DEPARTAMENTO DE INGENIERÍA ELÉCTRICA

DEVELOPMENT OF FERROELECTRIC NANOCOMPOSITE FOR CAPACITIVE PRESSURE SENSORS

POR

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ABSTRACT

The demand of flexible electronic devices led the scientific community to develop novel electroactive materials for various sensing devices to realize them in the potential applications in health monitoring, robotics, electronic skin and diagnostics. Especially, monitoring the human activities using integrated sensors are dedicated to non/invasive measurements such as pressure and force are seen in dielectric and piezoelectric applications. Currently, capacitive sensors with various dielectric materials with high sensitivity are realized as low power electronics devices in prosthetics, humanoids, structural health monitoring, biomedical and planter pressure monitoring in neurogenerative pathology applications. Materials for the capacitive sensors generally consist of electroactive polymers and ceramics as dielectric layer. Polymers which are flexible, robust are widely used and have low dielectric properties. On the other hand, ceramic having high dielectric properties are restricted its widespread usage due to brittle/rigid in nature. Currently, polymer nanocomposite with synergetic properties of polymer matrix and ceramic fillers are realized for capacitive pressure sensors.

The present work is intended to develop a polymer-ZnO based nanocomposite and to fabricate a flexible capacitive pressure sensor. Zinc oxide nanostructures modified with graphene greatly influenced the crystallinity and showed strong interaction with polyvinyldine fluoride matrix. Frequency dependent dielectric studies suggests the PVDF-ZnO-Gr nanocomposite shows the higher permittivity (~30 at 100 Hz) than PVDF-ZnO (~20 at 100Hz) nanocomposite. The electromechanical performance was investigated by measuring the change in capacitance response under various load conditions. The capacitive pressure-sensing response is considerably higher than that of the pristine PVDF-based device. The significant change in capacitance upon load is observed by the induced electrical potential due to displacement of electrodes and change in spacing between the fillers in the polymer matrix.

ABBREVIATIONS

AgNWs	Silver Nanowires
CNT	Carbon nanotube
CMOS	Complementary Metal Oxide Semiconductor
ICSS	Integrated Capacitive Strain Sensor
PFA	Perfluoroalkoxyalkane
PDMS	Polydimethylsiloxane
PVDF	Polyvinylidene fluoride
VACNT	Vertically aligned CNT
OFET	Organic field effect transistor
rGO	reduced Graphene Oxide
ZnO	Zinc oxide
Gr	Graphene

CHAPTER 1. INTRODUCTION

1.1 Flexible pressure sensors

Nowadays, flexible pressure sensors are becoming popular because they can be applied to a variety of systems including the touch on flexible displays, soft robotics, health monitoring, energy harvesting as shown in the Fig 1. The major advantage of a flexible pressure sensor is that it can be easily integrated into wearable devices. These flexible pressure sensors have various operating principles such as triboelectric, piezoelectric, optical, magnetic, piezoresistive, and capacitive for the measurement of the pressure. Among these, the capacitive pressure sensors are less sensitive to temperature, humidity, consume less power, and have a higher repeatability.[1]

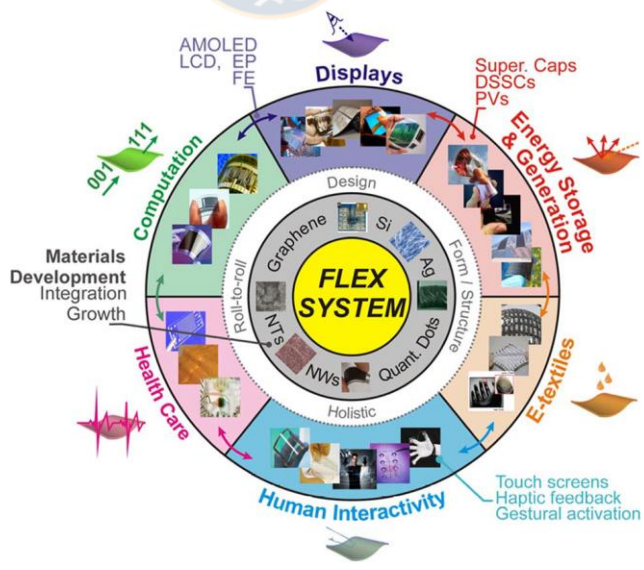


Fig 1: Next-generation flexible electronics systems and the key relevant sectors, the underlying materials [2]

Flexible pressure sensors are attracting great interest from researchers and are widely applied in various new electronic equipment because of their distinct characteristics with high flexibility, high sensitivity, and light weight; examples include electronic skin (E-skin) and wearable flexible sensing devices [3]. Challenges in developing high extensibility, high sensitivity, and flexible multi-functional sensing device still exist at present. Exploring new sensing mechanisms, seeking new functional materials, and developing novel integration technology of flexible devices will be the key directions in the sensors field in future.

CHAPTER 2. LITERATURE REVIEW

2.1 Sensors

Recent innovations in sensor technology are enabling smarter, safer, and more environmentally friendly electronics for business and consumers alike. Sensor is a device that when exposed to a physical phenomenon (temperature, displacement, force, etc.) produces a proportional output signal (electrical, mechanical, magnetic, etc.) shown in Fig 2.

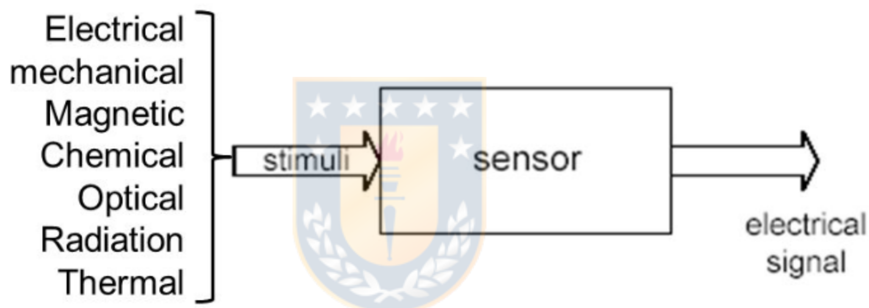


Fig 2: Physical phenomena of sensors

Different types of sensors that are commonly used in various applications. All of these sensors are used for measuring one of the physical properties like temperature, resistance, capacitance, conduction etc. Pressure sensors are used for many automotive, medical, industrial, consumer and building devices, which depend on accurate and stable pressure measurements to operate reliably. As more industries rely on pressure sensors to monitor and control their applications, demand for these technologies has greatly increased, putting estimations of the worldwide pressure sensor market at $11.4 billion by 2024.

2.1.1 Types of sensors

Various techniques have been developed in pressure sensors those are piezoresistive strain gauge pressure sensors, capacitive pressure sensors and piezoelectric pressure sensors. [3]

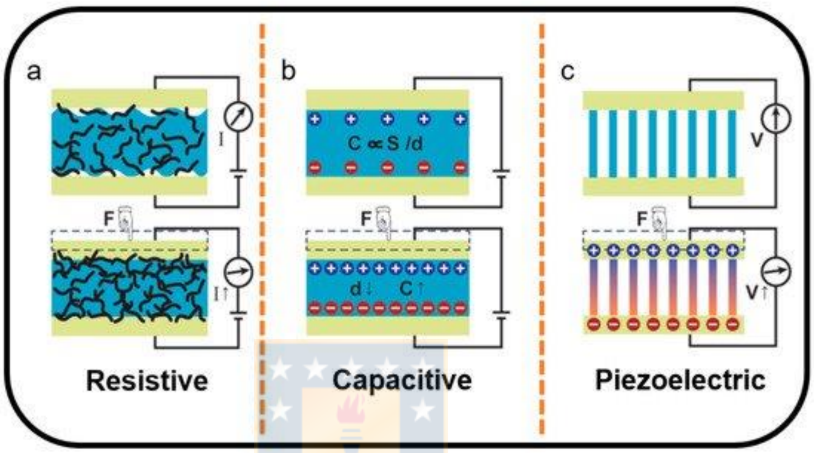


Fig 3: Schematic illustrations of the transduction methods: (**a**) resistive, (**b**) capacitive, and (**c**) piezoelectric [4]

The piezoresistive pressure sensor are low sensitivity and large size as compare with the capacitive pressure sensor. Many of the piezoresistive pressure sensors studies are trying to improve their low sensitivity using various materials [5]. In these piezo resistive sensors are robust with good resistance to shock, vibration, and dynamic pressure changes. The sensor output is temperature dependent. This can be a big disadvantage for applications such as tyre pressure measurement where there is much temperature changes over the operating cycle. On the other side, piezoelectric sensors consist piezoelectric elements those can be very small with an extremely fast response to changes in pressure. Few piezoelectric devices can measure rise times in the order of 1 millionth of a second, as a result piezoelectric sensors are used for mostly measuring dynamic pressures [6].

