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A Review on Properties and Applications of Polyvinylidene Fluoride (PVDF) and Metal Oxide Nanocomposites Thin Films

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Abstract

The different properties of PVDF nanocomposite thin films are influenced by the addition of nanofillers, as observed in various studies. PVDF nanocomposite films exhibit changes in structural, phase, frictional, optical, electrical and mechanical properties compared to traditional PVDF films. The table 2, given in this article gives brief information regarding the synthesis, different properties that has been deliberated and proved recently. The applications of PVDF with nanofiller nanocomposite thin films are discussed and it’s an astonishing concept that makes us to realize that there is an opportunity for us to use natural sources of energy to convert it into electrical energy and all under environment protection rules and regulations. That’s why PVDF nanocomposite thin films are playing a significant role in the energy conversion in the electrical vehicles, home appliances and other devices which are very useful for mankind.

Introduction:

Transportation is having important effect on the environment, because of which environmental pollution is becoming a big challenge to the government togovern and to help the people free from diseases due to air pollution, noise pollution, global warming and biodiversity loss. And as per the study 25% of total emissions and 33% of total energy consumption is due to transportation across the globe. So, we need to use sustainable transportation methods by using electric vehicles which can consume minimum sources of energy and protect the environment from pollution and reduces health effects from asthma, bronchitis, cancer and premature death.

As we know that, electric gadgets and electric vehicles have many benefits which includes environmental, economic and convenience advantages. EVs can be cheaper to run than petrol and diesel motor vehicles because electricity prices are lower than these non-renewable sources such as coal, petroleum products, coal products, crude oil etc. EVs can be charged at home or even at public charging stations with minimal expense, and they are easy to drive, quiet and sensitive. Now, the things to be taken care of are, to increase battery efficiency, safety. To achieve the goal in that direction, one of the elements that is PVDF with its nanocomposite thin films can used to do some miracles in increasing the capacity of the batteries.

Lithium-ion batteries were first developed in the year 1970 by Michal Whittingham. It was made up of graphite as cathode and lithium as anode. Now a days these batteries are made mainly for commercial purposes and used in home appliancesand also in electrical vehicles (EVs) and the current aim is to replace graphite and place silver for a stable and a consistent battery to work brilliantly! As we know lithium is the element which is having a good tendency to lose electrons compared to other elements. The electrochemical potentials of different metals are listed below. This clearly shows why lithium batteries are preferable than others.

Metals	Electrochemical potentials
Li	3.04V
Mg	2.37V
Al	1.66V
Zn	0.76V
Fe	0.44V
H	0V
Hg	-0.24V
Cu	-0.34V
Ag	-1.69V
F	-2.8V

Table: 1 List of metals with electrochemical potentials

Fabrication of a thin layer of PVDF nanocomposite with nanofillers creates an increase in the conductivity of the lithium batteries which indeed is of great demand to lead a comfortable life, on which most of the electronic equipments works, at home as well as at workplace.

Literature Review:

A comparative study on the different PVDF nanocomposite thinfilms mixed with metal – oxides and other nanocompositesto form thinfilms and to understand the variation in the properties of PVDF nanocomposite thinfilms in batteries.

Table: 2 List of PVDF nanocomposite thinfilms with synthesis methods and properties.

Sl. No.	Polyvinylidene Fluoride (PVDF)	Nanofillers	Method of Synthesis	The variations in the properties observed.
1	PVDF	1)Barium Titanate($BaTiO_3$) reinforced Poly Vinylidene fluoride co - hexafluoropropylene (PVDF – HFP)	Mixed solvent phase separation method (MSPS) and thermally induced phase separation thermally induced phase separation(TIPS) [1-4].	• In mechanical to electric conversion measurement, higher piezoelectric output is observed [1 - 4].
2.	PVDF	2)Barium Titanate	Solution casting	• The dielectric constant

