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# Polyvinylidene Fluoride-Praseodymium Oxide Nanocomposite Force Sensors for Monitoring Human Physiological and Muscle Motion Signs

[1,*] **Ashok BATRA,** [1] **James SAMPSON,** [2] **Kuzhivelil ARUN and** [3] **Aschalew KASSU**
[1] Materials Science Group, Department of Physics, Chemistry, and Mathematics
Alabama A&M University, Normal (Huntsville), AL 35762, USA
[2] Department of Physics, Sree Kerala Varma College, Thrissur, Kerala 680011, India
[3] Department of Mechanical, Civil Engineering and Construction Management
Alabama A&M University, Normal (Huntsville), AL 35762, USA
[1] Tel.: 2563728109, fax: 2563725622
E-mail: ashok.batra@aamu.edu

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**Abstract:** In the present investigation, praseodymium oxide ($Pr_2O_3$) nanoparticles embedded polyvinylidene fluoride (PVDF) thick films were fabricated via solution casting/intercalation technique. The $Pr_2O_3$ nanoparticles were synthesized by the hydrothermal technique. The Fourier Transform Infrared Spectroscopy (FTIR) has been recorded in the range 400 to 4000 cm$^{-1}$, and functional groups were identified in the nanocomposite films. Infrared vibrational spectroscopy (FTIR and Raman) curves revealed ferroelectric β-phase in the annealed nanocomposite films intrinsically. The electrode films so produced were sandwiched between Kapton film to form a sensing device. Based on reasonable linear piezo-capacitive behaviors obtained, PVDF-$Pr_2O_3$ nanocomposites films can be used to create highly flexible pressure sensors.

**Keywords:** PVDF, Praseodymium oxide, Nanocomposites, Solution casting, Pressure sensors.

## 1. Introduction

Electroactive polymers (EAPs) are gaining immense interest as smart materials [1]. There are many EAPs, namely, Nylon-11, polylactide and aniline pentamer copolymer, poly(lactic-co-glycolic acid) (PLGA), and poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (TrFE) [2-6]. However, PVDF and PDVF-TrFE exhibit the best electroactive properties, such as piezo-, pyro- and ferroelectricity, and optoelectronic. As a result, PVDF and its copolymers are of choice for the increasing number of possible organic microelectronics applications, such as electro-optic transducers, waveguides, sensors, actuators, energy harvesting, electro-optic memory, biomimetic robotics. PVDF is polar. With respect to the carbon atom in the unit, the hydrogen atoms are positively charged, and the fluorine atoms are negatively charged. The repeat unit of ($–CH_2–CF_2$_) or $CH_2CF_2$)n, in which the carbon-hydrogen bonds with the electrically polar carbon-fluorine, can take up several stable configurations determined by the treatment of the polymer. PVDF can be crystallized into at least four different polymorphous phases, depending on the film preparation conditions. Two forms β (or I) and α (or II) - are of particular importance. In form α, PVDF is non-piezoelectric, the bonds are in a trans-gauche-trans-gauche configuration, and the molecules are stacked, giving a nonpolar unit cell. The α phase can be converted into form β by stretching and electrically poling with a right field. In form β, the molecular groups are in an all-trans configuration, and the molecules are assembled to give a polar unit cell. Form β is orthorhombic with point group A $mm^2$. Several research investigations have highlighted the benefits of using nanoparticles, including carbon, dispersed in the polymer matrix to design and fabricate multifunctional materials with higher strength, including with above-cited properties in hybrid sensors or devices for medical and industrial applications. Tactile sensors, most commonly are referred to as strain, and pressure sensors, can obtain mechanical property data of the human body and local environment. It is recognized where contact, pressure, or traction is exerted on the skin and some internal organs. The tactile sense is one of the five traditional senses of the body. The tactile sense is received through millions of nerve ending on the skin, detecting even the slightest touch sensations and reporting it to the brain [1].

For brevity, we define four crucial attributes of smart materials [2-3]. *Piezoresistivity:* Tactile sensors based on piezoresistivity mechanisms change electrical resistance when the mechanical stimulus is applied. Piezoresistivity is the widely utilized technology to implement a tactile sensor due to its simple structure and cost-effective fabrication techniques. Based on the simple principle of operation of the sensor, few prototypes have been fully designed and developed. *Piezoelectricity*: It is the development of voltage, which is caused by electric dipole moments observed in some anisotropic crystalline materials, in response to mechanical stimuli and vice versa; and *Pyroelectricity:* It refers to electric polarization of certain smart materials to generate a transient voltage in response to applied temperature change. Thus, by converting thermal energy to electricity, the pyroelectric effect can be applied to build a self-powered temperature sensor that automatically detects temperature change without the need of an extra power supply or battery. *Piezocapacitive:* Pressure sensors based on piezo-capacitance mechanisms change electrical capacitance when the mechanical stimulus is applied.