2.1.2 Capacitive Sensors:

Recently, capacitive pressure sensors were realized and much beneficial for various applications those including biomedical and electronic fields. Typically, capacitive sensor consists of a thin dielectric layer sandwiched between the conductive electrodes similar like a capacitor as shown in Fig 4 Capacitive pressure sensor works on a principle by measuring the change in capacitance under applied pressure which causes the dielectric layer to deform. This capacitance change may or may not be linear and is typically on the order of several picofarads (pF) out of a total capacitance of pF.

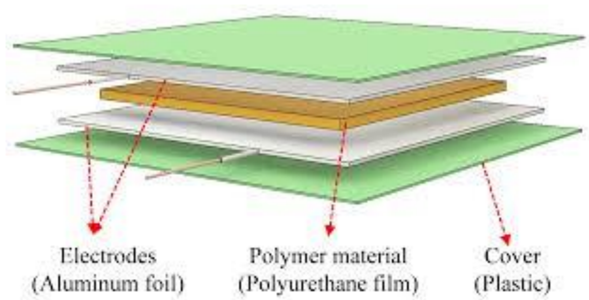
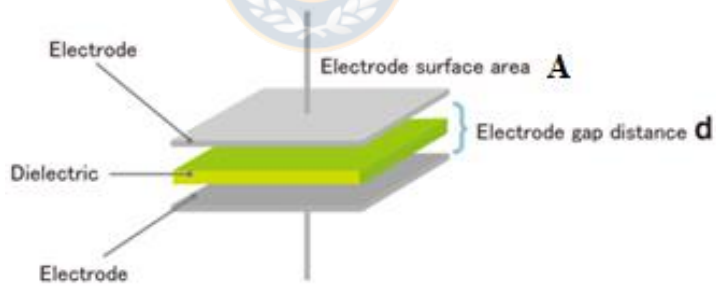


Fig 4: Flexible Capacitive Pressure Sensor [7]

The change in capacitance may be used to control the frequency of an oscillator or to vary the coupling of an AC signal through a network. The electronics for signal conditioning should be located close to the sensing element to prevent errors due to stray capacitance. Capacitive pressure sensing technique gains more importance in biomedical application due to high sensitivity and dynamic response[8]. Capacitive sensors are suitable for wireless applications. They can be used in an oscillator circuit to generate a signal, with a frequency proportional to pressure, that can be received wirelessly. The advantages of capacitive pressure sensors are having a very low power consumption because there is no DC current through the sensor element. Current only flows when a signal is passed through the circuit to measure the capacitance[9].

2.2 Dielectric materials for capacitive pressure sensors

The capacitive pressure sensor shows a simple structure, which is similar to that of a parallel plate capacitor. A thin dielectric material is placed between the two conductive electrodes as shown in the figure,



The parallel plate capacitor is defined by the following equation

$$\boldsymbol{C = \varepsilon_0 \varepsilon_r \frac{A}{d}} \qquad \textbf{............ (1)}$$

Where $\boldsymbol{\varepsilon_0}$ and $\boldsymbol{\varepsilon_r}$ are the vacuum dielectric constant and relative dielectric permittivity, respectively, **A** is the effective area of the parallel plate electrodes, and **d** is the distance between the two electrode plates. The Pressure sensitivity is one of the most important parameters of capacitive pressure sensor and is expressed as

$$S = \frac{\Delta C / C0}{\Delta P} \quad \text{............ (2)}$$

Where **P** is the applied pressure, **ΔP** is the change in pressure, **C0** is the initial capacitance of the capacitive pressure sensor without applied pressure, and **ΔC** is the change in capacitance.[10]

In general, dielectric materials for capacitive sensors are based on ceramics and polymers those are sandwiched between the conductive electrodes. Moreover, the materials selection depends on the type of application. Ceramics generally exhibits higher dielectric constant but are hard and brittle than any other materials which restricted their widespread usages. Besides, polymers have advantages like simple and low processing, high breakdown strength and their flexible nature make them attractive for many capacitive pressure sensors [11]. Despite the excellent physical properties, polymers suffer due to low dielectric properties than inorganic metal oxides. Also, at present nanocomposite materials with high dielectric properties are recognized as promising substitute materials for conventional electromechanical devices. These composite materials possess the synergetic properties of nanofillers as well as polymer matrix. The motive of the development of nanocomposite is to enhance the structural, mechanical and electrical properties with ease processing. Various fillers such as metals, ceramics and carbon-based materials were dispersed in the polymer matrix to develop nanocomposites with superior properties for capacitive pressure sensors. For instance, Seong *et al.* designed a waist belt type flexible capacitive pressure for a respiration signal monitoring shown in Fig 5. In this they are used PDMS based silver nanowire and carbon fibers thin films as electrodes. The sensor exhibited good performance with a high sensitivity of 0.161 kPa^{-1} for low pressure <10 kPa and a wide working pressure range up to 200 kPa with high durability of over 6,000 cycles [1].

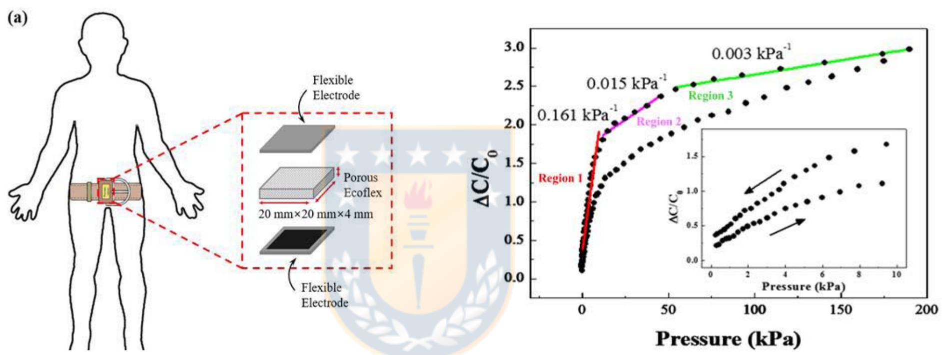


Fig 5: Diagram illustrating the sensor attached on the waist belt, capacitance change under varying applied pressure [1].

Pablo *et al.* [9] developed a portable and wireless capacitive Sensors Array for Plantar Pressure Measurement Insole fabricated with Flexible PCB. The designed PCB was pattern in Eagle software and user interface and data processing was developed in Python. The electro active ferroelectric film (EMFIT) was chosen as a dielectric material as shown in Fig 6. The performance of the sensors was tested for 1 minute 30 seconds under human activities such as standing and walking conditions and observed pressure zones on the insole diabetic foot conditions for the patients.

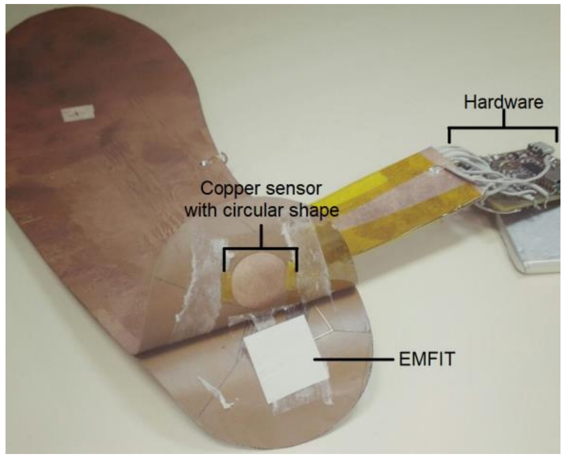


Fig 6: Insole fabricated with Flexible PCB

Shuai *et al.* developed a flexible pressure sensor designed by coating AgNWs on microstructured PDMS substrate and PVDF. AgNWs coated on PVDF was used as top electrode and AgNWs coated on microstructured PDMS was used as bottom electrode respectively shown in Fig 7. The sensor expressed a high sensitivity of 2.94 kPa^{-1}, low detection limit <3 Pa, short response time <50 ms, with excellent flexibility, and long-term cycle stability. The sensor also exhibited excellent resolution for real-time detection of voice vibrations, and air flow. [12]

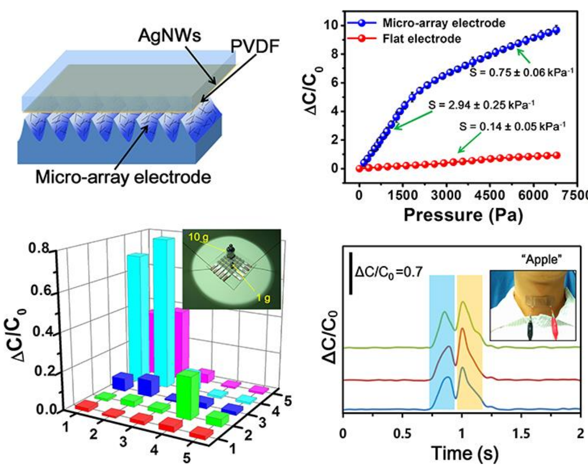


Fig 7: Microstructured flexible capacitive pressure for voice vibration detection[12]

Chen et al. investigated the capacitive pressure response of a Polymethylmethacrylate (PMMA) ZnO nanowire dielectric composite-based device with patterned electrode array. The device was realized by spin coating of PMMA-ZnO composite solution on a transparent glass/plastic substrate. The schematic illustration of pressure sensor is shown in Fig 8. The composite exhibited effective pressure response than pristine polymer due to geometry change in the capacitor and/or induced polarization of piezoelectric nanowires. The device showed a pressure sensitivity of 2.63×10^{-3} to 9.95×10^{-3} cm2 gf $^{-1}$[13].

