



FLEXIBLE PIEZOELECTRIC DEVICE ON PVDF/CNT  
FOR WIND TURBINE GENERATOR

By  
APHISAK KAEOPISAN

A Thesis Submitted in Partial Fulfillment of the Requirements for  
Degree of Doctor of Philosophy in Physics Program  
At Sakon Nakhon Rajabhat University  
November 2020  
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Aphisak Kaeopisan

ชื่อเรื่อง	การประดิษฐ์พีโซอิเล็กทริกชนิดโค้งงอจากวัสดุโพลีไวนิลลิดีนฟูออไรด์ สำหรับผลิตไฟฟ้าจากกังหันลม
ผู้วิจัย	อภิศักดิ์ แก้วไพศาล
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### บทคัดย่อ

พีโซอิเล็กทริกเป็นวัสดุที่สามารถเปลี่ยนพลังงานกลเป็นพลังงานไฟฟ้าและสามารถเปลี่ยน พลังงานไฟฟ้าเป็นพลังงานกล เป็นอุปกรณ์ที่ประดิษฐ์จากวัสดุพีโซอิเล็กทริก วัสดุอาจอยู่ใน รูปแบบของธาตุหรือวัสดุผสมโดยทั่วไปแล้วนั้นเป็นวัสดุชนิดหนึ่งเป็นตัวหลักและอีกชนิดหนึ่งเป็นวัสดุ ที่กระจายตัวในอีกชนิดหนึ่ง โดยใช้ผงโพลีไวนิลลิดีนฟูออไรด์ (PVDF,  $(C_2H_2F_2)_x$ ), PVDF 1% โดย น้ำหนักเติมผสมในสารละลายแบ่งเป็นทั้งหมด 6 ตัวอย่าง และถูกเติมด้วยผง ท่อคาร์บอนนาโนทิวบ์ (CNT) 0.001g 0.002g 0.003g 0.004g และ 0.005g ในสารละลาย N-Methyl-2-pyrrolidone [NMP ( $C_5H_9NO$ )] 20 mL. นำสารละลายเหลวหล่อเทปที่อุณหภูมิ 80 °C จากนั้นขึ้นรูปและรีดขึ้นรูป ให้หนา 200  $\mu\text{m}$  ฟิล์มได้รับการตรวจสอบโครงสร้างสารด้วยเครื่อง XRD, SEM, EDX, FTIR, UV-VIS, เพื่อเตรียมการทำขั้วไฟฟ้าด้วยกาวสีเงิน ดำเนินการจัดเรียงผลึกโพลด้วยสนามไฟฟ้า 1.5 kV /200 $\mu\text{m}$  วัดค่าสัมประสิทธิ์ไดอิเล็กทริก  $d_{33}$  -2.90 ถึง 9.77 pC / N สูงสุดของอุปกรณ์พีโซอิเล็กทริกเติม คาร์บอนนาโนทิวบ์ 3wt% ใน 6 ตัวอย่าง ค่าทางไฟฟ้าสูงสุดที่วัดได้ ความต่างศักย์ 21.2 V, กระแสไฟฟ้าที่ 0.3  $\mu\text{A}$ , กำลังไฟฟ้าสูงสุด 230  $\mu\text{W}$ , ความจุไฟฟ้า 0.1 $\mu\text{F}$  ตามลำดับ ผลจากการ ประยุกต์ใช้อุปกรณ์พีโซอิเล็กทริกกับกังหันลมแกนตั้ง 6 แกนใบพัด วัดความต่างศักย์ไฟฟ้าที่ 3V ที่ช่วงความถี่ 1-15Hz

**คำสำคัญ:** โพลีไวนิลลิดีนฟูออไรด์ คาร์บอนนาโนทิวบ์ เพอร์โรอิเล็กทริก ไดอิเล็กทริก โพลีเมอร์คอมโพสิต

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### ABSTRACT

Piezoelectric is a material that can convert mechanical energy into electrical energy. The composite material was polyvinylidene fluoride,  $(C_2H_2F_2)_x$ , (PVDF) power with 1g by weight. 6 samples of PVDF were doped with carbon-nanotube (CNT) powder with 0.000, 0.001 g, 0.002 g, 0.003 g, 0.004 g, and 0.005g. Each simple was added with N-Methy l-2-pyrrolidone,  $C_5H_9NO$ , (NMP) solution with 20 mL then rolled and casting tape at 80°C. Thin films are 200  $\mu\text{m}$  in thickness. XRD is applied for studying the structure. Thin films were prepared to make pole with silver glue then conducted to arrange the electrodes with 1.5 kV. The dielectric coefficients were -2.90 to 9.77 pC/N. The highest dielectric coefficients were found at thin films of 0.003 g. Thin film modules give maximum power at 230  $\mu\text{W}$  and maximum current at 0.3 $\mu\text{A}$ . The module was applied with wind turbine 6 axis propeller, connecting with the capacitance of 0.1  $\mu\text{F}$  and the potential difference at 2.9 V. The efficiency of piezoelectric module has 3 V at 1-15 Hz.