A great deal of research has been devoted to improving the outputs and piezoelectric properties of crystals and ceramic materials. In recent years, the ease of production and processing of PVDF films compared with piezoelectric crystals and ceramics, the relatively lower cost of polymer materials, the flexibility, and the sensitivity of PVDF nanocomposite polymer films are becoming an active area of research for developing sensors and functional devices. The piezo- and pyroelectric properties of PVDF polymer makes it an attractive polymer for various applications including energy harvesting [7-9], nanogenerators [7, 10], tactile sensors [11-14], humidity sensors [14], force sensors [15], capacitors [14], strain sensing [12, 16, 17], for developing wearable functional electromechanical devices [16, 18-22], for tissue engineering including regeneration and repair [10, 23].

In the biomedical domain, tactile piezoelectric sensors detect movements, including human body motion, and convert the deformations into electrical signals [13, 14]. Yu, *et al.* (2019) demonstrated the application of PVDF nanocomposite polymer films as nanogenerators producing usable energy from mechanical energy generated during running and walking [8]. Based on the study, the fabricated PVDF-nanofiber-based 'shoepad' nanogenerator produced about 6.45 μW output power with a 5.5 MΩ load resistance. The application of PVDF-based nanocomposite used for harvesting usable energy from regular human body motion and human biological activities, including respiration, for developing small size biocompatible nanogenerators to power wearable and implantable biomedical devices have also been demonstrated [9]. To enhance piezo-responses of PVDF-based nanocomposite, several design approaches, fabrication methods, and nanocomposite materials have been explored [16, 19].

PVDF has all the desired features to fabricate flexible pressure sensors such as the ultrahigh stretchability, bending, wearability, which can be easily integrated into artificial and electronic skins. Thus, it was thought exciting and worthy of exploring PVDF and its composite films embedded with $Pr_2O_3$ nanoparticles, in particular their suitability in pressure sensors for biomedical sensing. With this train of thought, we investigated piezo-capacitance relevant sensing characteristics under both Transverse and sheer stress.

## 2. Experimental

### 2.1. Fabrication of the Nanoparticle and Films

Praseodymium oxide nanorods were prepared by the hydrothermal synthesis method. In this study, 0.1 molar solution of Praseodymium chloride is mixed with 0.1 molar solution of Sodium hydroxide. The water used in this reaction was doubly distilled and deionized. By this method pH value of the solution was adjusted to 9. After stirring the colloidal reaction solution, it was transferred into an autoclave made up of Teflon lined stainless steel. Then the solution is subjected to heat at 300°C for 6 hours in an oven and subsequently cooled down to room temperature. The settled particles were collected and washed repeatedly with deionized water under vacuum. Praseodymium hydroxide nanoparticles were heated at 80°C. Hydroxide nanorods were turned into oxides after heating to a temperature of 300°C. Annealing of the sample to a temperature of 700°C was also conducted. It was found that annealing results in a change in color, which is an indication of the change in particle.

500 mg of PVDF was dissolved in 20 ml of DMF under vigorous stirring at 60˚C for the complete dissolution of PVDF in DMF. Then, a certain weight percentage of the Praseodymium oxide nanoparticles were added to the PVDF solution and vigorously stirred for one hour to obtain a homogeneous mixture. The nanocomposite films were prepared by casting the mixture in a properly cleaned and dried petri dish, and the solvent was evaporated at 90ºC in the oven. 1 wt%, with 2 wt%, 3 wt%, 4 wt% and 5wt% Praseodymium oxide nanoparticles loaded PVDF films were prepared. They were coded as PrO50; PrO100; PrO150; PrO200 and PrO250 respectively, including pristine PrO0.

## 2.2. Optical Characterization

Raman spectral analysis in the range from 250-2250 $cm^{-1}$ was carried out by using a Raman spectroscopy system (Enwave Optronics, Inc.) operating at 785 nm laser wavelength. The Fourier Transform Infrared Spectroscopy (FTIR) has been recorded in the range 400 to 4000 $cm^{-1}$. The surrounding medium was air, and all the measurements were performed at room temperature.