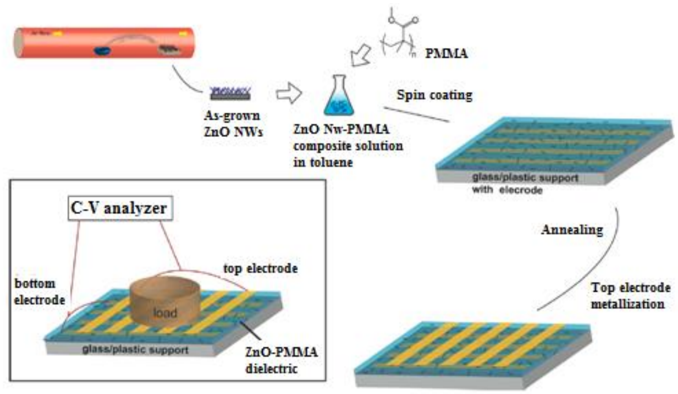


Fig 8: Schematic representation of preparation process and capacitance pressure sensor [11]

A stretchable and transparent thin film capacitive strain sensor based on patterned Ag NWs was demonstrated by Kim *et al.*[14] as shown in Fig 9. The ICSS had a good stable strain sensing performance during the repeated stretching test at strain (ε) values of 10% for 1000 cycles with no cross talk and can detect the finger and wrist muscle motions of the human body effectively.

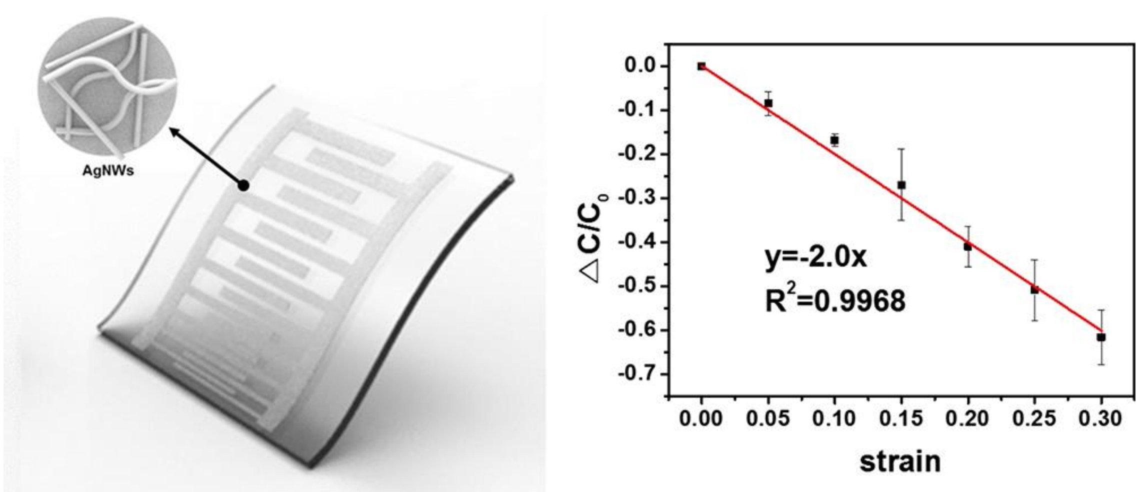


Fig 9: Schematic representation of parallel-plate-type capacitive strain sensor[14]

Kumar *et.al,*[15] developed a novel flexible paper-like hybrid device using ZnO nanowire and PVDF. The fabricated device showed high performance under uniaxial compression and generated an open circuit voltage 6.9 V and short circuit current 0.96 μA with an output power of 6.624 μW. James *et.al* developed a hybrid functional sensor by using a PVDF thin film, vertically grown ZnO nanorods and rGO electrode as shown in Fig 10 for monitoring independent temperature and pressure. They observed the enhanced dielectric permittivity of PVDF composite due to the piezoelectric barrier of ZnO, which made the device sensitive to pressure and temperature [16].

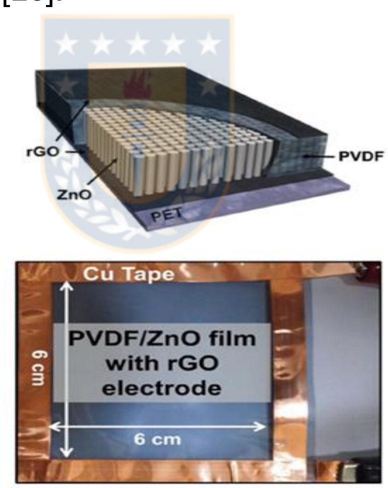


Fig 10: Schematic representation of PVDF-ZnO composite device [14]

A real time 5 × 5 flexible capacitive pressure sensor arrays was demonstrated by Peng *et al.* with good sensitivity. They have developed a 0.75 cm × 1 cm in size flexible printed circuit board integrated with CMOS switched-capacitor readout circuits for pulse measurement by placing the sensor array in contact with a subject's wrist [17]. Also, a highly sensitive piezoresistive strain based on the heterostructure of graphene and piezoelectric P(VDF-TrFE) thin film on a PDMS substrate was demonstrated by Kim *et al.* using a simple fabrication process shown in Fig 11. The sensor exhibited ultrahigh sensitivity of 0.76 kPa^{-1}, with measurement resolution of 1.7 Pa, signal to noise ratio greater than 60.8 dB and a fast response time is <100 ms [18].

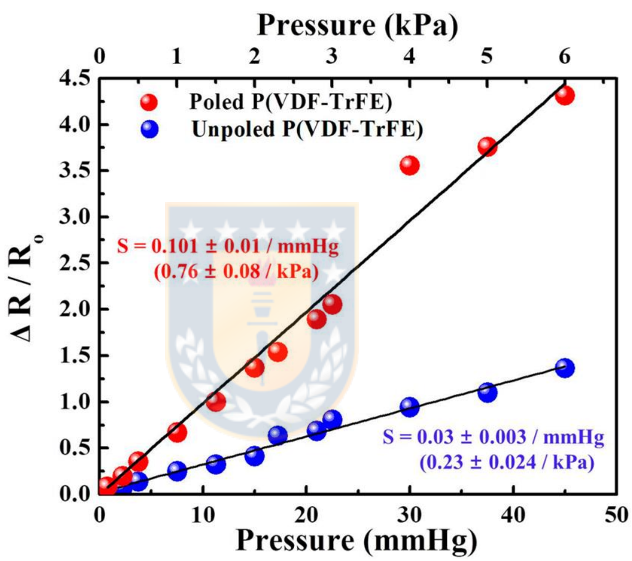


Fig 11: Change in resistance with applied pressure [16]

Li *et al.* demonstrated a flexible capacitive pressure sensor prepared by using silver nanowire paper-based surface as electrodes and PDMS as a dielectric layer. These sensor exhibited good sensitivity 1.05 kPa^{-1} in the dynamic range of 1 Pa to 2 kPa (shown in Fig 12) and has best potential for applying to artificial skin, movement monitoring and wearable devices [19]