**Keywords:** poly (vinylidene fluoride), carbon nanotubes, ferroelectric, dielectric constant, polymer composite.

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# CHAPTER 1

## INTRODUCTION

### RATIONALE AND MOTIVATION

#### Background and importance of the problem

Nowadays, energy shortage is considered an essential problem in the world. For this reason, the mechanical energy driven from the surrounding environment is an attractive alternative energy source. From significant mechanical energy sources found in nature, such as waterfalls, wind, and waves, too small energy sources such as energy obtained from mechanical vibrations in the engine building. Electrical appliances, air pressure as well as human movements. Which the device can generate power by itself by this little vibration It is another impressive technology. The material that can convert mechanical energy into electrical energy is called Piezoelectric materials. When waves or mechanical energy are generated on the material crystals, an electric current will flow in the contentor even in reverse When supplying electricity. The material can stretch or shrink at the nanometer level. At present, the science and technology of contents showing the Piezoelectric properties have advanced considerably by having research and development for various applications Continuously. For example, in sensors, actuators, and transducers, there is a piezoelectric. The main component, such as lead zirconium titanate (PZT) and barium titanate (BT), since these substances have outstanding electrical properties. Restrictions on flexibility in use There is a limit to use. From the said limitation, this research needs to invent the Modulus Piezoelectric Flexible, But still, the property of Piezoelectric By studying in the form of composite materials, this material is called Pyroelectrical composite (Piezoelectric composite) consisting of polymer Piezoelectric materials. Which is flexible and robust [3,4,5,6] because it combines the physical properties of nano and polymer materials One of the fundamental problems for small-scale applications is the design and selection of materials structures that are effective in converting mechanical energy into electrical energy. In this research, the composite piezoelectric composite was prepared by adding carbon nanotubes

(CNT) to the polyvinylidene fluoride (PVDF) and using the materials. Composite Piezoelectric was used to fabricate wind turbines from PVDF-CNT pistons. [12]

## DISSERTATION OBJECTIVES

1. To fabricate bent-shaped dielectric modules from polyvinylidene fluoride (PVDF) mixed with carbon nanotubes (CNT).
2. To study the microstructure and the electrical properties of the modulo-dielectric (PVDF/CNT).
3. To fabricate wind turbines from PVDF/CNTs modules.

## ANTICIPATED OUTCOMES OF THE DISSERTATION

1. Prepare composite polyvinylidene fluoride composite with carbon nanotubes using a tape casting technique. Film thickness in the ratio as follows.
  - FVDF/CNTs/NMP: 1/0.001/20g
  - FVDF/CNTs/NMP: 1/0.002/20g
  - FVDF/CNTs/NMP: 1/0.003/20g
  - FVDF/CNTs/NMP: 1/0.004/20g
  - FVDF/CNTs/NMP: 1/0.005/20g
  - FVDF/NMP: 1/20g
2. Examine the microstructure Physical and electrical properties of PVDF/CNT composite materials.
3. Use PVDF with the best piezoelectric properties to fabricate the piezoelectric modules.
4. Location of Alternative Energy Center of Sakon Nakhon Rajabhat University Nakhon Phanom University, duration eight months.
5. Build a horizontal axis wind turbine small size, low speed.
6. PVDF/MCNTs type PVDF/CNTs are installed on small wind turbines, wind speeds of 5-30 km h<sup>-1</sup>.

## DISSERTATION STRUCTURE

1. Composite polyvinylidene fluoride composite material can be prepared using nanotubes with thick film tape casting techniques.

2. The obtained polyvinylidene fluoride carbon-doped carbon nanotubes obtained by PVDF/CNT thick film casting techniques.
3. Obtain a low-speed wind turbine that uses piezoelectric.
4. Obtain guidelines for applying wind energy to convert to electrical power using piezoelectricity.
5. Obtain a low-speed wind turbine generator from the Piezoelectric PVDF/CNT module.
6. Publication of international academic works.



## CHAPTER 2

### LITERATURE REVIEWS

This chapter represents seven topics including, piezoelectric effect, the piezoelectric direction Polarization, PVDF piezoelectric, Polarization, Carbon nanotube, Properties of MWCNTs, Related research.

#### PIEZOELECTRIC EFFECT

##### Theory and research related

##### 1. Piezoelectric materials

There are both found in nature and from synthesis. The materials found in nature are mineral quartz, mineral quartz, tourmaline. Synthetic materials such as barium titanate, lead titanate, lead zirconated titanate (PZT) and polyvinylidene fluoride, etc. The Piezoelectricity of the substance can be divided into two characteristics, which are direct effect and reverse effect.