		$(BaTiO_3)$/ Montmorillonite (MMT)	method[2 ,4]	of the material increases with decrease of frequency at high temperature. [2, 4].
3.	PVDF	3)Barium Titanate $(BaTiO_3)$/Molybdenum Disulfide (MoS_2)	Solution casting method [3, 4].	• The **thermal stability** of the composite has been increased due to the addition of these nanofillers which indeed increases the thermal stability by 28°C to 30°C [3, 4]. • The incorporation of $BaTiO_3 – MoS_2$ nanofillers increases the **dielectric constant** which is very important for energy storage applications [3, 4]. • The addition of $BaTiO_3/MoS_2$ nanofillers activates β – phase of PVDF by a strong interaction and hence the magnetic properties increase and opens doors for many applications based on pressure sensors [3, 4]. • In gas sensing properties, the composite is used in detection of ammonia (NH_3) gas and among all the samples $PVDF/BaTiO_3–MoS_2$ nanocomposite sensor showed a fast response and recovery time. [3, 4]
4.	PVDF	PVDF/ZnO	Solution casting method[5-7]	• Optical, thermal and electrical properties were observed: UV–visible

				absorption spectroscopy is used to study optical properties and the addition of ZnO nano particles increases the absorption of UV radiation [5-7]. • The thermal stability of the PNC thin films was assessed using thermogravimetric analysis and the variation in decomposition temperature range has been observed [5-7]. • Variation in Dielectric constant, AC conductivity, Complex impedance and complex modulus measurements has been observed in the study [5-7].
5.	PVDF	PVDF/TiO_2	Solution casting method [8 - 10]	• Ionic conductivities were found using the formula$\sigma = l/(R_b \times A)$, where l represents the thickness, R_b is the bulk resistance, and A is the contactarea of the nanoparticle composite solid electrolytefilm during the experiment[8 - 10]
6.	PVDF	PVDF/MgO	Spin coating method [11]	• Dielectric constant: With the increase in MgO nanofillers in PVDF, dielectric constant increases as per the study [11]
7.	PVDF	Polyvinylidene fluoride-trifluoroethylene (PVDF/TrFE)	Spin coating method[12] (individual spin coating method)	• Dielectric constant in nanocomposites with PVDF and TrFE are observed to be having

				slightly higher dielectric constant [12]
8.	PVDF	PVDF/ PEO / WO_2	Spin coating method[13]	- **Optical properties:** There is a wide range of increase in the optical energy gap in the composite as the composition of the nanofiller varies[13]. - **Hall effect measurements:** It is also observed that altering the
9	PVDF	PVDF / NMFO	Sol – gel combustion method [14].	- A study on dielectric constant with the addition of NMFO has been made and according to the article and as per the study done by Wayne-Kerr LCR meter [14].
10.	PVDF	$LiNO_3$	Solution spin coating method[15]	- Electrical and electrochemical properties–$LiNO_3$ precipitated in 10LNO-SPE films, if we increase the temperature $LiNO_3$dissolution increases which generate additional charge carriers which increase ionic conductivity [15].

Applications:

1. Medical applications:

To check the heart beat/ pulse signal in the temple area or wrist area, the sensor must be placed in some specific tissue layer area of the body to receive the heartbeat signals. So, in this aspect, fabrication of a flexible electrospun cobalt ferrite($CoFe_2O_4$, CF) embedded polyvinylidenefluoride(PVDF) nanocomposite(NC) using an electrospinning technique can be prepared and additionally fabrication of triboelectric nanogenerator (TENG) using PVDF-CF (P-CF) NCas the tribo-negative layer and non-woven fabric of thermoplastic polyurethane (TPU) as the tribo-positive layerdevices. This application helps in identifying real-time sleeping disorders and respiratory monitoring [27].