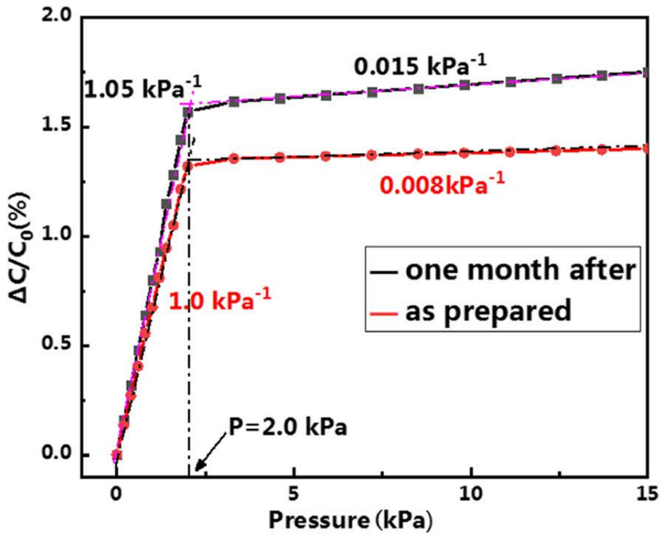


Fig 12: Response test of AgNW-paper-based capacitive FPS[19]

Wang *et al*. reported a thin film pressure sensor with double sensitive microstructured PDMS dielectric film and compared with single microstructured and flat surfaced PDMS dielectric film. The capacitance response of double and single microstructure films was much higher than the flat film. The study suggests that the design of multi-layer stack structure is an efficient method to improve the response of the thin capacitive pressure sensor.[20] Tien *et al.* [21]demostrarte a flexible sensor array, it detects pressure and temperatura using nanocomposite as dielectric material as shown in Fig. 13. These sensors reduce the mutual interference between pressure sensor and temperature sensor to accurately detect the pressure and temperature.

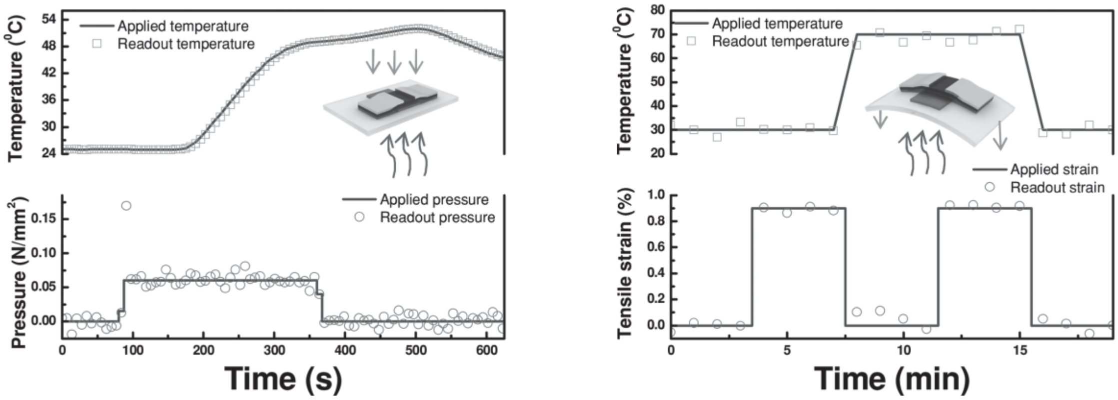


Fig 13: The image of an electronic artificial skin.[21]

Table 1: The reported performance of flexible pressure sensors [22]–[29]

Materials	Mechanism	Sensitivity	Min.detection	Max.detection
PFA	Piezoelectricity	15 V kPa^{-1}	-	2.5kPa
PVDF	Piezoelectricity	-	1 kPa	30kPa
ZNO nanorods	Piezoelectricity	-	3.5kPa	31.5kPa
VACNT/PDMS	Piezoresistivity	0.3 kPa^{-1}	2Pa	10 kPa
ACNT/G/PDMS	Piezoresistivity	19.8 kPa^{-1}	0.6Pa	0.3 kPa
CNTs/PDMS	Piezoresistivity	15.1 kPa^{-1}	0.2Pa	59 kPa
Graphene-paper	Capacitance	17.2 kPa^{-1}	2kPa	20 kPa
PDMS microstructure OFET	Capacitance	0.55 kPa^{-1}	3Pa	20 kPa

From the literature, various dielectric polymers such as PVDF and PDMS are used as active materials for flexible capacitive sensors. Also, the design of microstructured dielectric layer and significant electrode configuration evidenced improvement in the sensitivity for a great extent. Moreover, realizing nanocomposites as a capacitive sensor is one of the key challenges for processing and achieving optimal performance. Hence, research is still in progress day-by-day to develop active pressure sensing materials with highly sensitive and low cost for various biomedical applications those including wearable electronic devices.

2.3 Literature Summary

Nanocomposites have been explored for the fabrication of various electromechanical devices such as piezoelectric, piezoresistive and capacitive sensors. The mechanism involved in these devices such as charge separation and transportation to electrodes need to be studied. The major concern in these devices are to attain high sensitivity under the mechanical stimulus. The current studies about flexible capacitive pressure were mainly focused on polymer based dielectric materials, its microstructure and electrode configuration. Hence, the major scientific challenges are to develop novel nanocomposite sensors to achieve superior electrical and material properties with high sensitivity. The suitable electrode configuration and microstructure pattern of the nanocomposites need to be studied excessively to realize as flexible capacitive sensor for biomedical applications.

CHAPTER 3. PROJECT SCOPE

3.1 Hypothesis

The research is intended to fabricate flexible dielectric polymer nanocomposite by incorporating hybrid nanostructures into the polymer using low-cost processing technique. We hypothesize the dielectric polymer nanocomposite with hybrid nanostructures as nanofillers exhibit superior electrical properties such as permittivity, capacitance, impedance and electromechanical properties while retaining its structural properties than compared to another polymer nanocomposite and prinstine polymer without nanofillers. We hypothesis to develop flexible polymer nanocomposite having significant structural and electrical properties with electro-mechanical response to realize high performance capacitive pressure sensor in biomedical applications.

3.2 Objectives general

The current research is intended to develop highly sensitive nanocomposite dielectric layer as active sensing material with a special emphasis on design, development, and application as capacitive pressure sensor for microelectronic and biomedical applications.

3.3 Specific Objectives

• To synthesize metal oxide nanostructures (eg: ZnO, ZnO-Graphene) as active nanofillers for sensing applications.

• To develop flexible nanocomposite using synthesized nanostructures as nanofillers in the polymer matrix by low-cost processing techniques.

• To investigate the structural, material properties and electrical properties (such as permittivity, capacitance, impedance and electromechanical response) of the developed nanostructures and nanocomposites using sophisticated analytical techniques.

• To develop nanocomposite based capacitive pressure sensor by design of suitable electrode configuration.

• To investigate the electromechanical properties of the nanocomposite sensor subjected to mechanical stimulus.

3.4 Methodology

a) Development of ZnO nanostructures:

ZnO nanostructures will be prepared by nanotechnology buttom up approach using microwave method. The developed nanostructures will be hybridized using graphene nanosheets by insitu technique. The detailed materials characterization of developed nanostructures will be investigated by XRD, microscopy studies.

b) Fabrication of flexible dielectric polymer nanocomposite using ZnO based hybrid nanocomposite.

The development of flexible dielectric polymer nanocomposite will be carried out by incorporating hybrid nanostructures into the polymer using low-cost processing technique such as spin coating and solution casting. Nanostructures will be dispersed in PVDF (Polyvinylidene fluoride) or polydimethylsiloxane (PDMS) solution to obtain nanocomposite films. The nanocomposites will be put forward for various characterization techniques to study the interaction of fillers in the polymeric matrix. The electrical properties such as capacitance, impedance, permittivity etc. of the nanocomposite will be measured by using Impedance analyzer.

c) Design and fabrication of flexible pressure sensor using dielectric nanocomposite as active sensing material.

The proposed dielectric nanocomposite films will be used as an active dielectric layer for the fabrication of capacitive sensor. A suitable electrode configuration will be designed, and the the dielectric nanocomposite film is sandwiched between metal electrodes Cu tapes or thin films of Au (~ 50 nm). The Au electrodes deposition will be carried out using sputtering/thermal deposition techniques. The schematic representation of nanocomposite pressure sensor is shown below Fig 14.

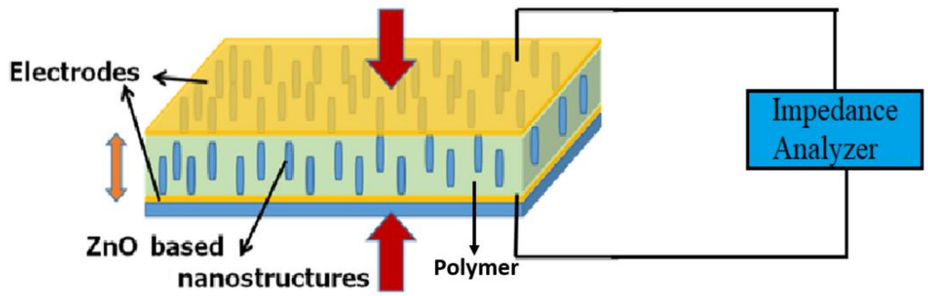


Fig 14: The schematic representation of nanocomposite pressure sensor

d) Performance evaluation of flexible capacitive pressure sensors for biomedical applications.