##### 2. Ferroelectric materials

phenomenon is a phenomenon of crystals that can polarize by themselves. Where there is no induction from the external electric field, this polarization can be switched in the direction of the external electric field provided. When appropriate external electric fields are provided.

3. This ferroelectric phenomenon was discovered by J. Valasek in 1921. It is found in the single crystal of Rochelle salt. In general, crystals can be divided into 32 groups according to Symmetry, And this number can be divided into crystals that are symmetrical through the center (11 groups of centrosymmetry), and 21 non-symmetric symmetry, in which this group can display 20 piezoelectric properties and only ten groups in this group can display the properties The Ferro Electric.

4. The direct effect is the property of a substance that can create electric charges to the surface when pressure is applied to the substance, as in Figure 1.

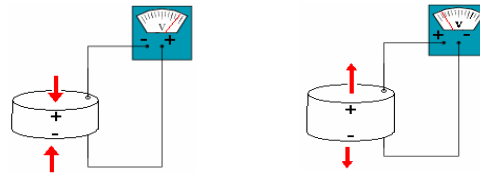


Figure 1 Direct Peculiar Properties.

Where the  $P$  symbol represents the vector of the electrode in the substance (Polarization) will say.

$$D = Q / A = dT \quad (1)$$

When  $T$  is the force acting on the cross-section (Stress) ( $\text{Nm}^{-2}$ )  
 $D$  Is the charge density on the surface of the dielectric (Dielectric displacement)

$Q$  Is the electric charge (Coulombs: C)

$d$  Is the Piezoelectric constant of the substance ( $\text{CN}^{-1}$ )

$A$  Is the cross-sectional area of the substance ( $\text{m}^2$ )

5. Indirect Piezoelectrical Properties (Reverse Effect) Indirect Piezoelectric Is the property of substances that can stretch or contract when under electric fields show as Figure 2.

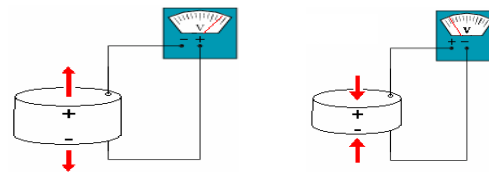


Figure 2 Indirect Piezoelectric Properties (Reverse effect).

Can write the equation as follows.

$$S = dE = \Delta L/L_0 \quad (2)$$

In which symbols  $d$  can be used to represent both direct and indirect piezoelectric constants. Because it is the ratio of energy transformation from equations 1 and 2, when considering the properties of elastic and dielectric values of the substance can be written as an equation The dielectric is as follows  
 $D = dT + \epsilon^T E$  (direct phenomenon) (1)  $S = s^E T + dE$  (indirect phenomenon)  
 $S = dE$

$$D = dT + \epsilon^T E \quad (3)$$

$$E = S^E T + dE \quad (4)$$

Where  $D$  is the charge density on the dielectric surface.

$E$  is the electric field ( $N C^{-1}$ ).

$T$  is the force acting on cross-sectional area (stress  $Nm^{-2}$ ).

$d$  is Piezoelectric constant ( $C N^{-1}$ ).

$\epsilon^T$  is the dielectric constant with the superscript symbol  
 Instead of the constant pressure.

$S^T$  is the coefficient of elasticity of the substance  
 (Elastic coefficient) by the superscript symbol For the  
 condition of a constant electric field.

## THE PIEZOELECTRIC DIRECTION OF POLARIZATION

The piezoelectric effect involves the interaction between the electrical and mechanical behaviors of a material. The material constants below describe that interaction. The direction of polarization is generally designated as the z-axis of an orthogonal crystallographic system. Material characteristics depend on the direction of the applied electric field, displacement, stress, and strain. Superscripts and subscripts are used to indicate direction.

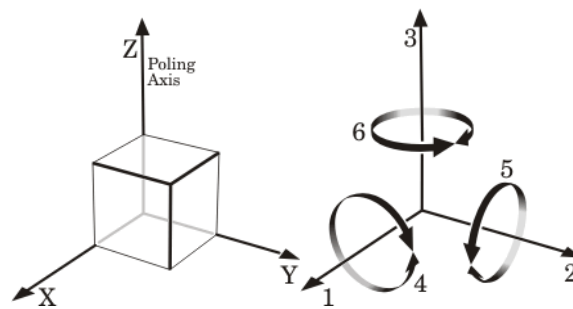


Figure 3 The axes x,y, and z are respectively represented as 1, 2, and 3 irections, and the shear about these axes are represented as 4, 5, and 6. Planar modes are expressed with a subscript p.