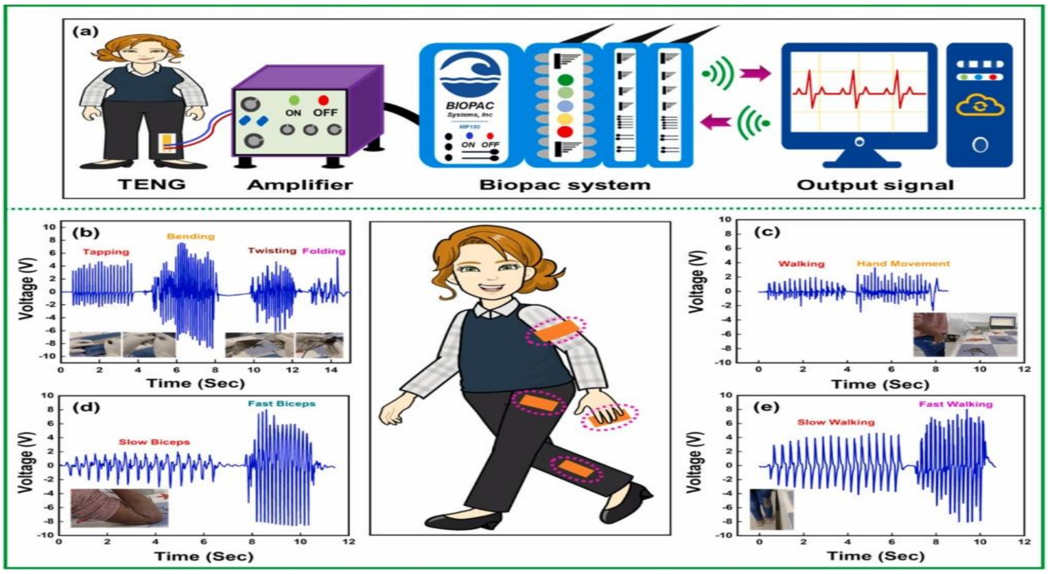


Fig: 1. (a) A schematic illustration of the experimental setup for detecting the biomechanical motion. Sensing ability of the P-CF-3/TPU-based TENG for various physical deformations: (b) Tapping, bending, twisting, and folding actions. (c) Walking and hand movement. (d) Slow biceps and fast biceps. (e) Slow walking and fast walking. (Signal condition: R_{in} 100 MΩ, gain = 0 dB, and 0.1–10 Hz and-pass filter). (Inset: Position of the device placed over different positions of the human body) [27].

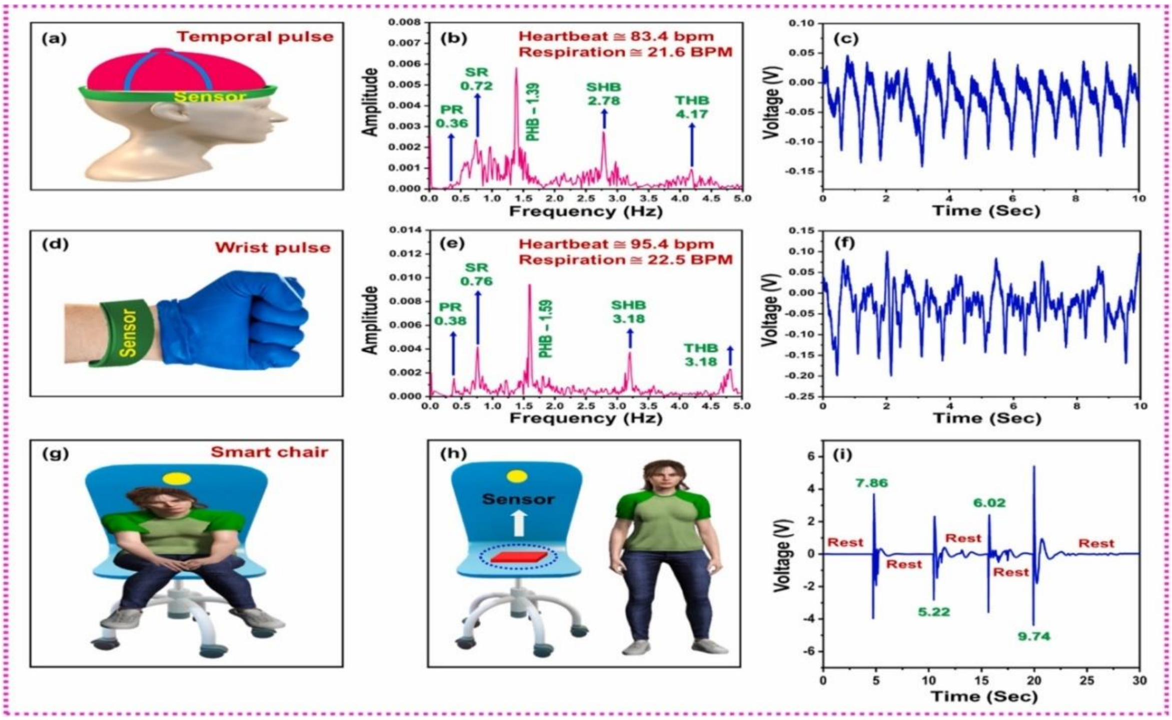


Fig: 2. Pulse detection by P-CF-3/TPU-based TENG. (a-c) The device attached over the temporal pulse site, FFT raw signals plot, and time domain raw voltage signals respectively. (d-f) A device attached over the wrist pulse site, FFT raw signals plot, and time domain raw voltage signals, respectively. (g and h) Sitting and standing position of the human subject in the smart chair, respectively. (i) Time domain raw voltage signal of periodic sitting and standing in the smart chair (Signal condition: Rin 100 MΩ, gain = 0 dB, and 0.1–10 Hz band-pass filter) [27].

