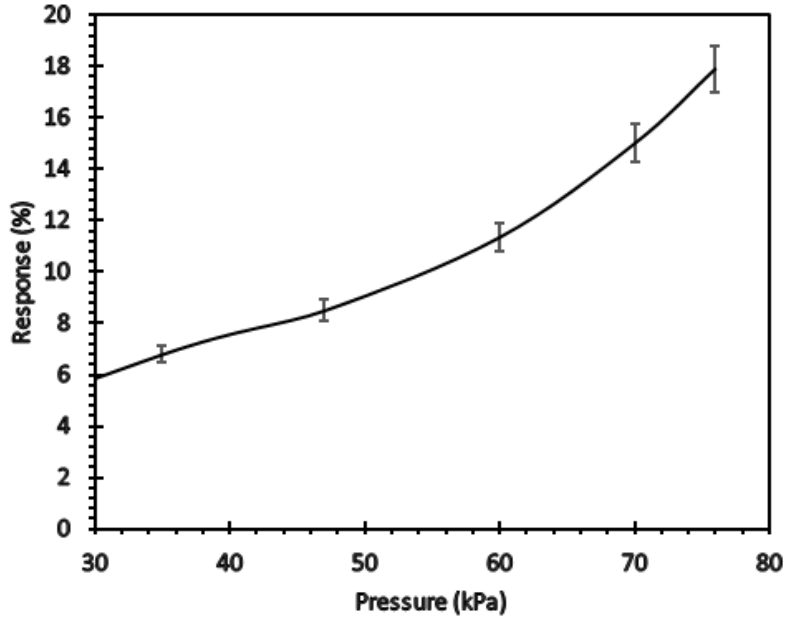


Fig. 6. Dependence of piezoresistive response on the pressure with error bars for the experimental data.

The response remained stable after a series of loading-unloading tests at the same pressure, this indicated that CB/PVDF had a high degree of repeatability and reproducibility which could be attributed to the firmness of the CB conductive layer. The sensing element was also evaluated by subjecting it to a vibrating device that had different vibrating modes suitable for the test. The vibration response was given in Fig. 7. showing that the sensor had a high degree of reproducibility and repeatability. The calculated frequency with that specific vibration mode was found to be about 16 Hz.

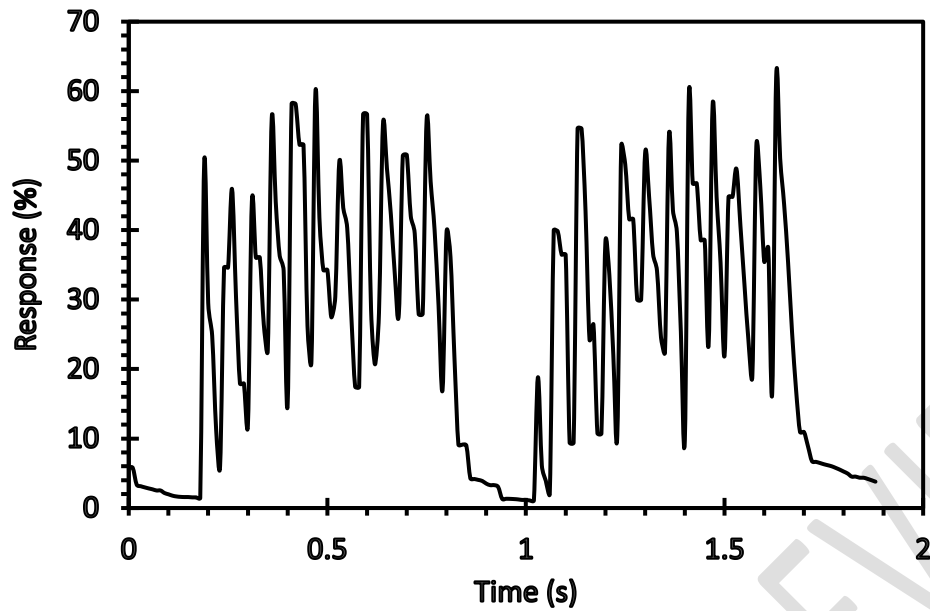


Fig. 7. Vibration response of the sensor when the thin CB/PVDF membrane was mounted a vibrating device, the frequency was estimated to be about 16 Hz.

4. Conclusion

A flexible pressure sensor was designed and fabricated using CB/PVDF composite film. The thin film was deposited on a PE substrate that provided flexibility to the sensor. The addition of PVDF to the conductive CB increases the adhesion of active material and the crosslinks between carbon black. This composite material exhibited a change in resistance significantly under loading, which creates film stretching. PVDF also provides an excellent mechanical property essential to generate a sensor signal under loading and unloading cycles. The dynamic characteristics of pressure sensors were also investigated. The sensor exhibited high sensitivity, fast response time, and a quantitative measurement capability of a wide pressure range. The reported pressure sensor demonstrates its high potential for developing piezoresistive pressure sensors and applications in flexible electronics such as wearable devices to monitor the movements of the human body.