## PVDF PIEZOELECTRIC

Polyvinylidene fluoride or polyvinylidene difluoride (PVDF)[1] is a highly non-reactive thermoplastic fluoropolymer produced by the polymerization of vinylidene difluoride. PVDF has four crystalline phases  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  depending on the chain conformation. Among them  $\alpha$  is thermodynamically most stable and non-polar in nature.  $\beta$  and  $\gamma$  are polar phases. Non-polar PVDF is used as an insulator and painting. Polar PVDF is used in energy harvesting, sensor, actuator, electronics e.t.c. PVDF has several properties like biocompatible, chemical resistance, good film-forming capability, cost-effectiveness e.t.c. Among four crystalline phase  $\beta$  is of great importance due to its spontaneous polarization and piezoelectric sensitivity. Because of this property, tremendous effort has been paid to induce the electroactive  $\beta$  phase in PVDF. Several methods are there to induce  $\beta$  phase in PVDF. It can be achieved by placing it into a high electric field, which randomly orients  $\text{CH}_2/\text{CF}_2$  dipoles along with the electrical field direction. Different types of doping (like metal nanoparticle, hydrated salt for avoiding poling step) also done for achieving the electroactive phase. The dielectric constant of PVDF is also high about 12, which makes it suitable to integrate with the device for getting the signal to noise ratio less. It has a glass transition temperature of  $-35^\circ\text{C}$ , which is much less than room temperature. So it is much flexible at room temperature. Nowadays, PVDF is largely used in nanogenerator applications due to its piezoelectricity. PVDF is non-toxic, flexible, easy to process make it suitable in nanogenerator applications. PVDF or polyvinylidene fluoride is a polymer material that shows piezoelectricity when pressure or mechanical

force applied to it. The material which shows piezoelectricity is called piezoelectric material. The piezoelectric material can be of crystals, ceramics, or polymer. Piezoelectric crystals are like quartz, berlinite, gallium orthophosphate, and tourmaline. Piezoelectric ceramics are like barium titanate, lead zirconate titanate, barium zirconate titanate. Some polymer (PVDF, PVDF - TrFE) also shows the piezoelectric effect. Based on these properties, a new type of technology arises today. This is called a nanogenerator. A nanogenerator is a type of device which generates voltage or power when a mechanical force or vibration applied to it. Among all piezoelectric material, polymer-like PVDF is most suitable because it is non-toxic, flexible, biocompatible, high piezoelectric voltage constant. As already told, PVDF exists in several forms:  $\alpha$  (TG<sup>+</sup>TG<sup>-</sup>),  $\beta$  (TTTT),  $\gamma$  (TTTGTTTG<sup>-</sup>), and  $\delta$  phases, depending on the chain conformations as trans (T) or gauche (G) linkages. Among them,  $\alpha$  does not show piezoelectric properties.  $\beta$ ,  $\gamma$ , and  $\delta$  phase shows piezoelectric properties. Generally, PVDF is present in the non-polar ( $\alpha$ ) phase. To make PVDF polar, several approaches are there like stretching, metal nanoparticle doping, hydrated salt doing, electrospinning process, e.t.c. Among all polar phases,  $\beta$  phase is most important due to its high remnant polarization and highest dipolar moment per unit cell ( $8 \times 10^{-30} \text{ cm}^2$ ) when compared to the other two phases. FTIR, bands, and X-ray diffraction peaks typically used for the identification of the phases. Many researchers are paying attention to nanogenerators (NGs) as an energy source in a self-powered micro-nano system. Nowadays, devices are gradually decreasing in size, and they need small power. In that case, a nanogenerator is useful as it generates a voltage in the range of micro and nano order. It is also used in small battery charging, wireless power transmission, LED light glow e.t.c.

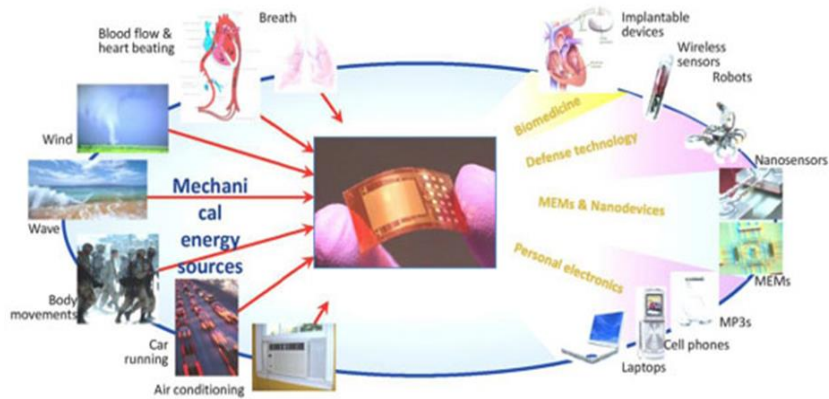


Figure 4 A different application of nanogenerator[1].

