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ORIGINAL RESEARCH

Flexible and Self-Powered PVDF-Nanosilica Based Piezoelectric Touch Sensor

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Abstract

Technological advances have profoundly influenced the design of wearable and flexible electromechanical sensors in piezoelectric materials technology. This article investigates the enhancement of the piezoelectric performance of polyvinylidene difluoride (PVDF) with the addition of nanosilica (SiO_2). The use of nanoparticles can overcome the difficulties associated with PVDF, and the touch sensor was fabricated using a sandwich-based assembly. A comparison of the piezo potential generated across the fabricated sensor samples with and without nanofiller was conducted. The experimental results demonstrate that the nanosilica addition improves the piezo-response of the touch sensor and thus has a promising application in the biomedical field.

Keywords Touch sensor · PVDF · Piezoelectric · Nanosilica · Nanocomposites

Introduction

Flexible and wearable touch sensors have emerged as a promising platform in personal healthcare, particularly prostheses. The demand for device flexibility is growing in tandem with the fast development of these technologies [1]. Improving the piezoelectric properties of the materials is crucial for enhancing the flexibility of the electromechanical sensors [2, 3]. PVDF and its derivatives are the appropriate materials for flexible device fabrication. These materials have high flexibility, high sensitivity, high ductility, wide frequency band, high thermal stability, good chemical resistance, and excellent biocompatibility with a good piezoelectric coefficient [4–6]. PVDF features a carbon chain as its basic skeleton, making it more flexible than single crystals or ceramics. Because of its greater flexibility, it can sustain more strain, making it ideal for touch-sensing applications that require bending and twisting. The polarity of the PVDF film is affected by defects in the polymeric chain, which increases the piezoelectric response [7, 8]. PVDF and its co-polymers have higher natural flexibility, manufacturing ease, and mechanical robustness than inorganic piezoelectric materials, making them more appropriate for flexible sensors [9, 10].

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Several optimization strategies have been devised to improve the piezoelectricity and hence the electromechanical efficiency of the PVDF. Since the fraction of β-phase structure determines the piezoelectric characteristics of this material, several research studies have focused on altering the structure of PVDF. Electric field poling or mechanical stretching can be used to produce PVDF with significantly improved β-phase content. But these methods can harm the sensor device during the process, as mentioned earlier. Piezoelectricity can be further enhanced by adding nanofillers into the PVDF matrix. This approach can alter the crystal structure of PVDF and enhance the β-phase proportion, which is essential for improving the electromechanical energy conversion. In addition to being superior to pure piezoelectric polymers, nanocomposites can have a higher dielectric constant and phase crystallinity [11, 12].

Nanosilica (SiO_2) is an attractive inorganic filler material that improves the ionic conductivity of PVDF polymer by altering their order packing tendency. Because of its appealing qualities, such as thermal stability, chemical inertness, low cost, non-toxicity, and ease of synthesis, nanosilica is vital for biomedical applications [13]. The nucleation of the β-phase in such nanocomposites can be attributed to effective interaction between CH_2 groups of the polymer chains having positive charge density and the surface of nanoparticles with negative charge density. Thus, the addition of SiO_2 to PVDF can induce the formation of the β-phase during the thin film fabrication process, making it an ideal method for preparing piezoelectric nanocomposites with the highest β-phase crystallinity and the best piezoelectric properties [14, 15].

This paper describes the fabrication and characterization of a PVDF-SiO_2-based piezoelectric sensor. Thin-film technologies, in particular, have been considered for use due to their versatility and ease of production. Furthermore, a bendable, self-powered tactile sensor with sensitivity, stability, and cycle life was developed for biomedical applications.

Device Architecture and Fabrication

Materials

PVDF powder was purchased from Alfa Aesar (Fisher Scientific). The nano-silica powder with 50 nm particle size was purchased from Sigma Aldrich, and N, N- dimethylformamide (DMF) solvent was purchased from Merck. Sylgard 184 elastomer and its curing agent were purchased and used as PDMS elastomers. All chemicals and solvents were used as received without any further processing.

