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Enhancement of β phase Crystal Formation in PVDF/MWCNT Fiber mat Sensor for Strain Sensing Application

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ABSTRACT

In this study, to enhance β phase crystalline formation in poly vinylidene fluoride (PVDF) by introducing Multi wall carbon nanotubes (MWCNT) at different preposition for strain sensing. β phase gives higher polarity due to its net dipole moment with increased its electrical conductivity and elastic lying. The MWCNT-PVDF fiber mat was fabricated using the electrospinner. The fabricated materials have been characterized by using X-Ray diffraction (XRD), and Scanning electron microscope (SEM). The prepared fiber mat specimens were embedded in the Glass Fiber Reinforced Polymer (GFRP), and the mechanical test had been conducted by three point bending test and tensile test, its corresponding electrical response were monitored. From these results the enhanced β phase crystalline form will give better electrical conductivity and elastic property to sense the damage more accurate.

Keywords - β phase, Electrospinning, Multi wall carbon nanotubes (MWCNT), Nanosensor, Structural Health Monitoring (SHM)

1. INTRODUCTION

Structures are precious parts of every living and nonliving thing. A minute fault inside a structure may lead to significant loss of property and human beings. According to safety and reliability, it is necessary to monitor the system for the safe operation. Structural Health Monitoring (SHM) technique is a process of implementing damage identification [1]. In the last few decades SHM has developed many approaches in different engineering fields to locate the damages in structures such as crack formation, corrosion, delaminating etc [2].

From the very beginning, the traditional Non Distractive Evolution (NDE) Method contributed to high safety and reliability but the periodic inspection of NDE could not address to the impact of damages and the increase of the system processing time and operating expenses. The Acoustic Sensing Method has long been used to detect and assess the damage through analysis of actively transmitted acoustic signals. This type of sensors is scanned over the structures and provides point by point representation of material properties and damaged locations [3]. The limitation of this method is that the scanning approach is not feasible for continuous and on board monitoring. It also needs more improvement in characterization, miniaturization, rugged and embedding sensors.

Conventional sensors such as thermocouples, strain gauges and accelerometers have also been used for SHM. One major issue for such sensors is that it needs to route large number of wires to provide power and data transmission [4]. Moreover, this is the difficult problem when retrofitting these sensors such as shuttle or aging aircraft fleet. To overcome these disadvantages and the limitations of conventional sensors, the wireless technology and Non-contact sensor system had been developed. Here the sensors are not physically in contact with the structures and the number of sensors is minimized in case of these techniques. Hence the fault zone detection expected is not that much precise and full scale structure sensing is yet to be developed. So the embedding sensor technique has been adopted for SHM and this embedding sensor will increase the sensitive of the sensors, meanwhile the embedded sensor may downgrade the material properties [5]. In order to overcome such drawbacks, N.D Alexopoulous adapted the new technique where Polyvinyl alcohol- multi-wall carbon nanotube (PVA-MWCNT) fiber is embedded in the nonconductive glass fiber material in order to determine the strain through measurement of electrical resistance of the embedded structure and later he sought the electrical response of untreated and pre-stretched PVA- MWCNT fiber [6, 7].

Nanofibers from polymers with piezoelectric effect will make the resultant Nanofibrous devices piezoelectric [8, 9]. According to flexibility and excellent piezoelectric, pyroelectric properties, PVDF (Poly vinylidene fluoride) is one of the interesting materials to make sensors and electronic devices [10]. It exhibits good stability and does not depolarize when subjected to very high alternating electric fields [11]. To produce high electromechanical coupling and large force generating capabilities the piezo electric properties of PVDF has been enhanced.