Reference

- [1] S. J. Park, J. Kim, M. Chu, and M. Khine, "Flexible Piezoresistive Pressure Sensor Using Wrinkled Carbon Nanotube Thin Films for Human Physiological Signals," *Adv. Mater. Technol.*, 3 (2018) 17001508.
- [2] X. P. Li, Y. Li, X. Li, D. Song, P. Min, C. Hu, H. B. Zhang, N. Koratkar, Z. Z. Yu, "Highly sensitive, reliable and flexible piezoresistive pressure sensors featuring polyurethane sponge coated with MXene sheets," *J. Colloid Interface Sci.*, 562 (2019) 54.
- [3] A. Rinaldi, A. Tamburrano, M. Fortunato, and M. S. Sarto, "A flexible and highly sensitive pressure sensor based on a PDMS foam coated with graphene nanoplatelets," *Sensors (Switzerland)*, 16 (2016) 2148.
- [4] H. Bin Yao, J. Ge, C. F. Wang, X. Wang, W. Hu, Z. J. Zheng, Y. Ni, S. H. Yu, "A flexible and highly pressure-sensitive graphene-polyurethane sponge based on fractured microstructure design," *Adv. Mater.*, 25 (2013) 6692.
- [5] Y. Wang, L. Wang, T. Yang, X. Li, X. Zang, M. Zhu, K. Wang, D. Wu, H. Zhu, "Wearable and highly sensitive graphene strain sensors for human motion monitoring," *Adv. Funct. Mater.*, 24 (2014) 4666.
- [6] Y. Ma, N. Liu, L. Li, X. Hu, Z. Z. Zou, J. Wang, S. Luo, And Y. Gao, "A highly flexible and sensitive piezoresistive sensor based on MXene with greatly changed interlayer distances," *Nat. Commun.*, 8 (2017) 1207.
- [7] S. Gong, W. Schwalb, Y. Wang, Y. Chen, Y. Tang, J. Si, B. Shirinzadeh and W. Cheng, "A wearable and highly sensitive pressure sensor with ultrathin gold nanowires," *Nat. Commun.*, 5 (2014) 1.
- [8] Y. H. Wu, H. Z. Liu, S. Chen, X. Chu Dong, P. P. Wang, S. qi Liu, Y. Lin, Y. Wei, L. Liu, "Channel Crack-Designed Gold @PU Sponge for Highly Elastic Piezoresistive Sensor with Excellent Detectability," *ACS Appl. Mater. Interfaces*, 9 (2017) 20098.
- [9] C. L. Choong, M. B. Shim, B. S. Lee, S. Jeon, D. S. Ko, T. H. Kang, J. Bae, S. H. Lee, K. E. Byun, J. Im, Y. J. Jeong, C. E. Park, J. J. Park, U. I. Chung, "Highly stretchable resistive pressure sensors using a conductive elastomeric composite on a Micropyramid array," *Adv. Mater.*, 26 (2014) 3451.
- [10] Y. Pang, H. Tien, L. Tao, Y. Li, X. Wang, N. Deng, Y. yang, and T. L. Ren, "Flexible, Highly Sensitive, and Wearable Pressure and Strain Sensors with Graphene Porous Network Structure," *ACS Appl. Mater. Interfaces*, 8 (2016) 26458.
- [11] X. Wu, Y. Han, X. Zhang, Z. Zhou, and C. Lu, "Large-Area Compliant, Low-Cost, and Versatile Pressure-Sensing Platform Based on Microcrack-Designed Carbon Black @Polyurethane Sponge for Human–Machine Interfacing," *Adv. Funct. Mater.*, 26 (2016) 6246.
- [12] Y. Huang, D. Fang, C. Wu, W. Wang, X. Guo, and P. Liu, "A flexible touch-pressure sensor array with wireless transmission system for robotic skin," *Rev. Sci. Instrum.*, 87 (2016) 065007.