In this stage, the electromechanical response of the nanocomposite based capacitive sensor will be studied under mechanical stimulus by impedance analyzer. After successful investigation, the nanocomposite capacitive sensor will be put forward for real time applications in biomedical engineering.

CHAPTER 4. EXPERIMENTAL WORK

4.1 Synthesis of Nanostar like ZnO nanostructures

ZnO nanoparticles were synthesized by chemical route using microwave method. Initially, 3.285 g of zinc acetate dihydrate (Merck, ≥98%) was added in 15 mL of hydrazine hydrate (Merck, ≥99% purity) and under magnetic stirrer at 400 rpm for 15 min. Thereafter, the white precipitate obtained was quenched by adding deionized water and under magnetic stirrer at 400 rpm for another 5−10 min. After that, the white precipitate disappeared and reappeared. Thereafter, the solution was placed in commercial microwave oven to instant heating of about 5 mins. The solution was cooled and washed with deionized water and ethanol several times and dried at 50 °C for 12 h to obtain ZnO nanostructures.

4.2 Synthesis of Nanostar like ZnO-Gr nanostructures

Initially, 10 mg of graphene (Gr) nanoparticles (prepared by modified Hummer method) were added in hydrazine hydrate (15 mL) separately and under magnetic stirrer at 400 rpm for 15 min. Then, zinc acetate (3.285 g) was added to the graphene nanoparticles solution and under magnetic stirrer at 400 rpm for another 15 min. After that, deionized water was added to the above solution and under magnetic stirrer at 400 rpm continued for another 15 min. Thereafter, the solution was placed in commercial microwave oven to instant heating of about 5 mins. The solution was cooled and washed with deionized water and ethanol several times and dried at 50°C for 12 h to obtain ZnO-Gr nanostructures.

4.3 Preparation of PVDF based zinc oxide and zinc oxide graphene nanocomposite films

The composite films were fabricated by using a solution casting technique. In brief, PVDF (Sigma-Aldrich) was dissolved in Dimethylformamide (DMF) under continuous stirring. ZnO (20 wt.%) were dispersed in DMF and transferred to the above PVDF solution separately. The composite solution was stirred and sonicated to obtain homogeneous dispersion and thereafter poured into a glass dish (diameter 96 mm) and dried in the oven for overnight at 65 °C. A similar procedure was followed to prepare PVDF-ZnO-Gr nanocomposite film by adding 20 wt.% of ZnO-Gr nanostructures in PVDF solution. The schematic preparation process of nanocomposite films is shown in the Fig 15 and the developed flexible nanocomposite film as show in Fig 16.

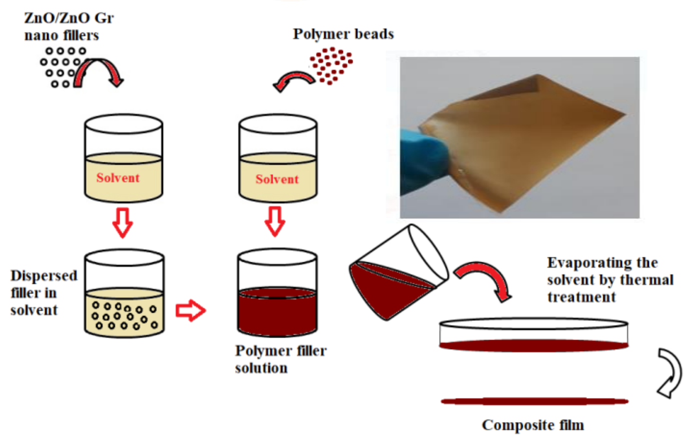


Fig 15: Schematic view of nanocomposite films preparation process

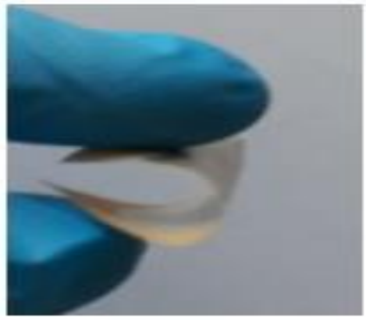


Fig 16: Developed flexible nanocomposite film

4.4 Fabrication of capacitive pressure sensor device

The developed composite films were cut in to 20 mm× 20 mm in size. The surface of the composite films was sputter-coated with Au electrode on both sides. Thereafter, the films were sandwiched with conducting Cu tape to give electrical contacts. The device was covered with Kapton (polyamide) tape both sides to make it more robust as shown in the Fig 17.

Fig 17: Developed capacitive pressure sensor device

CHAPTER 5. CHARACTERIZATION TECHNIQUES

5.1 X-ray diffraction:

X-ray diffraction (Fig 18) is a powerful tool to analyze the crystal structure of crystalline materials by means of X-rays, directed towards a crystal of known wavelength (λ). The interaction of the beam with solid material produces diffraction pattern, which is dependent on the crystal structure of the material. The X-ray diffraction is used to demonstrate the periodic arrangements of atoms in the materials by knowing the lattice parameters and the interplanar spacing which is of the order of X-ray wavelength. The diffraction pattern follows the condition of Bragg's law i.e. $2d\sin\theta = n\lambda$, where n is the diffraction order, λ is the wavelength, d is the spacing between consecutive parallel planes and θ is the glancing angle. The structural identification made from the diffraction pattern is further correlated with the international recognized database Joint Committee on Powder Diffraction Standards (JCPDS).

X-ray diffractometer (XRD) from Phillips (PW3050/60) as well as Bruker D8 advance are used in this research. The measurement was performed by using 40 kV, 30 mA Cu Kα incident beam (λ=1.54 Å). The measurements were conducted at scan rate of 0.02 °/s and 2θ range from 5° to 90°.

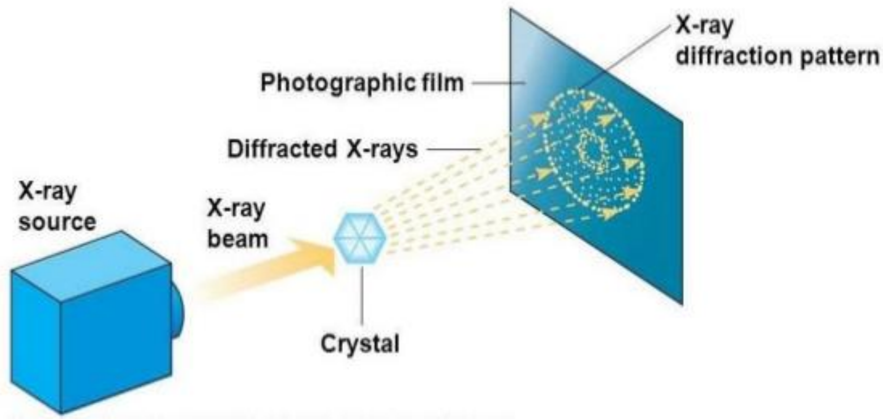


Fig 18: A Schematic diagram of X-ray Diffraction [30]

5.2 Scanning Electron Microscope

Scanning electron microscope (SEM) (Fig 19) is a powerful technique, which is basically used for examining the property of the materials in the field of metallurgy, geology, biology, and medicine etc. The scanning electron microscope (SEM) utilizes a focused beam of high-energy electrons to generate different types of signals on the surface of a particular specimen which is directed towards the specimen. The signals which are generated from electron-sample interactions gives the information about the materials like external morphology (texture or surface property), chemical composition (EDAX), and crystalline structure and orientation of materials. Some common signals like secondary electron, backscattered electrons and the X-rays generated for imaging the sample. In the study of SEM technique, when the electron beam incident on the sample, it penetrates some distance before the collision of the surface atoms. The secondary electrons generally created from the inelastic scattering depend on the greater number of electrons reaches on the detector and depend on the incident angle which is responsible to generate the topographic information.