2. Gesture recognition technique in human- machine interaction(HMI):

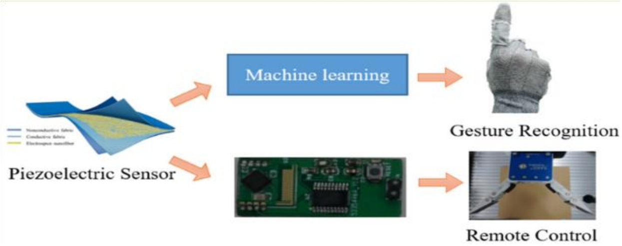


Fig: 3. Gesture recognition technique [28]

Wearable human – Machine gesture interaction based on fabric piezoelectric sensor can be used for real time hand and face gesture recognition techniques which indeed help a lot to many people who cannot talk properly and convey what actually they are having problems like for example in some patients in rehabilitation centers the patients cannot speak properly and thus they cannot share their problems, So this can be solved using HMI devices which is fabricated using PVDF/$BaTiO_3$nanocomposite membrane sensors[28].

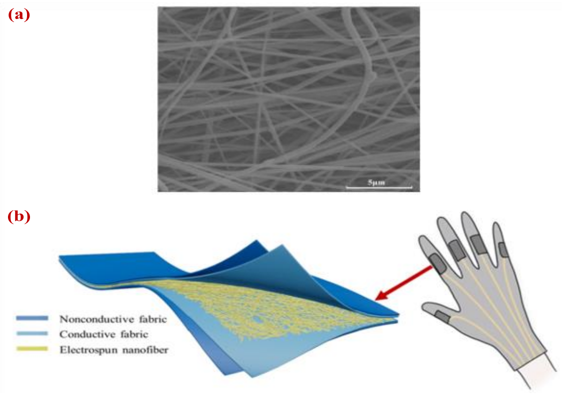


Fig: 4. Proposed fabric piezoelectric sensor. (a) SEM image of electrospun nanofibers. (b) Schematic of the fabric piezoelectric sensor structure[28].