The electrical properties of PVDF can highly influences the crystalline structure. PVDF can have five possible crystalline phases like α, β, γ, δ, and ε. Among these β phase of PVDF has more attractive type than others. It has trans planar zig-zag arrangements and all its fluorine atoms are located in the same side [12]. Due to its high polarity, β phase has strong piezo electricity than other phases. When enhancing this β phase crystal formation in PVDF structure, the electrical conductivity of the material and elastic lying get increased and it will decrease the Young's modulus of the material [13] which will provide the necessary properties of PVDF for various applications. The addition of MWCNT with PVDF can enhance the β-phase content by acting as a nucleating agent [14, 15], and therefore enhance the piezoelectric property of the materials. In this paper MWCNT has been chosen because they have a better reinforcement property than that of single walled carbon nanotubes. To make sensors with nanofibers, Electrospinning is one of the important techniques to produce the ultrafine fibers [16]. By this method the diameter and the morphology of the fiber can be controlled as well as increase its effectiveness and economic efficiency [17]. In this paper PVDF and MWCNT were used to make a sensor. The enhancement of β phase crystal formation in PVDF/MWCNT fiber mat probably increases the electrical conductivity of the structure, and it will also enhance other properties like dipole moment, structural health and so on. The enhanced electrical conductivity of the PVDF/MWCNT fiber mat will sense the damage with more accuracy and effectiveness. Through this we can develop sensors and other structural health monitoring devices. Finally this prepared fiber mat was embedded with glass fiber reinforced polymer (GFRP). And then tensile and three point bending test was carried out. Based on these result the enhanced crystalline phase was analyzed and the sensing capability, accuracy were further discussed.

2. MATERIAL SELECTION

The PVDF pellets with average molecular weight (Mw) of 1, 80000 were purchased from Sigma Aldrich. The MWCNT which were used in this paper were supplied by Sigma Aldrich. The average fiber diameter is 6nm -8nm having purity ≥99% and length 2.5-20μm which is synthesized by chemical vapor deposition method. The DMSO (Dimethyl sulfoxide) used as a solvent supplied by Sigma Aldrich under the trade name of VETEC® with purity of ≥99% . The acetone as a another component of solvent was purchased from Nice Chemicals Pvt. Ltd under the trade name of Nice®. Epoxy resin-Araldite LY556/hardener HY951 supplied by Huntsman and mixed with the ratio of 100:12. Silicon glass fiber with 0-90^{0} orientation had chosen to prepare the composite plate.

3. MATERIAL MANUFACTURING

3.1 Preparation of PVDF/MWCNT solution

The PVDF/MWCNT composites with different MWCNT concentration were first prepared into films with the thickness of 40 to 80 nm via solution casting method. In this study the MWCNT concentration taken as 0, 0.01, 0.5, and 1 wt% respectively. The PVDF pellets were dissolved by adding 50% of total weight percentage (wt %) of DMSO and 50% of total weight percentage of acetone. This solution was stirred using magnetic stirrer under the controlled temperature of 160^{0} C with 850rpm for 120 mins in the closed bottle in order to avoid evaporation. Simultaneously, MWCNT is mixed with the remaining 50% of total weight percentage of DMSO and acetone with 2 wt% of surfactance (SDS) is added together and sonicated for 45mins at 70^{0} C to disperse the particles. Then the PVDF/MWCNT solutions were mixed together and this mixture was kept again in magnetic stirrer for 24hrs to ensure the substrates dissolve well in the solvents.

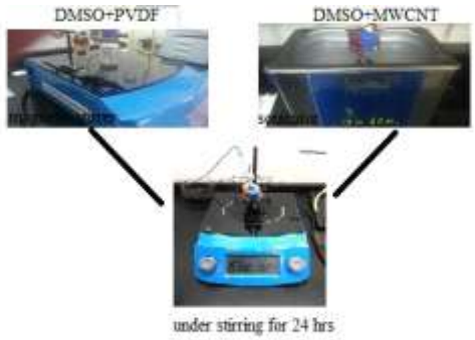

Fig 1. Solution preparation via solution casting method

The mixed solution was completely sealed in a container in order to prevent evaporation effects at room temperature. The same steps were repeated in different trials with different wt% of MWCNT and PVDF. The detailed concentration of MWCNT and PVDF are shown in Table 1.

3.2 Electrospinning process of PVDF/MWCNT

Electrospinning is the effective method to obtain nanofibers also it is less expensive and simpler than the conventional spinning process. In electrospinning process, the PVDF/MWCNT composite solution was filled into the syringe without air bubbles. Polymer can influence the formation of droplet on the tip of the needle and Taylor cone. When high voltage is applied the electrical force and the gravitational force works against the surface tension. The parameters of the process flow rate are 0.5ml/hr. under the temperature of 23^0c and 39% humidity level. The needle tip to the collector drum distances 18cm and the voltage of 21kvolts.The collector drum with the diameter of 25mm covered with aluminum foil in order to avoid improper peeling of fiber mats .After optimization the pump started to push the solution on the collector drum. The spinneret is formed due to the high potential difference between the tip of the needle (+ve charged electrode) and the collector (-ve charged electrode). Finally the fibers from the syringe will be collected in the form of fiber mat .Repeat the same steps for remaining solution of different wt%.