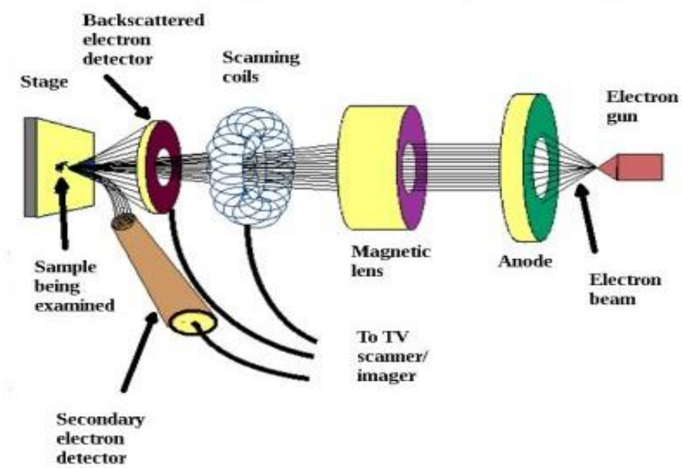


Fig 19: A Schematic diagram of Scanning Electronic Microscope [31]

The sample used in the SEM technique must be electronically conductive to avoid the charging effects. To prevent this charging effects, nonconductive sample must be coated with conductive material of nanometer thickness. In the present study, the morphology of the developed samples was determined by using scanning electron microscope.

5.3 Dielectric/ Impedance spectroscopy

Impedance spectroscopy is a powerful tool to identify electrical properties of materials. This technique is applicable for both solid and liquids. This spectroscopic study is widely used to examine the intrinsic electric behavior of materials such as complex permittivity $\varepsilon^*(\omega)$, conductivity $\sigma^*(\omega)$, and capacitance etc. in a broad range of frequencies. With the known sample dimensions, dielectric spectroscopy measures the impedance spectrum (Z*(ω)) of the material and thereby gives the electrical properties.

Various other parameters like time, DC bias, and AC field strength can also be determined. The measurement setup of dielectric spectrometer is shown in Fig 20.

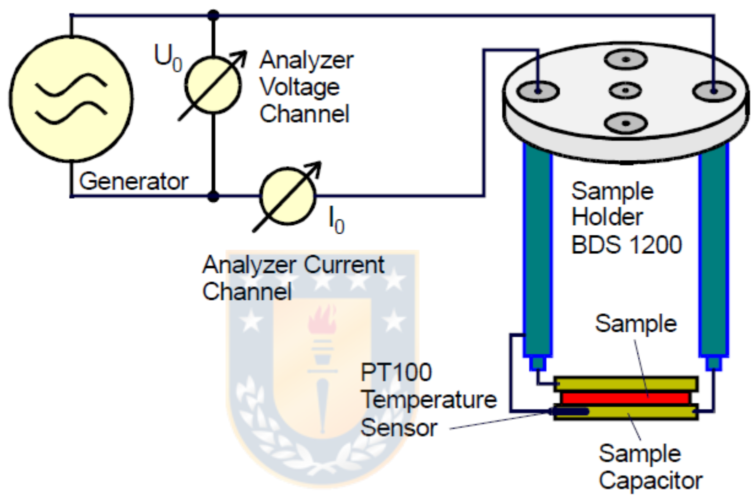


Fig 20: Dielectric measurement setup [32]

The sample material is placed between two electrode plates in a sample holder. An external voltage U_o with fixed frequency is applied to the sample and caused current I_o in the sample. In general, a phase shift exists between voltage and current with phase angle ø. The ratio between the applied voltage and current gives the complex impedance of the sample.

$$Z^* = \frac{U^*}{I^*}$$

Where $U^* = U_o$ and $I^* = I' + iI''$; $I_o = \sqrt{I'^2 + I''^2}$; $\tan(\emptyset) = \frac{I''}{I'}$

And the complex permittivity (ε^*) is expressed in terms of impedance (Z^*) and empty sample cell capacitance (C_o) as

$$\varepsilon^* = \varepsilon^{'} - i\varepsilon^{''} = \frac{-i}{\omega Z^*(\omega)}\frac{1}{C_o}$$

In the present study, broadband dielectric spectroscopy (BDS) studies were carried out to measure the complex permittivity and electric modulus of the samples by using a Novocontrol broadband dielectric spectrometer with an Alpha-A analyzer. The composite films were cut in to 20 mm diameter and the thickness of the films were measured. The samples were ensured to be in electric contact by applying silver paste on both sides and placed between gold plated copper electrodes. The measurements were performed by applying AC voltage ~1_{rms} to the sample. In addition, the capacitive pressure sensing response was investigated by measuring the capacitance of the device with respect to the different load conditions at a constant frequency of 1 kHz using a 2-wire electrode system of impedance analyzer and LCR meter. [10]

CHAPTER 6. RESULTS AND DISCUSSIONS

6.1 X-ray diffraction studies

X-ray diffraction patterns of PVDF-ZnO and the PVDF-ZnO-Gr nanocomposite films are shown in Fig 21. All the diffraction patterns were indexed as wurzite structure of ZnO [32]. Both the nanocomposites shown the crystalline peaks of ZnO in the semicrystalline PVDF polymer. The XRD pattern of semi crystalline PVDF showed diffraction peaks at two theta 18.2º (100) and 20.2º (110) correspond to α-PVDF and β-PVDF respectively. The crystallinity is enhanced in the nanocomposites due to the addition of ZnO and ZnO Gr in PVDF matrix. The major characteristic peaks of ZnO were observed at two theta 31.6º, 34.3º and 36.3º in addition to the diffraction peaks of PVDF. The crystallite size of ZnO and ZnO-Gr in PVDF was determined by Debye- Scherrer equation:

$$\mathbf{D = (K\,\lambda)/\,(d\,\cos\theta)}$$

where, K is the shape factor - 0.9, λ = 1.54060 Å (in the case of CuKa), d is the full width and half maximum. The average crystallite size is 0.415 nm for PVDF-ZnO nanocomposite and 0.421 nm for PVDF-ZnO-Gr nanocomposite film.

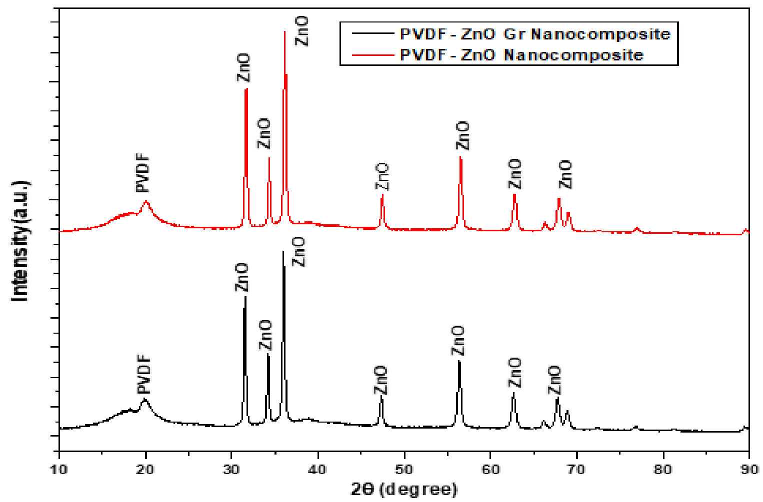


Fig 21: X-ray diffraction (XRD) pattern of PVDF- ZnO based nanocomposite films.

6.2 Microscopic Studies

Scanning Electron Microscopic (SEM) studies were carried out for developed ZnO and ZnO-Gr nanostructures and are shown in Fig 22 SEM images (Fig 22 (a), (b)) of ZnO suggested the formation of nanostar like morphology observed at different magnification. The average diameter of the ZnO nanorod was estimated to be ∼200 nm.

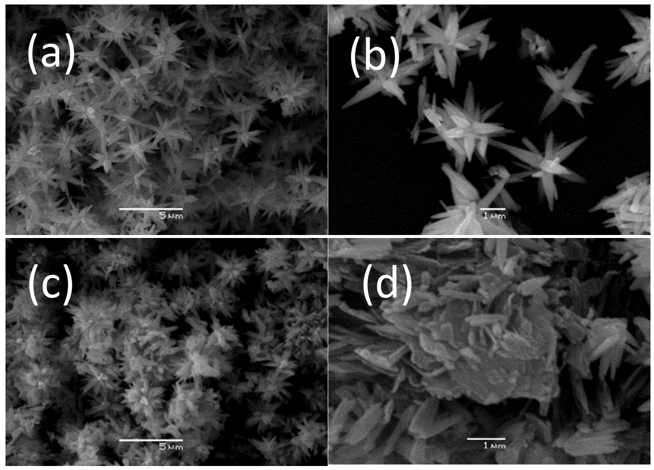


Fig 22: SEM images of (a) ZnO nanostructures (b) ZnO nanostructures with high magnification c) ZnO-Graphene nanostructures (d) ZnO - Gr nanostructures with high magnification

The microscopic results suggest that formation of stable and uniform size nanostructures. Fig 22 (c), (d) shows the SEM image of ZnO-Gr nanostructures and suggested the formation of nanostar like morphology observed at different magnifications and the ZnO nanostars are modified with graphene layers. These microscopy results suggest strong interaction of ZnO nanostructures and graphene.