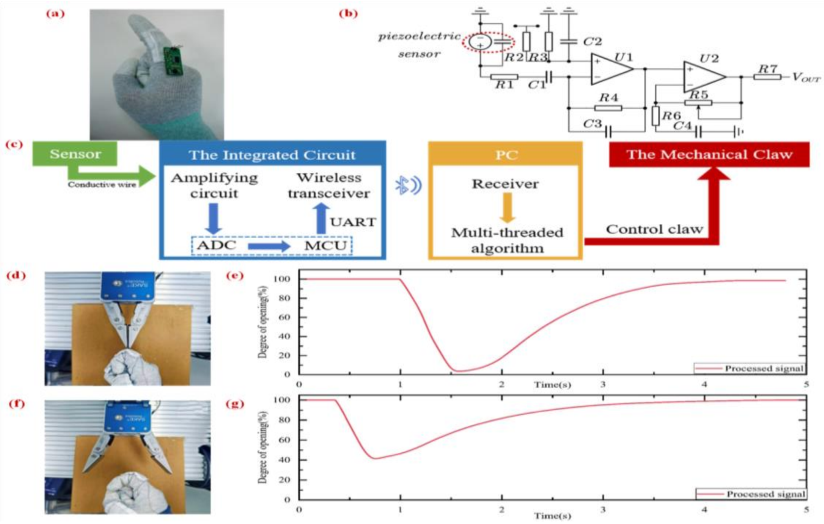
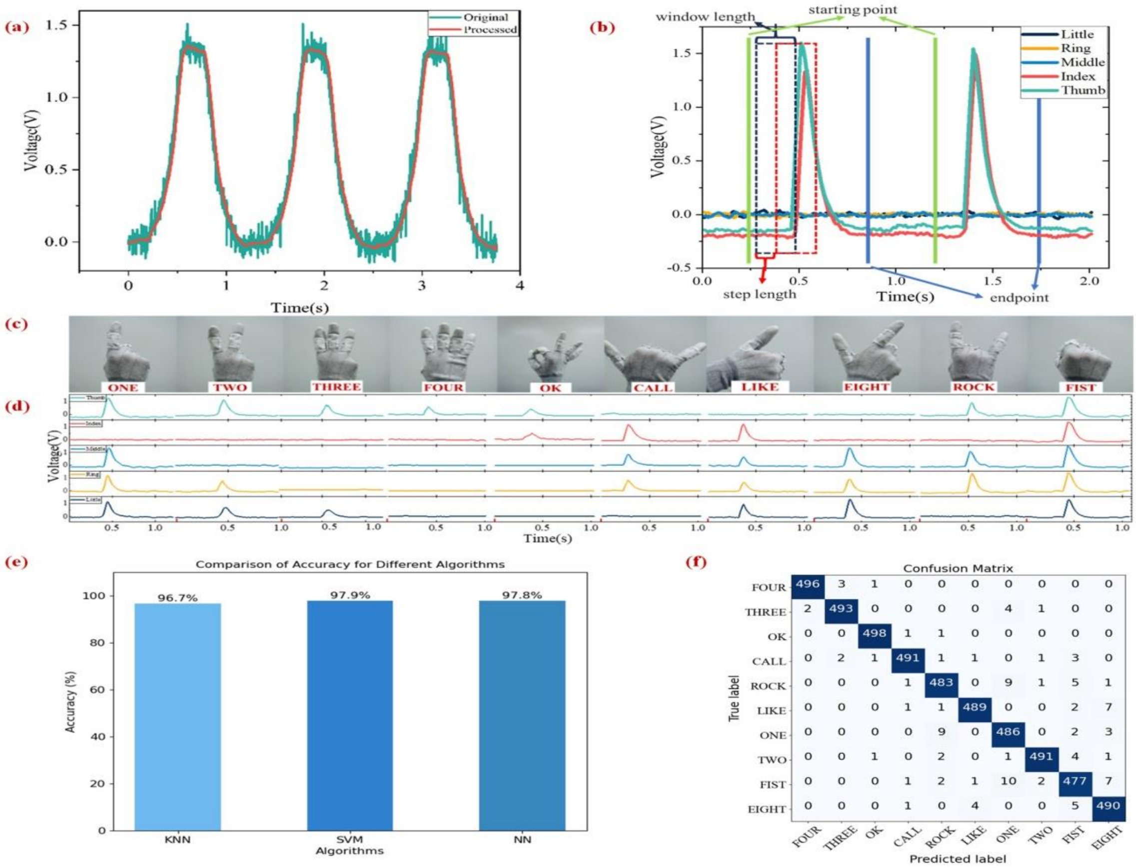


Fig: 5. Mechanical claw control system. (a) Image of the sensor and control circuit. (b) Amplifier circuit. (c) Block diagram of the mechanical claw control system. (d) and (f) Images of the mechanical claw under finger bending at different angles. (e) and (g) [28]



Confusion Matrix

True label \ Predicted label	FOUR	THREE	OK	CALL	ROCK	LIKE	ONE	TWO	FIST	EIGHT
FOUR	496	3	1	0	0	0	0	0	0	0
THREE	2	493	0	0	0	0	4	1	0	0
OK	0	0	498	1	1	0	0	0	0	0
CALL	0	2	1	491	1	1	0	1	3	0
ROCK	0	0	0	1	483	0	9	1	5	1
LIKE	0	0	0	1	1	489	0	0	2	7
ONE	0	0	0	0	9	0	486	0	2	3
TWO	0	0	1	0	2	0	1	491	4	1
FIST	0	0	0	1	2	1	10	2	477	7
EIGHT	0	0	0	1	0	4	0	0	5	490

Fig: 6. Gesture recognition. (a) Signal filtering. (b) Signal feature extraction. (c) Proposed ten types of gestures. (d) Signal output graph corresponding to ten types of gestures. (e) Classification accuracy of different algorithms. (f) Gesture classification confusion matrix of SVM[28].

3. Humidity sensor applications:

Polyvinylidene fluoride(PVDF), Polymethyl methacrylate (PMMA) thin film in a range of ZnO nanofillers were fabricated and used as a high-performance humidity sensor.ZnO is having wide band gap of about 3.37eV which makes it highly sensible to humidity[31].