## 2.3. Electrical Characterization

LabVIEW interfaced Quadtech LCR Bridge network can be used to conduct the dielectric study, and FTIR study provides the normal vibrational modes of PVDF and nanocomposites. The real and imaginary parts of the dielectric permittivity (ε' and ε") can be obtained by measuring terminal parallel capacitance CP and loss tangent at a fixed measurement frequency of 1 kHz using LCR meter, and measurements were taken during heating run with temperature controller. A thermocouple installed near the sample, and the temperature can be measured with the help of a digital multi-meter. The details of the setup are described elsewhere [5]. The relevant parameters required or infrared sensing and energy harvesting, which include the dielectric constant ($\varepsilon'$) and pyroelectric coefficient ($p$) were calculated. A real part ($\varepsilon'$), imaginary part ($\varepsilon''$) of the dielectric constant were determined as:

$$\varepsilon' = \frac{C_p d}{\varepsilon_0 A}, \quad (1)$$

$$\varepsilon'' = tan\delta \cdot \varepsilon', \quad (2)$$

where $C_p$ is the parallel capacitance of the sample at a signal frequency of 1 kHz, $tan\delta$ is the dielectric loss, $A$ is the electrode area of the silver electrode, $d$ is the thickness of the sample, $\varepsilon_0 = 8.854\times10^{-12}$ F/m is the permittivity of vacuum.

Piezocapacitance response is calculated as $\Delta C / C_o$; where $\Delta C$ is the change in capacitance on applied force.

## 2.4. Force Measurement Custom-Made Apparatus

Custom-made setups shown in Fig. 1 were designed and fabricated for testing these nanocomposite pressure/strain film sensors for use in human motions and robotics. Set I consist of a Starrett Press and Force indicator. With set up I, one can apply force on the device under test (DUT) placed between the two holders and note down corresponding capacitance. We apply a transverse force from 0 to 100 N. Thus, DUT can be used for measuring transverse pressure. Set II consists of a custom-made feature to apply sheer force on a curved device under test. This type of sensor can be used to mimic finger motion. The device is held with the help of two jaws, and sheer pressure is applied with the help of a cylinder placed under the device. By moving the cylinder upward, pressure can be applied on the device under test, and accordingly, the capacitance can be measured.

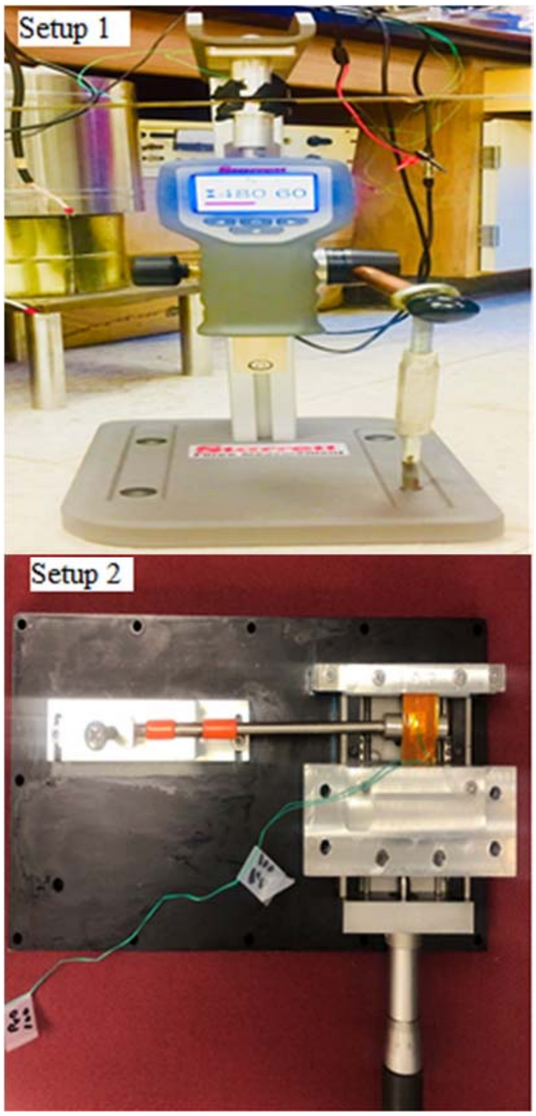


**Fig. 1.** Custom-made sensor performance determination setups: Setup 1(transverse pressure), Setup 2 (shear).

Custom-made setups shown in Fig. 1 were designed and fabricated for testing these nanocomposite pressure/strain film sensors.

## 3. Results and Discussions

From the recorded Fourier Transform Infrared (FTIR) and Raman spectra in the range of 400 to 4000 cm$^{-1}$, functional groups were identified in the nanocomposite films (Fig. 2). Infrared vibrational spectroscopy (FTIR) revealed ferroelectric β-phase in the annealed nanocomposite films intrinsically around 840 cm$^{-1}$ [24, 25].