6.3 Dielectric Studies

The electrical studies like frequency-dependent real part of dielectric permittivity of the PVDF-ZnO & PVDF-ZnO-Gr nanocomposite films are shown in Fig 23. The dielectric permittivity of PVDF-ZnO & PVDF-ZnO-Gr nanocomposite films were measured by using broadband dielectric impedance analyzer in the frequency range of 10 Hz to 10 MHz. The nanocomposite films showed the permittivity is decreasing with increasing the frequency. At higher frequency, the permittivity is low because the diploes do not have much time to polarize and showed strong orientational polarization. Whereas at lower frequencies the permittivity is higher because the dipoles have enough time polarize showing strong space charge polarization and interfacial polarization. And also PVDF-ZnO-Gr nanocomposite film shows higher permittivity compare to the PVDF-ZnO nanocomposite which is due to the strong interaction of PVDF and ZnO modified with graphene which further increase the polarization.[32]

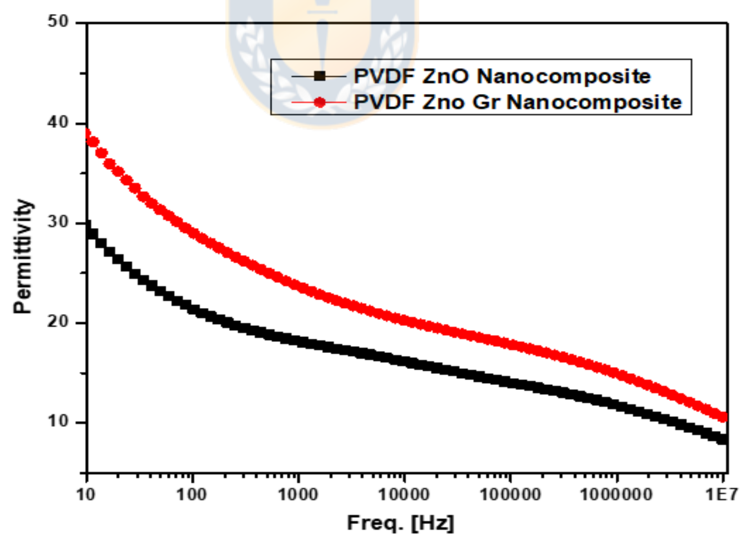


Fig 23: Frequency dependent permittivity of PVDF-ZnO & PVDF- ZnO-Gr nanocomposite film

Fig 24 shows frequency dependent dielectric loss tangent of PVDF-ZnO & PVDF-ZnO-Gr nanocomposite films. The observed dielectric losses are less which is <

1 for both the nanocomposites in the frequency range. The dielectric loss is expressed as the ratio of imaginary permittivity to real permittivity. The dielectric loss of tangent is expressed as

$$Tan\ \delta = \frac{\varepsilon''}{\varepsilon'}$$

Where ε' and ε'' are the real and imaginary parts of complex permittivity

With increasing frequency, the dielectric loss is drastically decreased in PVDF-ZnO-Gr nanocomposite film and there after slightly increased with increasing the frequency. At 1000Hz the dielectric losses of PVDF-ZnO-Gr is around 0.4 and PVDF-ZnO is 0.15. The increase in dielectric loss in PVDF-ZnO-Gr than compare to PVDF-ZnO nanocomposite is due to addition of graphene in ZnO which increase the conductivity. [32]

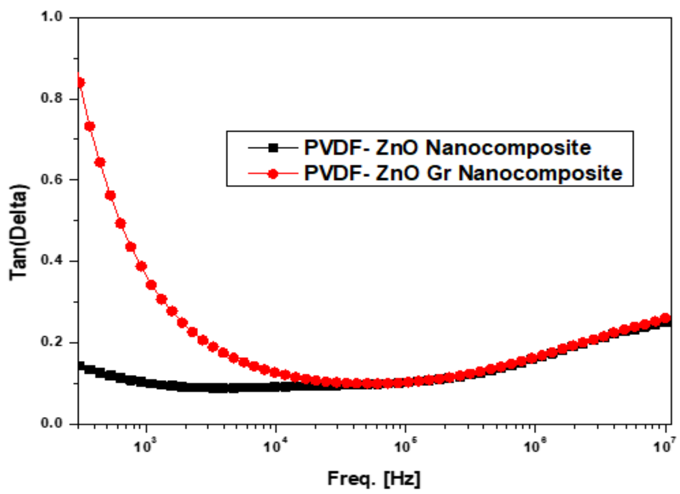


Fig 24: Frequency dependent dielectric loss tangent of PVDF-ZnO & PVDF-ZnO-Gr nanocomposite film

6.4 Electromechanical studies

After successful investigation of physical and electrical properties, the PVDF-ZnO-Gr shows better material and electrical properties and were used to fabricate a capacitive pressure-sensing device. The film was sandwiched between the metal electrodes (Au and Cu) and acted as a parallel plate capacitor. Thereafter, pressure sensing response was investigated by measuring the capacitance and impedance of the nanocomposite film device at a frequency of 1 kHz of bias 1 Volt (AC) with respect to the tapping load. The schematic device measurement is shown below Fig 25. Also, the device was tested with increasing load of 4 Kg and measured the capacitance by using impedance analyzer. The schematic representation of a developed device is shown in the Fig 25.

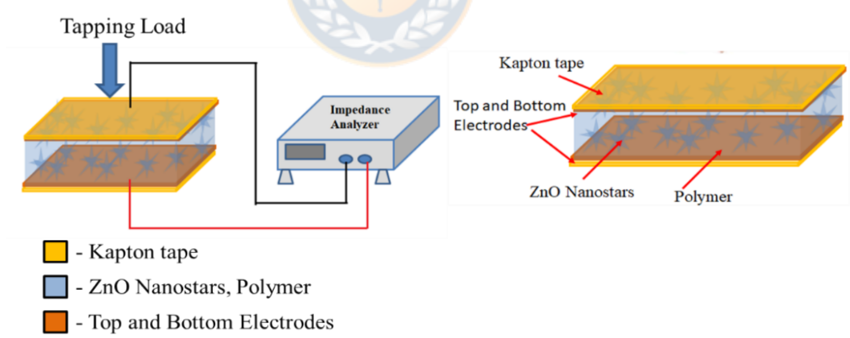


Fig 25: Schematic measurement set up nanocomposite capacitive pressure sensor

The capacitance was measured at various load conditions by using an impedance analyzer. In percepts, the capacitance is comparative to the spacing between the parallel metal electrodes. The change in capacitance with respect to load (10 g) is caused by the reduction of the spacing between the electrodes, which tends to cause a geometrical change in the device. The PVDF-ZnO graphene device was subjected to sequential compressive stresses and the capacitance were recorded at 1000 Hz with respect to time as shown in the Fig 26.

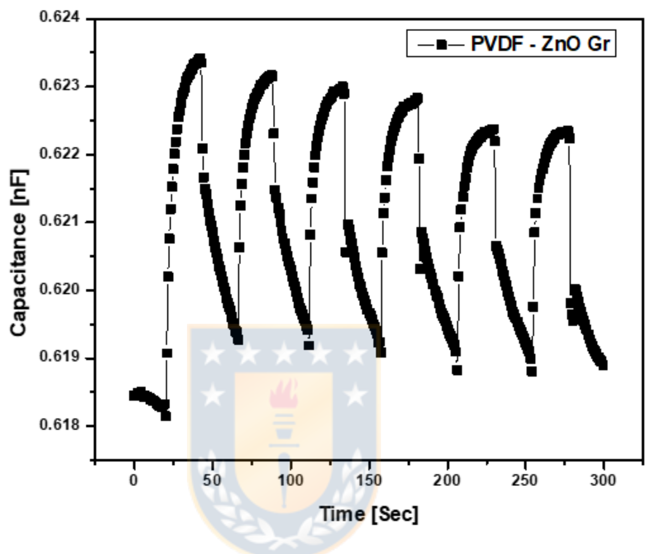


Fig 26: Capacitance response of PVDF-ZnO Graphene device measured under mechanical load and unload.

The observed capacitance at no load is 0.618 nF and the capacitance is increased to 0.628 nF under load conditions. The change in capacitance is due to the geometrical changes in the capacitive sensor and due to the strong polarization induced in the nanocomposite due to the addition of ZnO modified with graphene.