Polyvinylidene fluoride or polyvinylidene difluoride (PVDF) is a highly non-reactive thermoplastic fluoropolymer produced by the polymerization of vinylidene difluoride. As already told, it has four crystalline phases depending on the chain conformation structure. When poled, PVDF is a ferroelectric polymer, exhibiting efficient piezoelectric and pyroelectric properties. These characteristics make it useful in sensor and battery applications. PVDF has a glass transition temperature ( $T_g$ ) of about  $-35\text{ }^\circ\text{C}$  and is typically 50–60% crystalline. Unlike other popular piezoelectric materials, such as PZT (lead zirconate titanate), PVDF has a negative  $d_{33}$  value. Physically, this means that PVDF will compress instead of expanding or vice versa when exposed to the same electric field. PVDF is a specialty plastic used in applications requiring the highest purity, as well as resistance to solvents, acids, and bases. Compared to other fluoropolymers, like polytetrafluoroethylene (Teflon), PVDF has a low density ( $1.78\text{ g/cm}^3$ ). It is available as piping products, sheets, tubing, films, plate, and an insulator for premium wire. It can be injected, molded or welded and is commonly used in the chemical, semiconductor, medical and defense industries, as well as in lithium-ion batteries. It is also available as a crosslinked closed-cell foam, used increasingly in aviation and aerospace applications.

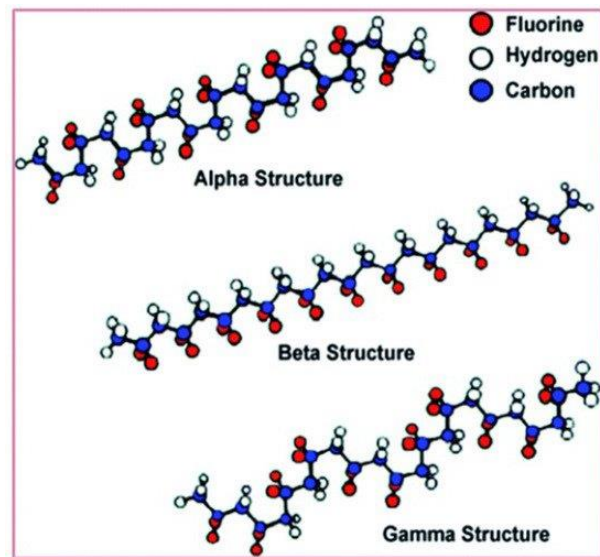


Figure 5 The three primary polymorphic crystalline phases of PVDF[2].

Piezoelectricity is the ability of certain material to generate an electrical voltage when a mechanical force or pressure applied to it. Material, which shows this kind of behavior is called piezoelectric material. PVDF is also a piezoelectric polymer material. As already mentioned,  $\alpha$  phase of PVDF is non-polar, so it does not show the piezoelectric effect.  $\beta$  and  $\gamma$  phase is responsible for generating piezoelectricity in it. Normally the charges of piezoelectric crystals are balanced even they are not symmetrically arranged. The effects of charges exactly cancel out, leaving no net charges in it. When pressure or mechanical force applied to it, the charges are become out of balance. This effect of charges does not cancel each other, so net charges appear on both sides of crystals. In such a way, a voltage can be generated in it by simply pressing it. Now the piezoelectricity generation depends on the electroactive phase and crystallinity of PVDF material. Usually, PVDF material is not piezoelectric because it is in the non-polar phase. It is produced in large thin clear sheets, which are then stretched and poled to give it the piezoelectric properties. Materials that have crystalline lattice structure that is a three-dimensional geometric arrangement of atoms in a molecule which repeats itself from molecule to molecule (unit cell). Piezoceramics are solid mixtures of minute piezo crystallites. Dipoles are initially randomly oriented. Responses of these dipoles to the externally applied electric field would tend to cancel one another, producing no gross change in the dimensions of the piezoceramics. They do not have piezoelectric behavior at the macro level. In order to obtain a useful macroscopic piezoelectric response,

dipoles must be permanently aligned with one another. A process called poling is used for this purpose. A piezoelectric material has a characteristic Curie temperature. When heated above this temperature, dipoles can change orientation in the solid phase of the material. In the polling process, the material is heated above its Curie temperature, and a strong electric field is applied. The direction of the electric field is the polarization direction, and the dipoles shift into alignment with it. Keeping the electric field constant, the material is cooled below its Curie temperature, with the results that the alignment of dipoles is permanently fixed. In this case, material is said to be poled.