Fabrication of PVDF-SiO_2 Nanocomposite Thin Films

SiO_2 nanoparticles were dispersed in 10 mL of DMF solvent using probe sonication for 15 min, followed by bath sonication for 30 min. These procedures ensure that nanoparticles disperse uniformly at room temperature. The PVDF powder was then added to the prepared solution and stirred continuously for 3 h with a magnetic stirrer set to 700 rpm. The solution was then spread onto a glass mold and cast with a clean glass blade. The resultant nanocomposite polymer solution was kept at a temperature of 60 ℃ for 4 h to remove all possible residues and then dried in the vacuum. The dried thin film was then peeled off and kept in a vacuum oven for annealing at a temperature of 90 ℃ for 2 h. The thickness of the prepared film is around 100 µm. The experiment was then repeated to prepare other nanocomposite thin films by varying the SiO2 composition (1%, 1.5 %, and 2%).

Sensor Assembly and Packaging

PVDF- SiO_2 nanocomposite thin film was diced into 1 cm ×1 cm ×100 µm dimensions. After cleaning and drying, thin copper foils with a thickness of 50 µm were chosen to make connecting leads. Flexible and compressible polymer nanocomposite thin films were shielded by bendable conducting copper plates with conducting strips. The SiO_2 concentration was opted based on the ATR-IR characterization results. The sensor film was sandwiched between copper foils and sealed with non-conductive tape. Another sensor using a pure PVDF thin film was also developed using the same fabrication steps mentioned above.

Sensor Film and Device Characterization

Fabricated thin films were analyzed using an FTIR spectrophotometer (JASCO FTIR-4700) to identify the optimum composition of the nanosilica filler in the PVDF matrix. After determining the optimum filler composition, the pure PVDF and PVDF- SiO_2 (with optimum SiO_2 concentration) films were analyzed using Differential Scanning Calorimetry (DSC) (DSC Q20 TA) to identify the change in crystallinity and melting temperature. Thermal gravimetric analysis (TGA) was also performed on the samples to investigate the thermal properties of the film. The schematic of the touch sensor operation is illustrated in Fig. 1. A 3D-printed sensor stand supports the sensor during the tapping operation for device characterization. The experiment setup consists of a universal vibration apparatus, a force-sensing resistor (FSR-402), an Arduino board, a mixed signal oscilloscope (MSO) (Keysight-MSOX3014T), and a PC.