Table 1 Weight % of MWCNT and PVDF for solution preparation

Samples	MWCNT (wt%)	PVDF (wt%)	DMSO (wt%)	Acetone (wt%)	Surfactance (wt %)
Solution 1	0	12.72	41.14	41.14	5
Solution 2	0.1	12.62	41.14	41.14	5
Solution 3	0.5	12.22	41.14	41.14	5
Solution 4	1	11.72	41.14	41.14	5

Fig2.Fiber mats which is collected from electrospinning unit

3.3 Characterization

Surface morphology and MWCNT dispersion were investigated by scanning electron microscopy (SEM). Surface and cross section images were taken for analyze the surface morphology. Before SEM observation, the samples were merged into liquid nitrogen for 20 min and sputtered with a thin layer of gold. The phase behaviors and crystallization of PVDF/MWCNT films was examined by using X-ray diffraction (XRD) techniques. These experiments were performed at room temperature with Cu target Ka radiation using a Discover2000 X-ray Diffractometer system in IIT Madras. The wave length of the X-ray was 0.154059nm. All XRD data were collected from 2θ=0-90° with a step interval of 0.02.

3.4 Embedding fiber mat in GFRP

The collected fiber mat was embedded with GFRP (glass fiber reinforced polymer) by using vacuum resin transfer method (VRTM). To embed fiber mat in glass fiber has been cut into 10 plies at the dimensions of 300* 300 mm.10 plies of fabric, oriented at 0/90.

During the lay-up, the first 9 plies were laid and the wrap faces were alternated upwards and downwards and resulting in a cross-ply balanced and symmetric laminate. The PVDF–MWCNT fiber mats were placed between the ninth and the last ply of the glass fiber.In total nine PVDF–MWCNT fiber mats were used to manufacture composite plate; this permitted the manufacturing of nine testing specimens with one embedded fiber mat per specimen. And then the manufactured composite plate with PVDF/MWCNT fiber mat was cut according to ASTM D3039 specifications and edges were polished. The dimensions of the testing specimens were length*width = 150mm *25 mm. silver paste were covered at the two marks of each specimen. The two cable connectors had been added again with silver paste and the millimeter is attached at the end of the cable to measure the resistance.

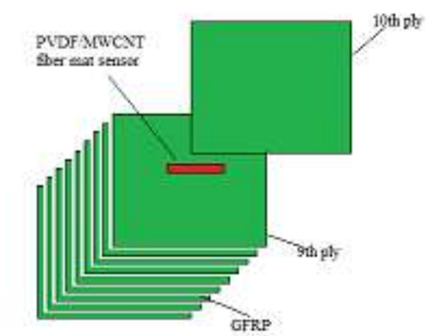

Fig 3. Embedding fiber mat in GFRP

4. EXPERIMENTAL PROCEDURE

4.1 Tensile tests

Mechanical test for the specimens were conducted in order to determine its tensile behavior. The two different approaches were examined;(i)Monotonic tensile test till the specimen fracture. (ii)Incremental-decremental tensile testing till the specimen fracture. These entire tests were performed in 100KN Instron servo hydraulic testing machine at IIT madras.

(i) Monotonic tensile test

Monotonic tensile test were performed to 9 specimen and its modules of elasticity (E) and tensile strength (Rm), elongation to fracture (A) were found and shown in the Table 2.

(ii) Incremental tensile loading and unloading

To seek the fibers response, different quasi static incremental loading and unloading steps had been made to different specimen embedded with PVDF/MWCNT fiber mat. Incremental loading steps had been conducted to specific levels of tensile fracture stress of the material and the testing machine was controlled by load. For incremental unloading the specimen had been made to zero loading state of machine.