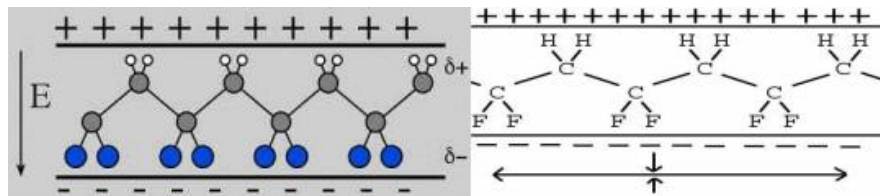


Figure 6 The electric field is in the opposite direction of the poled direction, and the sheet is stretched length[2].

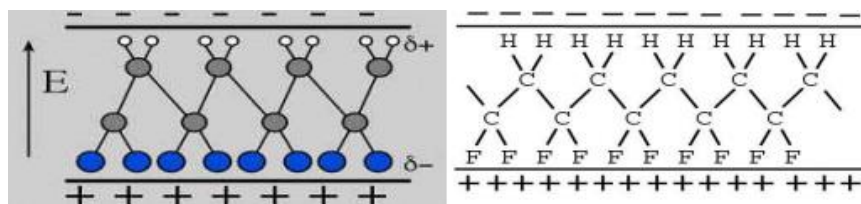


Figure 7 The electric field is in the same direction of the poled direction, and the sheet is contracted in length[2].

A Nanogenerator is a type of technology that converts mechanical/thermal energy as produced by small-scale physical change into electricity. It has three typical approaches: piezoelectric, triboelectric, and pyroelectric nanogenerators. Both the piezoelectric and triboelectric nanogenerators can convert mechanical energy into electricity. However, pyroelectric nanogenerators can be used to harvest thermal energy from time-dependent temperature fluctuation. Different materials like zinc oxide nanowire, lead zirconate titanate, barium titanate nanowire, PVDF e.t.c. are used for nanogenerator preparation. Nanogenerator is expected to be applied for various applications where the periodic kinetic energy exists, such as wind and ocean waves, on a large scale to the muscle movement by the beat of a heart or inhalation of the lung in a small scale. It is generally



used in Self-powered nano/microdevices, Smart Wearable Systems, Transparent and Flexible Devices, Implantable Telemetric Energy Receiver, e.t.c.

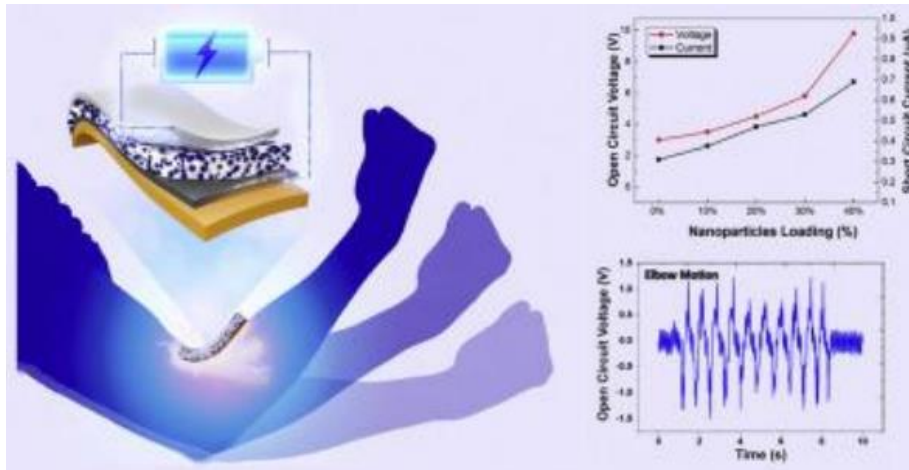


Figure 8 Nanogenerator gives output current from hand movement[3].

of PVDF. Due to specific chain conformation in the crystal unit cell and providing the highest remnant polarization,  $\beta$  phase has attracted more attention than the others ( $\gamma$  and  $\delta$ ). A variety of methods have been developed to obtain such electroactive  $\beta$ -phase. The beta phase can be generated directly from the electrospinning process. It generates fiber-like structure and for nanogenerator preparation anode and cathode is placed on both side of.