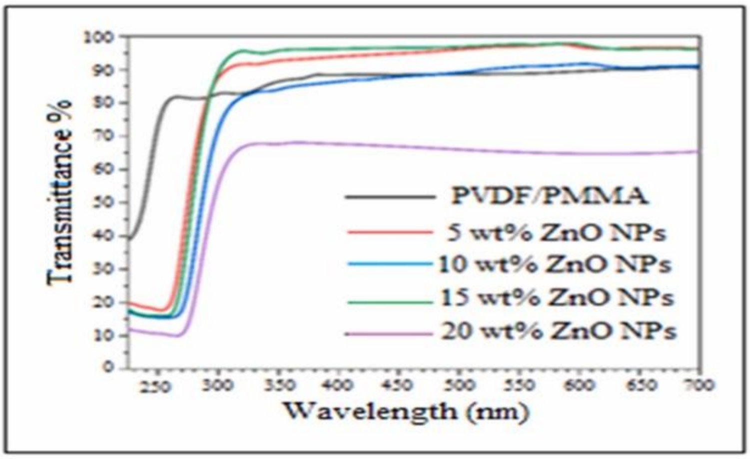


Fig: 7. Transmittance spectra of PVDF/PMMA//ZnO NPs composite thin films with different weight ratios of ZnO NPs.

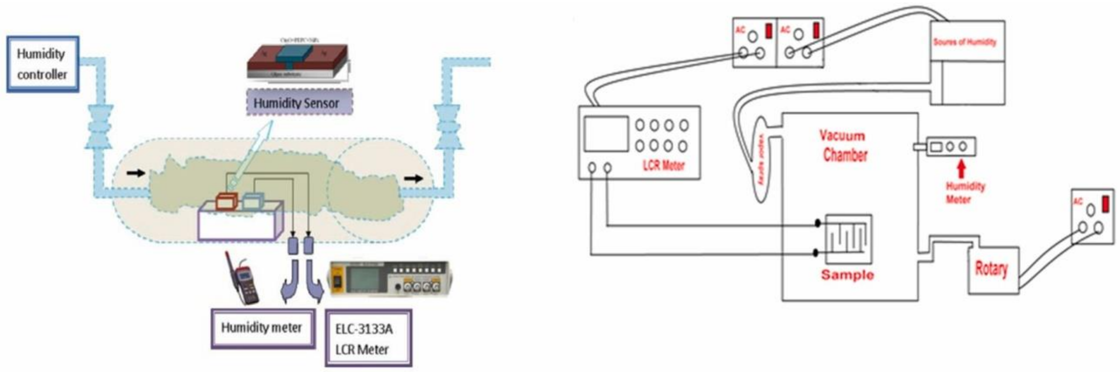


Fig: 8. Experimental setup used for the characterization of humidity sensors[31].

4. Biocarbon-Enhanced Flexible Nanofiber Mats for Sustainable Energy Generation and Wearable Device Applications:

This study involved the fabrication of PVDF nanofiber membranes incorporating 12% activated nanobiochar through electrospinning, with variations in thickness. The activated pyrolyzed biomass consistently exhibited a size range of 70–90 nm, it is advisable to keep the fiber membrane thickness within this range. The composite membrane displayed significant piezoelectric behaviour under applied pressure, and the output voltage exhibited a proportional increase with thickness. With increasing pressure, the output voltage for the 0.5, 0.9, and 1 mm PVDF/ nanobiochar composite device gradually rose by 4.8, 6.4, and 8.5 V, respectively[30].

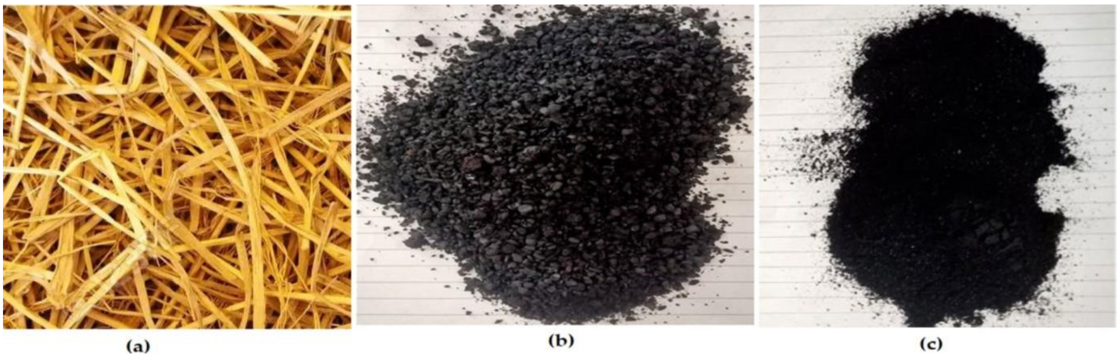


Fig: 9. Production stages of Biochar from agriculture wastes recycling (photographs are in the scale 2.5 cm width); a fibrous residue of sugarcane stalks, b biochar produced by pyrolysis process, and c. nanobiochar produced by milling process [30].