Table 2. Monotonic test results

Sample	E (GPa)	Rm (MPa)	A (%)
PVDF/0wt% MWCNT	20.482	489	2.32
PVDF/0.1%MWCNT	21.823	492	2.34
PVDF/0.5wt% MWCNT	22.761	496	2.45
PVDF/1wt% MWCNT	23.456	499	2.62

4.2 Three point bending test

The embedded MWCNT fiber mat specimens were carried out for three point bending test under two different cases. For the first case, the fiber was placed in the bottom of the specimen to develop the tensile stress. While in the second case, the fiber was placed at the top of the specimen to develop the compressive stress over the fiber's region. The nominal stress of the fiber σ_{fib} has been calculated by the equation:

$$\sigma_{fib} = (M_b/Iz) * y_{fib}$$

Where M_b is the maximum bending moment at the specimen, Iz is the moment inertia and y_{fib} the distance of the MWCNT fiber from the middle thickness of the specimen.

5. RESULT AND DISCUSSION

5.1 Morphological analysis and phase behaviors

(i) SEM image

The SEM images show the typical surface morphology of PVDF- MWCNT fiber mat which is obtained by electrospinning. This SEM images revealed that fibers were of long and uniform shaped. The MWCNTs are uniformly dispersed in the whole PVDF matrix due to the surface modification and solution blending. The synthesized PVDF-MWCNT fibers had a diameter of 50 µm indicating their micro dimensions. The fiber mat possesses a smooth, continuous and interconnected structure that increases the electron-conductivity.

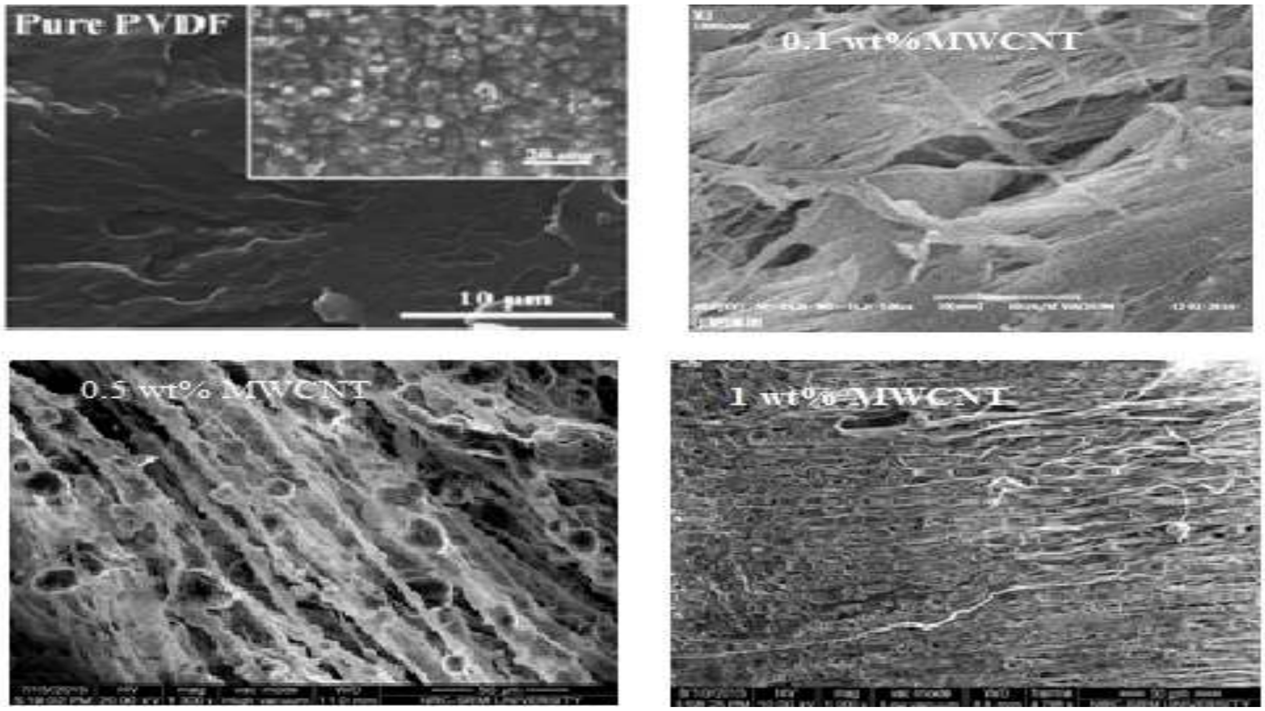

Fig. 4 SEM images of PVDF/MWCNT with different concentration of MWCNT

(ii) XRD graph

The crystalline structures of PVDF/MWCNT fiber films are characterized by XRD spectrum. In fig 5 the XRD patterns reveals that β phase crystal formation was increased in 1 wt% of MWCNT also it shows the characteristic peak around 2Θ=19.12° where the β phase (001) formation occurred.