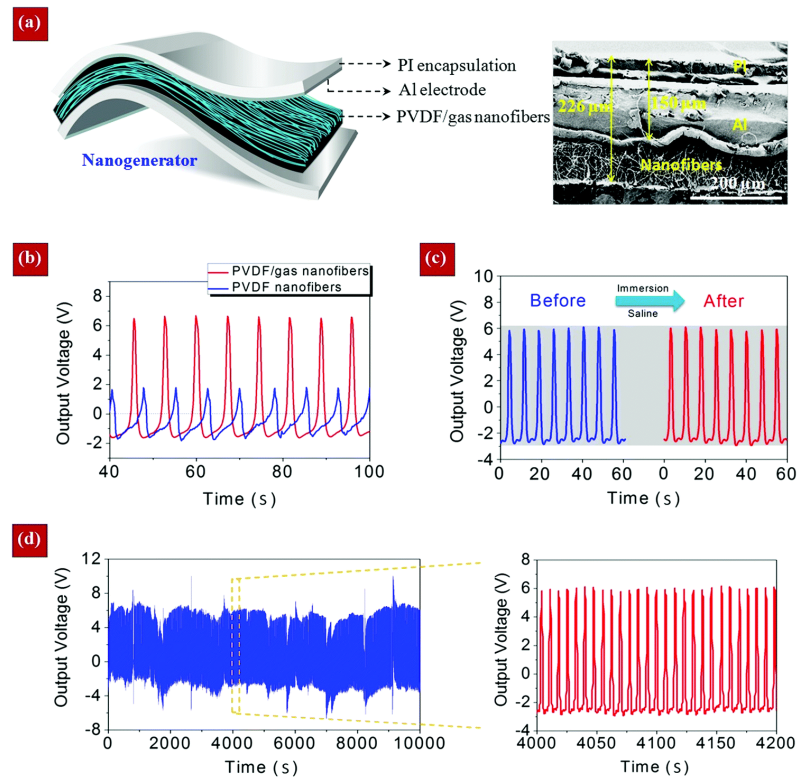


Figure 9 Pure OPM nanofibers with high piezoelectricity designed for energy harvesting in vitro and in vivo[4].

The output voltage can be generated from this nanogenerator by applying mechanical force or vibration on it. It can be placed in our human body, and it generates voltage from human body motion due to its flexibility. Due to its biocompatible nature, it can be placed inside our human body, and from inside human body motion, it generates a voltage. PVDF based nanogenerator is used in different applications like LED light glow, capacitor charging, wireless transmission.

PVDF generated a voltage when pressure or mechanical force applied to it. The reverse process is also true. That is when a voltage is applied, it will vibrate. The first property is applied in sensor application, and the reverse process is applied in the actuator. For its biocompatible property, it is used in biomedical sciences, like immunoblotting, as an artificial membrane. PVDF membrane is also used in filtering devices. Piezoelectricity output depends on the percentage of the electroactive phase in it. More electroactive phase generates more output voltage. Different materials are used to be doped with PVDF for getting more.

## piezoelectric voltage

Piezoelectric materials can be used in a variety of electronic devices, depending on the change of phenomena. If the pressure is fed to the material causing deformation or mechanical force occurs, it can be used as a transducer in ultrasonic medical devices, microphones, and actuators, which are important components of the printer shutter. In-camera Hydraulic valve (Hydraulic valve), etc., and in the case of the force of the material causing the electric force can be used as a gas igniter in stoves, heaters used as a generator, as a pressure sensor, etc.

2.6 Spontaneous Polarization from the crystallization, 20 crystals are showing the piezoelectric properties, but only ten groups of crystals can polarize by themselves. Among the 20 symmetrical groups showing the piezoelectric phenomenon, the crystals of this symmetry group have a single axis of rotation, but there is no reflection plane perpendicular to this axis. Along this axis of rotation, the atomic arrangement at one end is different from the other (opposite end). This crystal is called the polar crystal, which shows the spontaneous polarization.

## POLARIZATION

The polarization is the value of the dipole moment per volume unit or the value of a charge per unit area on the surface perpendicular to the polarization axis. In most cases, the polarization axis is usually in line with the crystal core, although the crystal with the polar axis shows the piezoelectric phenomenon. But does not require the vector of polarization. Since the result of the electric moment along all the polar axis may be equal to zero. Therefore, only crystals with a single polar core show their polarization vector (PS). In general, this polarization cannot be measured directly from the charge on the crystal surface. Because this charge is compensated by internal or external conductors that carry electric current or by the charge on the joint of the twin crystals (Twins), the crystals are showing their polarization consist of positive and negative ions. At some point, the temperature of this ion is at a balanced position with the lowest free energy of the crystals, and the center of the positive charge is not limited by the center of the negative charge. Shows the crystal structure of Barium titanate, above the Curie temperature of 120°C. The original crystal structure is a cubic containing  $Ba^{2+}$  ions are at the corner of the cube.  $O^{2-}$  ions are

at the center of the face, and  $Ti_4 +$  ions are at the center of the cube. And at lower temperatures, curie the structure will be slightly deformed with the substitution of  $Ba_2 +$  and  $Ti_4 +$  ions in relation to  $O_2-$  ions by polarization, each pair of positive and negative ions may be seen as electric dipole and polarization. (Momentary polarity per unit volume) is caused by this group of polar pairs. (Pointed in the same direction) The change in polarization, when there is a change in temperature, is called the pyroelectric phenomenon. (Pyroelectric effect), in which the pyroelectric effect was discovered in the Tourmaline by Theophrastus (314 BC) and named by Brewster in 1824. Thermodynamic theory. The first Thermodynamic theory was presented by Thompson (later Lord Kelvin) in 1878 and developed by Voigt in 1897. Quantum theory in terms of Crystal lattice dynamics and quantum mechanics was developed by Born in 1945. The pyroelectric phenomenon (Pyroelectric effect).