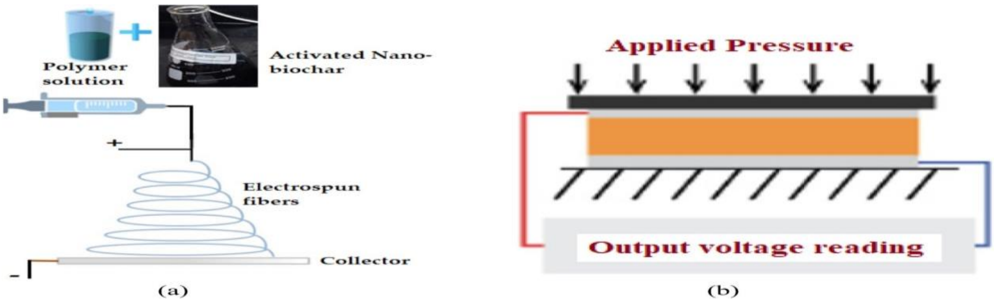


Fig: 10. Schematic diagrams: a. the electrospinning setup and b the electrical response of the membranes.

5. Wearable Piezoelectric sensors:

In this application, piezoelectric and heat-dissipating boron nitride nanotube (BNNT)/polyvinylidene fluoride (PVDF) nanocompositethin films having superior properties for wearable sensing applications are introduced and studied[29].

"In this research, BNNT/PVDF nonporous thin films fabricated by a novel approach based on gel nanofibers are introduced to apply for thermal, mechanical, and moisture-resistant piezoelectric wearable sensor applications requiring high sensitivity to pressure.Fabricated BNNT2.5 and BNNT5.0 showed highly enhanced piezoelectricity, mostly depending on the BNNT amount and BNNT-induced β phase formation in the polymer matrix. Through the good dispersion and semivertically connected alignment of BNNT and BNNT superior properties, ~8 times enhanced thermal conductivity were observed with BNNT2.5." [29].

In this application BNNT is introduced in a new method (dispersing 2.5 and 5.0 wt % of BNNT, (NanoBorNT-80, Naieel Technology)[29]and based on the amount of dispersion of BNNT's, mechanical properties of thin films has been observed."Both BNNT2.5 and BNNT5.0 also showed humidity resistance with a stable hydrophobic water contact angle on its surface" [29].

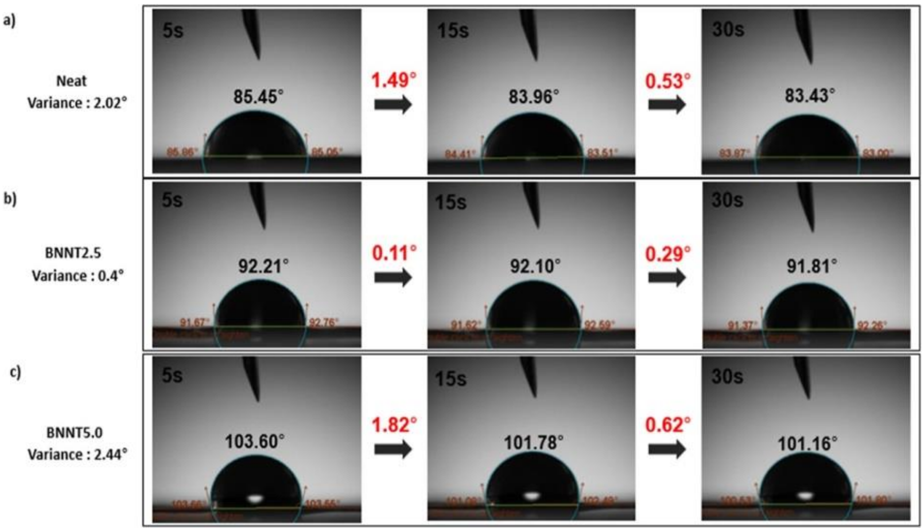


Fig: 11. Water contact angles of (a) Neat, (b) BNNT2.5, and (c) BNNT5.0 in 5, 15, and 30s [29].

6. Pressure sensors:

In addition, by an application of mechanical force, the crystal structure of the PVDF/$BaTiO_3$–MoS_2 films was deformed and the external pressure creates a potential in the $BaTiO_3$/MoS_2 composites, which aligns the dipoles in the PVDF matrix. The findings indicate that, these types of nanocomposites are appropriate for use in self-charging battery separators, bridges, shoes, footpaths, and cars as pressure sensors.[3][32].