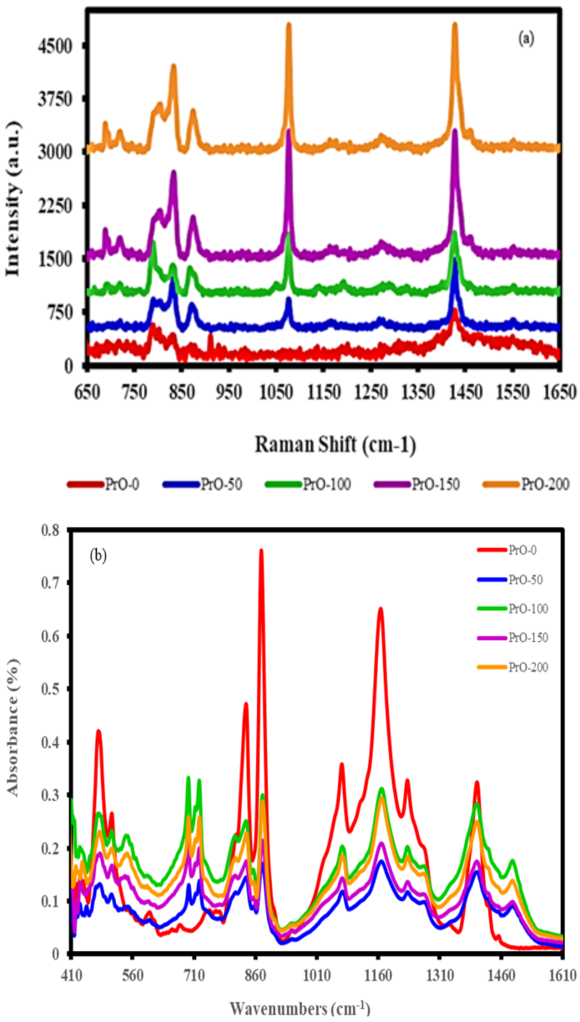


**Fig. 2.** Raman spectra (a) of PVDF thin film measured with a Raman system equipped with 785 nm wavelength laser and FTIR spectra (b).

For piezo-capacitive results, pressure was applied from below the electroactive nanocomposite samples via the cantilever in the earlier mentioned experimental setup initially displayed in Fig. 1. As the cantilever changes position, and consequently mechanical force, a measure of the change in dielectric capacitance is measured for the two nanocomposite thin-films named PrO-100 and PrO-200. The relative DC electrical capacitance/sensitivity change versus position is first recorded in this manner. Secondly, electrical capacitance/sensitivity change versus force applied in Newtons is recorded utilizing a Starrett force materials testing system and graphically presented as well. Polymer composite material consisting of an insulating polymeric matrix and conductive reinforcing nanoparticles have a total resistance that is due to both components present. Assuming the resistance of the matrix be constant, the total resistance of the nanocomposite smart material will depend on number of particles as well as conducting paths present. That being said, the characteristics of the implemented conductive network will be the main factors which may ultimately determine the total resistance of the composite materials. The cantilever/position method exhibits the properties of the material under flexion, while the Starrett method utilizes applied mechanical force to exhibit the behavior of the nanocomposite-film under compression. Fig. 3 exhibit the experimental results in relation to the PrO-100 nanocomposite. Fig. 4 displays result of nanocomposite PrO-200.