Also, electromechanical studies of capacitive pressure sensor is shown by measuring impedance with respective time under mechanical tapping load. Both devices showed a significant response to the applied stress. The Fig 27 suggested impedance with respective time of PVDF-ZnO nanocomposite film at no load condition is 220 kΩ and impedance is increasing to 245 kΩ under tapping load. And also, Fig 28 PVDF-ZnO-Gr nanocomposite film shows at no load condition is 278 kΩ and impedance is increased to 308 kΩ under load condition. Moreover, the initial response to the load is higher in PVDF-ZnO-Gr compared to that of the PVDF-ZnO device and is due to the strong interaction of PVDF and ZnO modified with Gr.

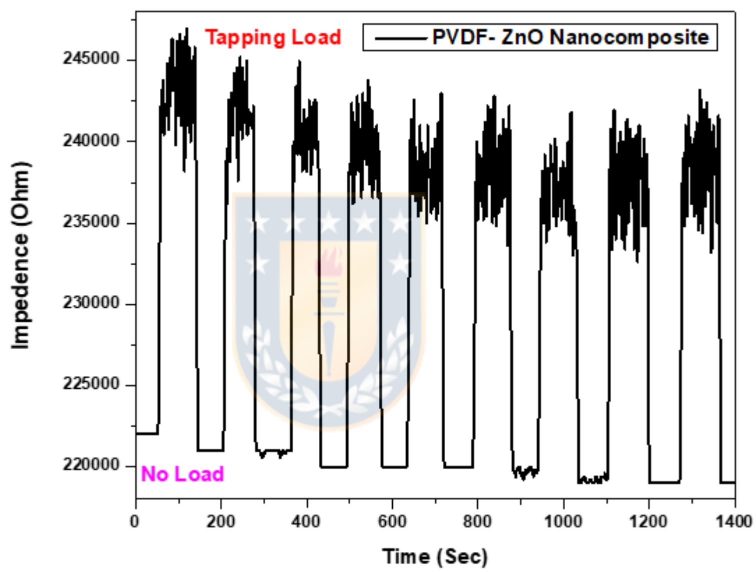


Fig 27: Impedance response of the PVDF-ZnO Nanocomposite sensor at tapping load

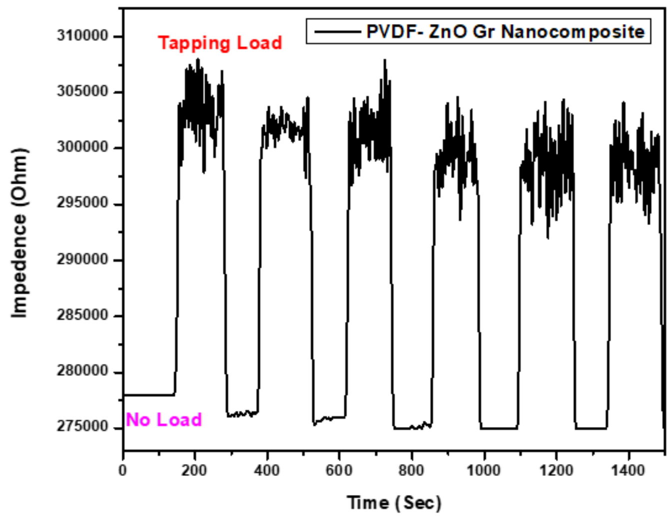


Fig 28: Impedance response of the PVDF-ZnO-Gr Nanocomposite sensor at tapping load

Electromechanical measurement of the developed nanocomposite device at increasing load (0.61kg – 17 kg) obtained by measuring the capacitance at 1000 Hz as shown in the Fig 29. The significant change in the capacitance was observed with increasing the load up to 17 Kg and the induced slope of PVDF-ZnO-Gr is determined as shown in the Fig 30 and is 1.124×10^{-14}. Overall, the composite exhibits change in capacitance with respective applied pressure.

Fig 29: Electromechanical mesurement step-up of capacitive sensor

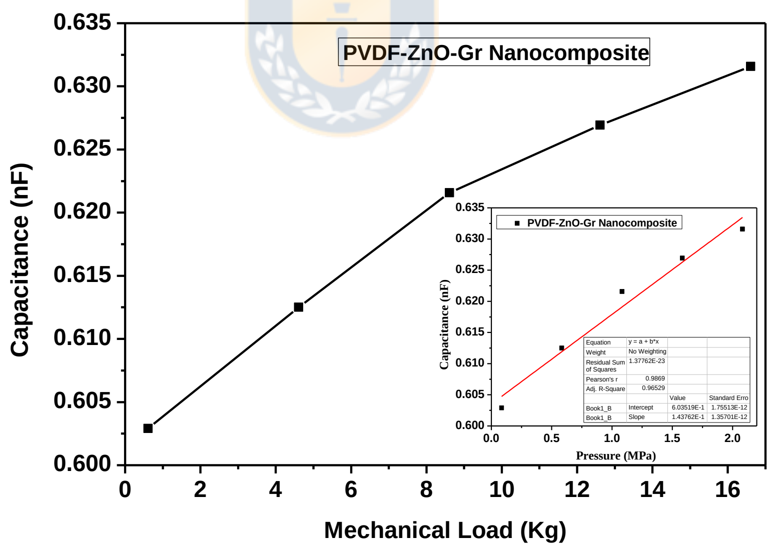


Fig 30: Average capacitance response of the PVDF-ZnO-Gr Nanocomposite sensor at various load

CHAPTER 7. CONCLUSIONS

Dielectric nanocomposites with high permittivity and reduced dielectric loss are desirable for various electromechanical applications. However, the processing of dielectric nanocomposites with desired properties is challenging. The present work focused on the design and development of ZnO based nanocomposites with superior electrical properties as capacitive pressure sensing applications. The ZnO based hydride nanostructures were developed by addition of graphene using simple facile chemical route to form nanostar like ZnO-Gr nanostructures. Flexible PVDF-ZnO based nanocomposite films were synthesized by solution casting process. The developed ZnO nanostructures and PVDF-ZnO nanocomposites were characterized by using sophisticated analytical techniques to understand the crystal structure, morphology, and electrical properties. After modification of ZnO with graphene, the hybrid ZnO-Gr nanostructures evidenced strong interaction with the PVDF matrix, which significantly improved the dielectric properties (ε' ~27, tan δ ~ 0.3 at 1000 Hz) then compared to PVDF-ZnO nanocomposites (ε' ~22, tan δ ~ 0.1 at 1000Hz). Thereafter, the developed flexible nanocomposite films were fabricated as capacitive pressure sensor device. The capacitance at no load is 0.618 nF and the capacitance was increased to 0.628 nF under load conditions in PVDF-ZnO-Gr nanocomposite films. Also, electromechanical studies of capacitive pressure sensor device were analyzed by measuring the impedance with respective time under mechanical tapping load. Both devices showed a significant response to the applied stress. Moreover, the modification of ZnO with Gr shows higher impedance (308 KΩ). Overall, nanostar like ZnO-Gr based nanocomposite devices exhibited improved significant change in the capacitance was observed under applied load which can be put forward for various biomedical applications.

CHAPTER 8. FUTURE SCOPE OF WORK

A flexible capacitive pressure sensor device was fabricated by using the developed nanocomposites. As justified in this work, dielectric properties of the nanocomposites depend on the morphology of the fillers, dispersion, and interaction of fillers with matrix. In addition, the dielectric properties such as permittivity, dielectric loss and other electrical properties influence the device performance. Moreover, future work may extend to integrate the nanocomposite capacitive pressure sensor with laboratory available electronic PCB and may evaluate the device performance of dielectric nanocomposites by placing the nanocomposite sensors in the insole to monitor the foot pressure. A low-cost in-shoe wireless device for measuring plantar pressures can be designed and realized using nanocomposite based capacitive sensors.

CONFERENCES & PUBLICATIONS

Conference:

"Flexible Nanocomposite Based Capacitive Sensor for tactile pressure measurements in Biomedical Applications", Poster Presentation at Virtual Online Conference on Nanotechnology, Nanomedicine and Smart Materials, September 24, 2020.

Publications (WoS):

1. "Polarization-Induced Quantum-Mechanical Charge Transfer in Perovskite−Graphene Nanocomposites with Superior Electro-optic Switching Modulation", J. Phys. Chem. C, 2020, 124,26648-26658.

2. Investigation and Performance of PVDF-ZnO Graphene Nanocomposite Capacitive Nanocomposite Sensor, (Manuscript under preparation)

3. A Review on Electro Active Polymers and their Nanocomposites for Sensors (To be submitted)

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