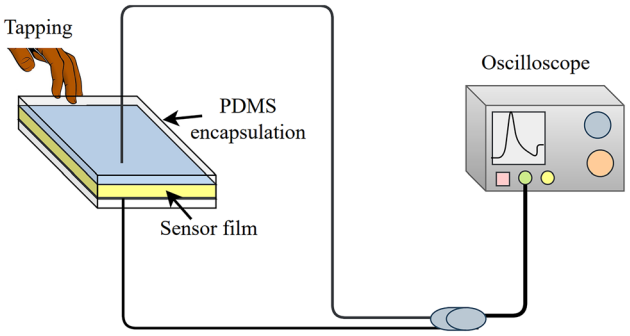

Fig. 1 Schematic of piezoelectric PVDF-nanosilica based touch sensor

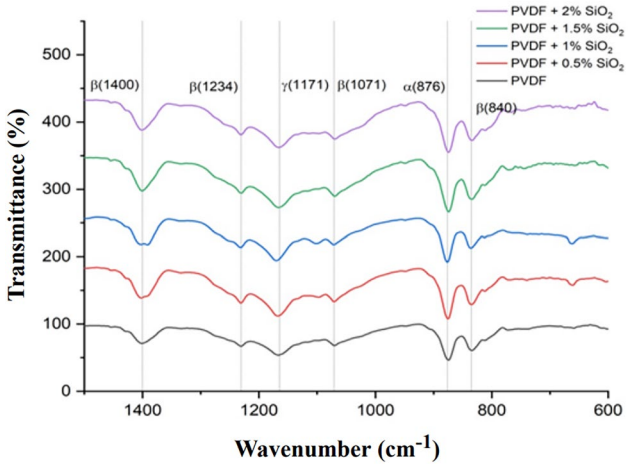

Fig. 2 ATR-IR spectra of PVDF and PVDF-SiO_2 nanocomposite films

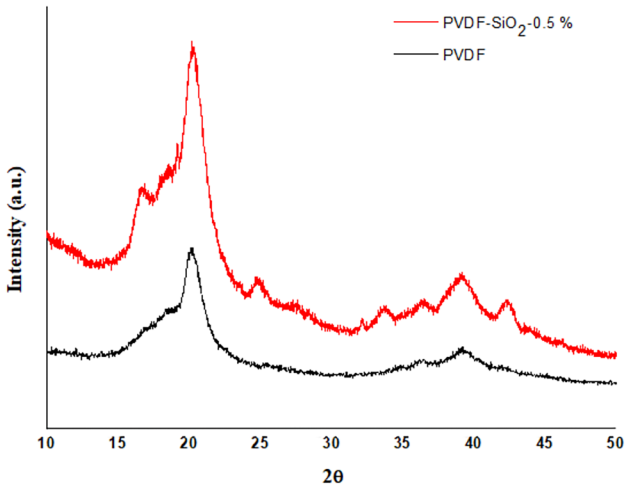

Fig. 3 XRD of PVDF and PVDF-SiO_2 nanocomposite films

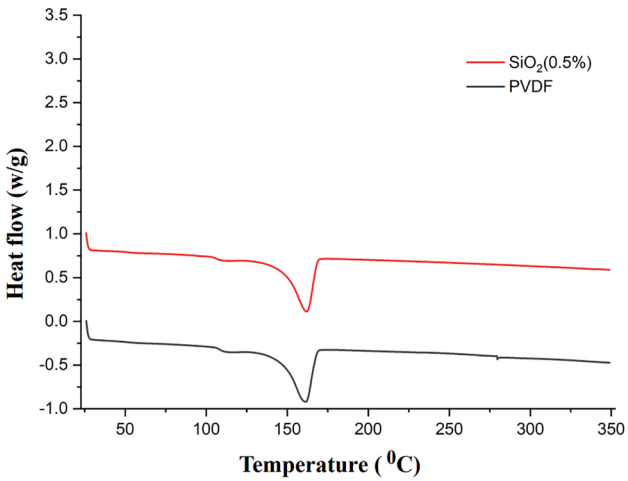

Fig. 4 DSC curves for the PVDF and PVDF-SiO_2 film

Results and Discussions

The ATR-IR spectra were analyzed to determine the piezoelectric β-phase improvement due to the addition of SiO_2. Based on the ATR-IR results, the optimum concentration of the SiO_2 in the PVDF matrix was identified. The weight percentages of SiO_2 varied from 0.5 wt % to 2 wt %. The thin film was analyzed in the 600 to 1500 cm-1 range. The peaks represent the β-phase at 840, 1071, 1234, and 1400 cm-1. Figure 2 depicts the ATR-IR results. The results confirm the improvement of the β-phase, and the progress is more significant with the PVDF-SiO_2 (0.5 wt%) composite. The comparison can be viewed in Fig. 2. The optimal nanosilica concentration restricts the agglomeration of SiO_2 in the PVDF matrix. Accumulation reduces the flexibility and strength of the composites, significantly reducing sensor performance.

The XRD pattern of the pure PVDF and PVDF-SiO_2 (0.5 wt %) composite films are shown in Fig. 3. The strong XRD peaks of PVDF-SiO_2 at 2θ=20.7° corresponds to (110) and (200) planes and additional peaks at 36.9° and 41.1° were also observed which shows the β-phase crystallization of PVDF-SiO_2 composite.