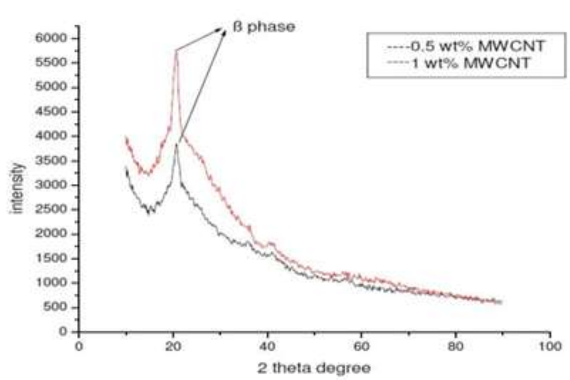

Fig 5. XRD diffractions of PVDF/MWCNT fiber mats

5.2 Tensile tests

(i) Monotonic tensile test

While monotonic tensile test, the modulus of elasticity E and tensile strength Rm, elongation of fracture ʌ as well as strain energy density W were tabulated in Table 2 and plotted in Fig. 6. Fig. 6 shows the graph between modulus of elasticity and the wt% of MWCNT. This graph clearly shows, When the weight % of MWCNT increased in the specimen its modulus of elasticity were increased. The 1 wt% of MWCNT specimen given the max % of E which is 23.456 Gpa.

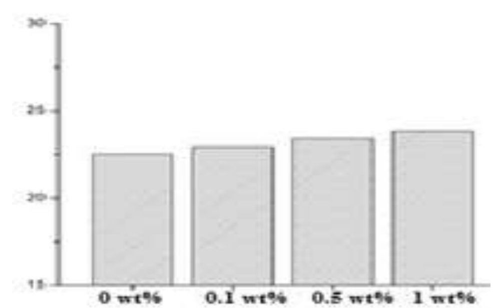

*Fig 6. Monotonic tensile te*st graph

(ii)Incremental tensile loading and unloading

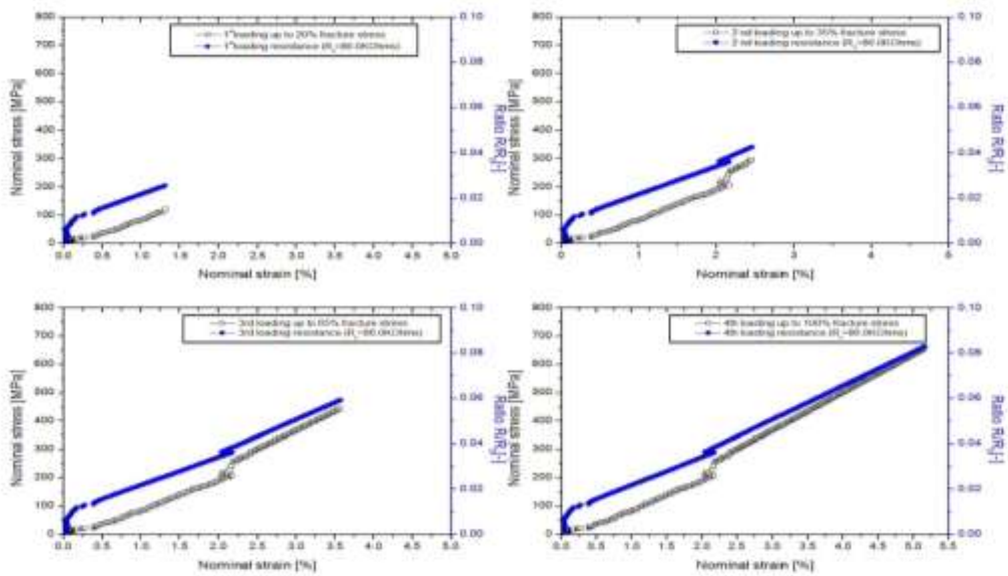

Fig 7. Graph of Incremental tensile loading and unloading tests for PVDF/MWCNT fiber mat