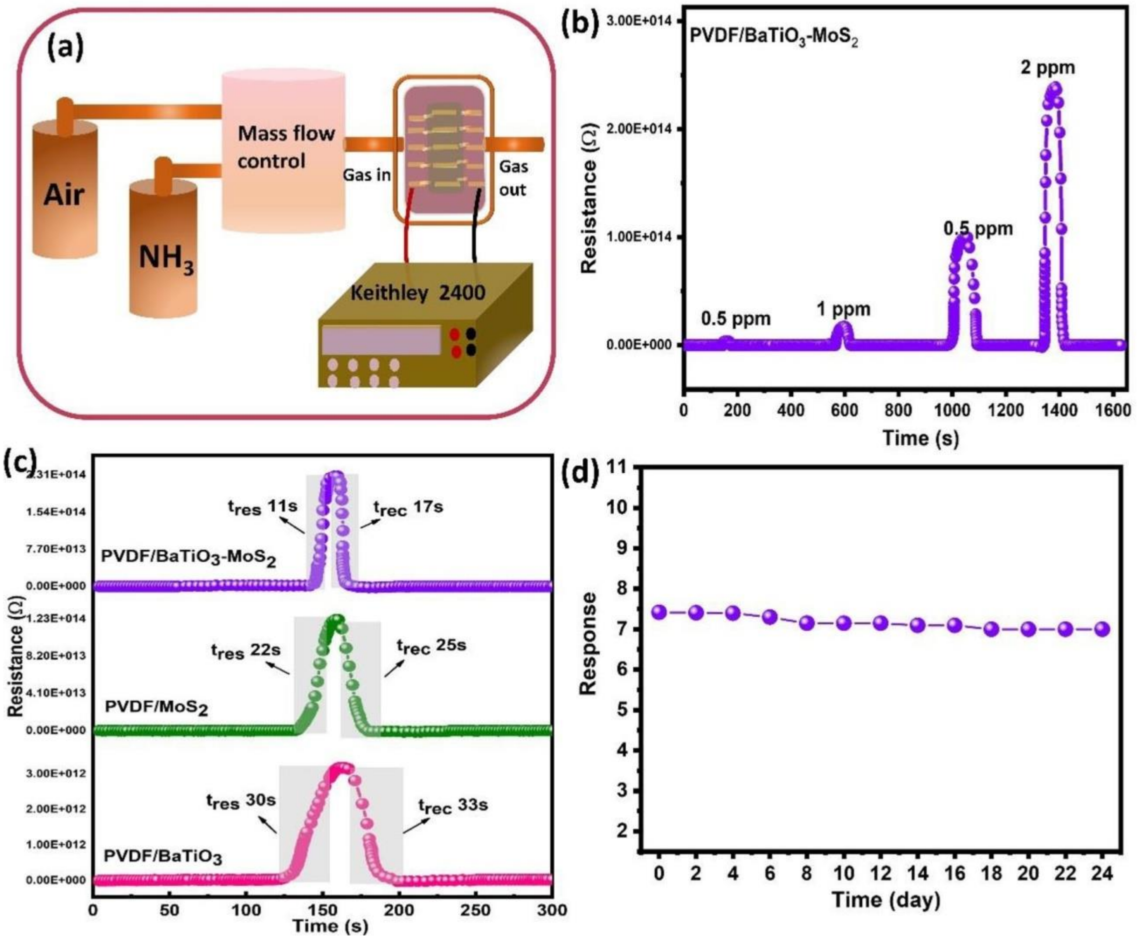


Fig: 12. a An illustration showing techniques to test NH_3 gas with a sensor, b Response of a room temperature, PVDF/ $BaTiO_3$–MoS_2 composite sensor to NH_3 gas concentrations, c Response and recovery behaviour of PVDF nanocomposites, d Long-term sensor stability at 2 ppm NH_3 at ambient temperature[3].

Conclusion:

This review article involved quick review on PVDF nanocomposite thin films with different nanofillers like $BaTiO_3$, ZnO, TiO_2, MnO etc when they are combined in different ratio, how the variations in the properties like mechanical, optical, electrical and thermal properties changes and leading to good research in increasing the capacity of the electric batteries can be scrutable. Also, the applications PVDF nanocomposites in many fields has been highlighted to understand the importance of the composite in the research area.

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