The thermal transitions and crystallinity properties were investigated using the DSC technique. The analysis was performed at a heating rate of 10 ℃ in N_2 atmosphere. The effect of nanosilica on the crystallization and melting temperature of the composite film is revealed by DSC analysis. The impact can be seen clearly in the DSC plot (Fig. 4), and the findings can be seen in Table 1. The melting and crystallization temperatures of the composites were affected by the addition of fillers. The variation is due to the uniform dispersion of nanosilica particles across the PVDF matrix. The all-trans structure is more densely packed and has a greater melting temperature. As a result, the melting point fluctuation indicates the formation of the β-phase in the composite

Table 1 DSC results of thin sensor films

Thin film	Tm (℃)	Tc (℃)	Melting Enthalpy(J/g)	Crystallinity (%)
PVDF	161.73	133.68	50	47.75
PVDF-SiO_2	162.93	134.12	51.28	48.90

films. The analysis shows an increase in the crystallinity of the nanocomposite samples compared to pure PVDF thin films.

Tensile test results for pure PVDF and PVDF-SiO_2 nanocomposites are shown in Table 2. According to the findings, the addition of nanosilica to the PVDF increased the tensile strength of the films. This indicates that the nanoparticles can act as temporary cross-linking agents between the PVDF chains and can create localized regions of improved strength, imparting a reinforced effect in the film. But the presence of more SiO_2 concentration in the PVDF polymer can make them less flexible and brittle by lowering the elongation break points.

TGA helps to get the thermal stability analysis of the films. The selected samples were dried using a vacuum oven at 70 ℃ overnight. TGA was performed in the range of 0–750 ℃. Thermograms of the sample are shown in Fig. 5. The pure PVDF film started to degrade at 406 ℃, whereas the degradation temperature increased to 420 ℃ for PVDF-SiO_2 (0.5 wt %) composite film.

A single taxel of the sensor comprises a piezoelectric sensing layer sandwiched between copper electrodes encapsulated inside a PDMS layer. When a contact force is applied, the piezoelectric sensor layer deforms, resulting in a polarization shift on its surface. This induces a voltage on the film surface corresponding to the applied external force. The dynamic piezoelectric response of the fabricated sensors was obtained by applying continuous tapping forces externally using universal vibration apparatus. The tapping force measurement setup consists of a force-sensitive resistor (FSR-402), and the associated electronic circuitry.

The sensor response was quick and gave a similar response to the same applied force, making it reliable. The generated results were observed using an MSO. The sensor

Table 2 Tensile strength analysis of thin films

Thin film	Tensile Strength (MPa)
PVDF	33.5
PVDF-SiO_2 (0.5%)	37.5
PVDF-SiO_2 (1%)	46.5
PVDF-SiO_2 (2%)	49.5