The Incremental tensile loading and unloading test were conducted to with and without embedding of PVDF/MWCNT specimens. Typical axial nominal stress-strain diagram for the four incremental loading – unloading steps shown in fig 7. As the test were load controlled after the unloading the specimen which returns to zero loading condition. Incremental tensile loading steps of addition of 200MPa each, introduce the damage to the specimen that can be noticed as residual strain measurement after every unloading. Depending on the magnitude of the peak load value, a different type of damage has created in the specimen (ie) deboning matrix and matrix cracking. Meanwhile the change in resistance between the conductive cable the value did not return to zero, the residual resistance measurement value is 4% higher after the 4th loading condition.

5.3 Three point bending test

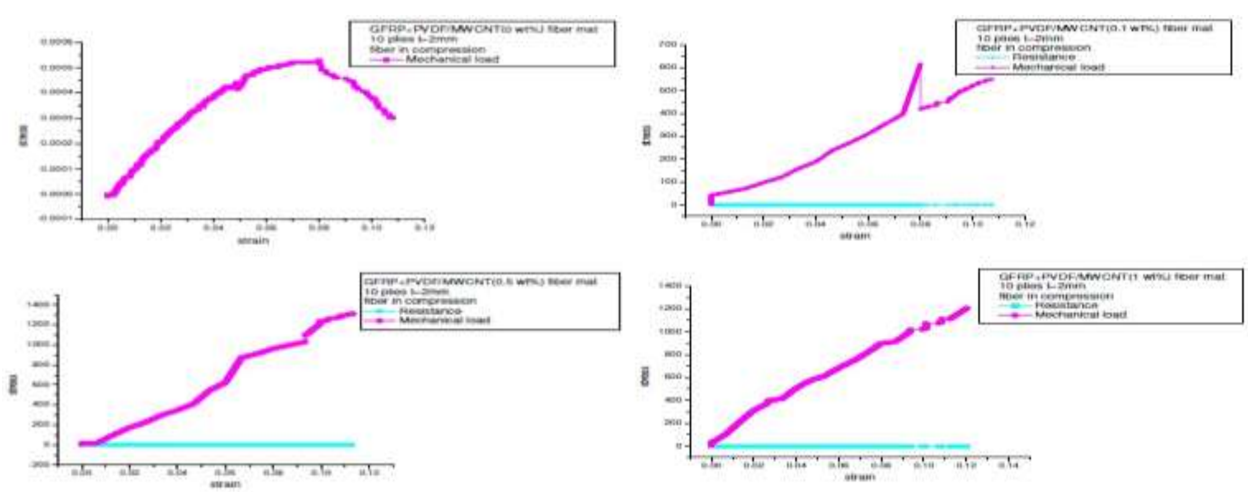

Fig 8. Typical three-point bending mechanical and electrical resistance results of the GFRP material with embedded CNT fiber in the compressive region

The specimens embedded with PVDF/MWCNT fiber mat were tested in three point bending test under compression. Fig 8 is the graphical representation of strain-stress relationship according to electrical response of the fiber mat when under mechanical loading. The results of the mechanical stress–strain as well as the $\Delta R/R_o$ measurements for the monotonic loading up to fracture can be seen in Fig 8. It is clear that during the continuously increasing mechanical load of the specimen’s region with the PVDF/MWCN T fiber, the readings of the electrical response (resistance) of the fiber is decrease. Initially the change in resistance value of all graphs is zero. It seems there is no resistance between the two spots of PVDF/MWCNT fiber mat which is embedded in GFRP. So the conductivity of the fiber mat is high Also conductance of PVDF/MWCNT fiber mat getting increased when the MWCNT wt% is increased in PVDF.

6. CONCLUSION

The following conclusions were obtained:

- When increasing MWCNT wt% in PVDF/MWCNT solution, its certainly increases the β phase crystalline formation and modulus of elasticity in the resultant fiber.
- Through electrospinning process the structural morphology of the fiber and the cell dimensions is modifiable.
- Increasing β phase crystal formation in PVDF/MWCNT fiber mat will increase the electrical conductivity of the PVDF/MWCNT fiber mat. Increased electron-conductivity reduces the resistance of the fiber mat, decreased electron-conductivity change in resistance value turn to more accurate sensing capability.

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