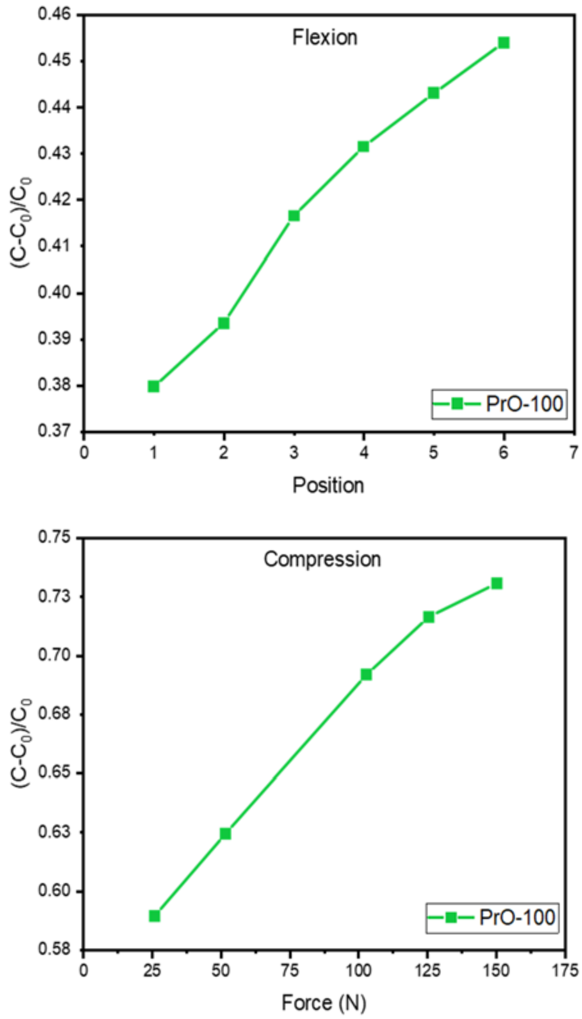


**Fig. 3.** Capacitance-change under flexion vs. position (arb. Units) and compression for PrO-100 versus force (N).

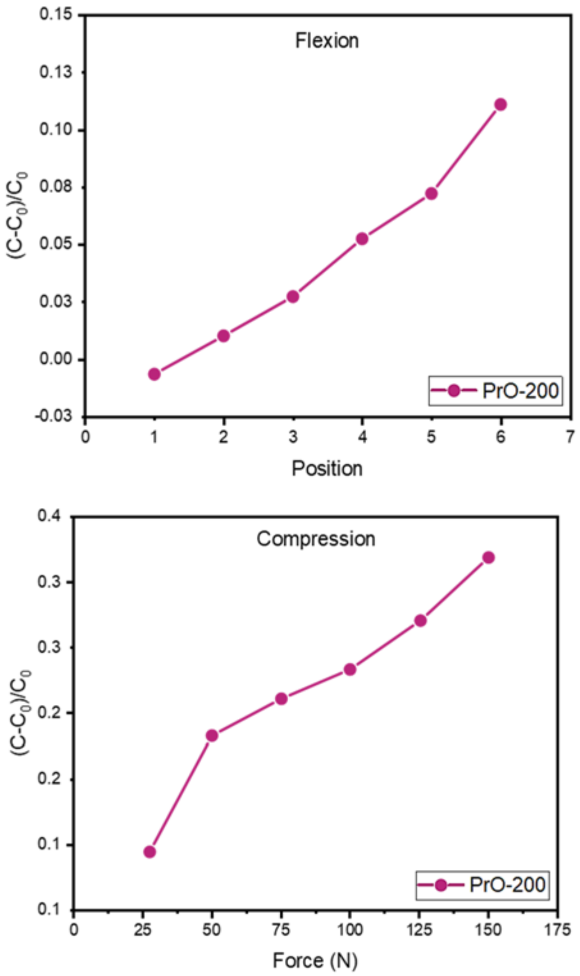


**Fig. 4.** Capacitance-change under flexion (shear stress) vs. Position (arb Units) and compression for PrO-200.

Stress and strain are the main driving forces and concepts in question when investigating piezo-capacitive and piezo-resistive characteristics of smart materials. The strain has three general categories, depending upon the change produced in a body and the type of stress applied. In terms of strain, there is longitudinal strain; volume strain; and shearing strain. As far as stress is concerned, there are five types of stress: tensile, compressive and shear, torsional, and bending. The results obtained using our custom-made experimental setups are indirectly related to these kinds of stress/strain parameters as well. By simulating stress/strain upon the nanocomposite film samples, information regarding their optimal placement and integration into systems as small biomedical energy harvesters or sensors can be determined. In terms of piezocapacity, common medical devices such as pacemakers could be attuned with small piezoelectric energy harvesters where the force from the flexion and compression of the contractions of the heart and pacemaker could be utilized to create an endless battery and functioning life. Piezoresistive/piezo-capacitive based smart materials would prove useful in the example of a medical patient recovering from recent knee replacement surgery. These smart devices integrated into the artificial knee could help a physical therapist track patient's the knee strength and progression of a patient during their road to recovery.

## 4. Conclusions

In this study, good quality and homogeneous nanocomposite PVDF films embedded with $Pr_2O_3$ nanoparticles have been fabricated. We have demonstrated that technology based on $Pr_2O_3$ nanoparticles embedded in flexible PVDF matrix has proven successful in developing flexible pressure sensors. From the results of the FTIR analysis of the fabricated PVDF-praseodymium nanocomposite polymers films, we can clearly see the band at 840 $cm^{-1}$, confirming the formation of the β-phase in the films [23-28]. It is worth mentioning that compared to resistive sensors, capacitive sensors generally have higher sensitivity and lower detection limits [29, 30]. However, their inadequate linearity response and the presence of parasitic capacitance can be a significant challenge in practical applications.

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