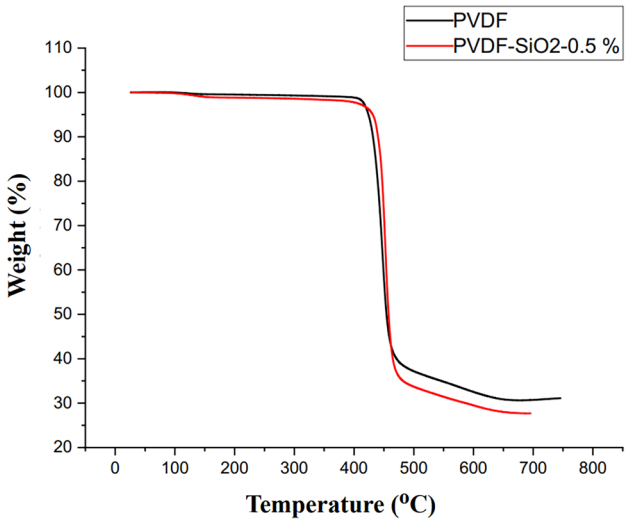

Fig. 5 TGA curves for PVDF based sensor films

devices were placed over the noise shielding sheet to avoid the intrusion of unnecessary noise input from nearby equipment. The oscilloscope was utilized to record the electrical signal generated by the sensors. The measurement setup for sensor characterization is shown in Fig. 6. The results show an improvement of 1.6 times higher signal response for a PVDF-SiO_2-based sensor compared to a pure PVDF-based device for the same applied force (15 N). All the tapping experiments were conducted in ambient laboratory conditions. The surface area to volume ratio of PVDF increased as SiO_2 nanoparticles were added, allowing more charges to populate the sensing film surface, and thus the addition of SiO_2 has a significant role in improving the β-phase of the PVDF thin film. The rapid and repeated experimental analysis shows a clear influence of SiO_2 filler addition on device-level piezoelectric performance due to enhanced β-phase. The responses of the sensors to a load of 15 N are shown in Table 3.

Conclusion

PVDF polymer is crucial in the current context for developing flexible device designs due to its exceptional characteristics. Simple, flexible, and self-powered prototypes of a PVDF-SiO_2 nanocomposite-based touch sensor have been evaluated experimentally. Sensors were fabricated using optimum filler percentage and encapsulated with a thin PDMS layer for protection. The repeated experimental analysis reveals a clear impact of nanosilica addition on the PVDF due to increased β-phase formation. The research findings should encourage and guide the emergence of

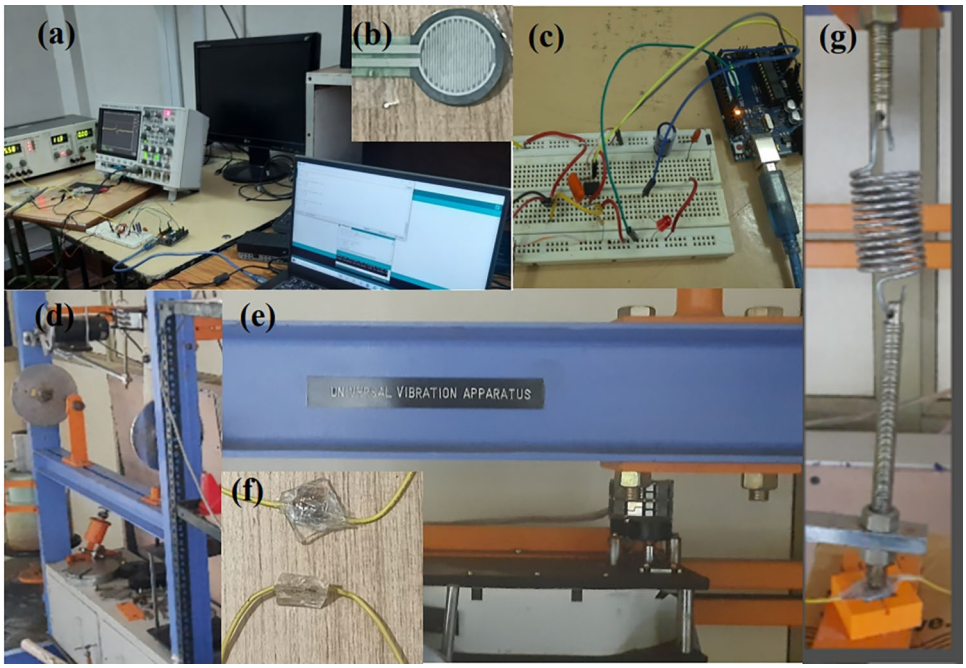

Fig. 6 **a** Experimental setup for calibrating FSR **b** FSR-402 **c** Arduino based electronic setup for calibration **d** Setup for measuring contact force using vibration apparatus **e** Universal vibration apparatus **f** Fabricated and packaged sensor assembly **g** Vibrating tip of the setup for tapping on the top surface of the device

Table 3 Sensor response to repeated tapping input

Sensor film	Filler	Concentration (wt %)	Output (mV)
PVDF	–	–	548
PVDF	SiO_2	0.5	886

various sophisticated touch-sensing units with improved sensitivity for healthcare applications.

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Declarations

Conflict of Interest The authors declare that they have no conflict of interest.

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