- [13] H. Park, Y. Ra Jeong, J. Yun, S. Y. Hong, S. Jin, S. J. Lee, G. Zi, and J. S. Ha, "Stretchable Array of Highly Sensitive Pressure Sensors Consisting of Polyaniline Nanofibers and Au-Coated Polydimethylsiloxane Micropillars," *ACS Nano*, 9 (2015) 9974.
- [14] Y. E. Shin, J. E. Lee, Y. Park, S. H. Hwang, H. G. Chae, and H. Ko, "Sewing machine stitching of polyvinylidene fluoride fibers: Programmable textile patterns for wearable triboelectric sensors," *J. Mater. Chem. A*, 6 (2018) 22879.
- [15] L. Pan, A. Chortos, G. Yu, Y. Wang, S. Isaacson, R. Allen, Y. Shi, R. Dauskardt, Z. Bao, "An ultra-sensitive resistive pressure sensor based on hollow-sphere microstructure induced elasticity in conducting polymer film," *Nat. Commun.*, 5 (2014) 1.
- [16] S. Patel, H. Park, P. Bonato, L. Chan, and M. Rodgers, "A review of wearable sensors and systems with application in rehabilitation," *Journal of Neuro Engineering and Rehabilitation*. 9 (2012) 21.
- [17] A. J. Bhandarkar and J. Wang, "Non-invasive wearable electrochemical sensors: A review," *Trends in Biotechnology*. 32 (2014) 363.
- [18] S. Majumder, T. Mondal, and M. J. Deen, "Wearable sensors for remote health monitoring," *Sensors (Switzerland)*. 17 {2017} 130.
- [19] Y. Huang, X. Fan, S. C. Chen, and N. Zhao, "Emerging Technologies of Flexible Pressure Sensors: Materials, Modeling, Devices, and Manufacturing," *Advanced Functional Materials*. 29 (2019) 1808509.
- [20] X. H. Zhao, S. N. Ma, H. Long, H. Yuan, C. Y. Tang, P. K. Cheng, Y. H. Tsang, "Multifunctional Sensor Based on Porous Carbon Derived from Metal-Organic Frameworks for Real-Time Health Monitoring," *ACS Appl. Mater. Interfaces*, 10 (2018) 3986.
- [21] C. Cui, X. Wang, Z. Yi, B. Yang, X. Wang, X. Chen, J. Liu, and C. Yang, "Flexible Single-Electrode Triboelectric Nanogenerator and Body Moving Sensor Based on Porous Na₂CO₃/Polydimethylsiloxane Film," *ACS Appl. Mater. Interfaces*, 10 (2018) 3652.
- [22] S. H. Park, H. B. Lee, S. M. Yeon, J. Park, and N. K. Lee, "Flexible and Stretchable Piezoelectric Sensor with Thickness-Tunable Configuration of Electrospun Nanofiber Mat and Elastomeric Substrates," *ACS Appl. Mater. Interfaces*, 8 (2016) 24773.
- [23] S. Stassi, V. Cauda, G. Canavese, and C. F. Pirri, "Flexible tactile sensing based on piezoresistive composites: A review," *Sensors (Switzerland)*. 14 (2014) 5296.
- [24] W. Zhang, Q. Liu, and P. Chen, "Flexible strain sensor based on carbon black/silver nanoparticles composite for human motion detection," *Materials (Basel)*., 11 (2018) 1836.
- [25] S. Chang, J. Li, Y. He, H. Liu, and B. Cheng, "A high-sensitivity and low-hysteresis flexible pressure sensor based on carbonized cotton fabric," *Sensors Actuators, A Phys.*, 294 (2019) 45.
- [26] J. L. Yao, X. Yang, N. Shao, H. Luo, T. Zhang, and W. G. Jiang, "A Flexible and Highly Sensitive Piezoresistive Pressure Sensor Based on Micropatterned Films Coated with Carbon Nanotubes," *J. Nanomater.*, 2016 (2016) 5.

- [27] O. Y. Kweon, S. J. Lee, and J. H. Oh, "Wearable high-performance pressure sensors based on three-dimensional electrospun conductive nanofibers," *NPG Asia Mater.*, 10 (2018) 540.
- [28] E. I. Materials and A. Oxide, "<2012010818323103.Pdf>," 08, pp. 4–6.
- [29] P. Singh, H. Borkar, B. P. Singh, V. N. Singh, and A. Kumar, "Ferroelectric polymer-ceramic composite thick films for energy storage applications," *AIP Adv.*, 4 (2014) 087117.
- [30] M. Pawlyta, J. N. Rouzaud, and S. Duber, "Raman micro-spectroscopy characterization of carbon blacks: Spectral analysis and structural information," *Carbon N. Y.*, 84 (2015) 479.
- [31] T. Ungár, J. Gubicza, G. Ribárik, C. Pantea, and T. W. Zerda, "Microstructure of carbon blacks determined by X-ray diffraction profile analysis," *Carbon N. Y.*, 40 (2002) 929.
- [32] H. Horibe, Y. Sasaki, H. Oshiro, Y. Hosokawa, A. Kono, S. Takahashi, and T. Nishiyama, "Quantification of the solvent evaporation rate during the production of three PVDF crystalline structure types by solvent casting," *Polym. J.*, 46 (2014) 104.
- [33] L. Wang, T. Ding, and P. Wang, "Effects of compression cycles and precompression pressure on the repeatability of piezoresistivity for carbon black-filled silicone rubber composite," *J. Polym. Sci. Part B Polym. Phys.*, 46 (2008) 1050.
- [34] L. Wang, T. Ding, and P. Wang, "Thin flexible pressure sensor array based on carbon black/silicone rubber nanocomposite," *IEEE Sens. J.*, 9 (2009) 1130.
- [35] Z. Shi, A. H. Jayatissa, and F. C. Peiris, "Fabrication of semiconducting pyrite thin films from hydrothermally synthesized pyrite (FeS₂) powder," *J. Mater. Sci. Mater. Electron.*, 27 (2016) 535.