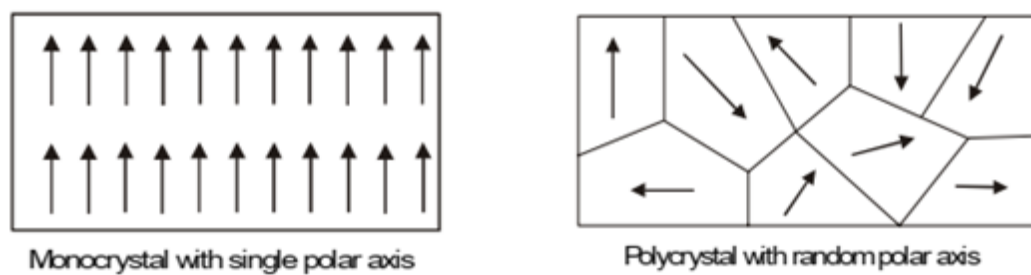


Figure 10 The pyroelectric phenomenon (Pyroelectric effect) Polarization from external electric field of piezoelectric materials[5].

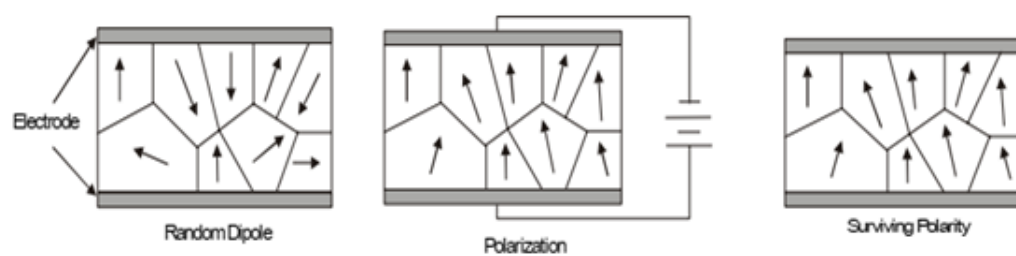


Figure 11 Polarization caused by an external electric field[5].

Polyvinylidene difluoride (Polyvinylidene difluoride; PVDF) [5]

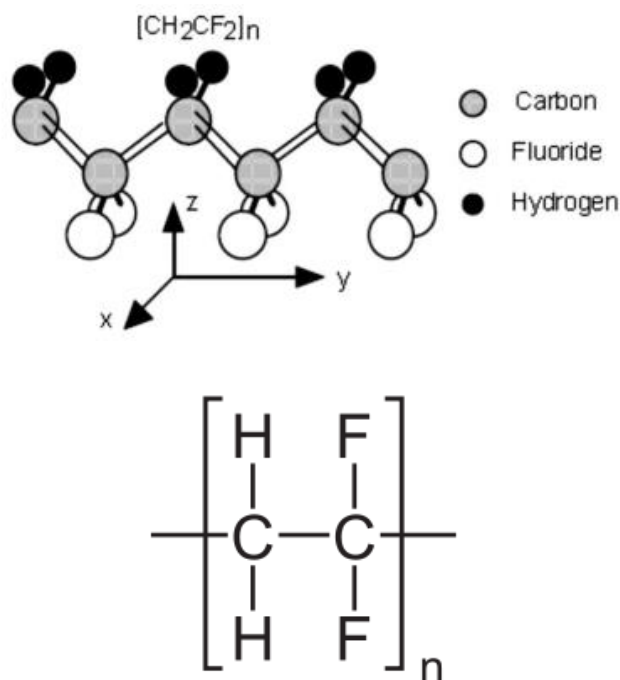


Figure 12 The structure of the polyvinylidene dihydrogen fluoride PVDF[5].

Table 1 Piezoelectric properties of PVDF compared to PZT and BaTiO<sub>3</sub> at 20°C

Property	Unit	PVDF	BaTiO <sub>3</sub>	PZT
Dielectric Constant				
Piezoelectric Charge Constant		12	600-1200	<1000-4000
Electromechanics Coupling Factor	PC/N%1010	$d_{31}=20$	-30 - -60	-100 ->-600
Young's Modulus	N/m <sup>2</sup> 106	$d_{33}=-30$	<100-150	-200 ->600
Acoustic Impedance	kg/(m <sup>2</sup> s)*kg/m <sup>2</sup>	11	21	30-75
Density		0.3	11-12	6-9
		2.3	25	30
		1780	5300-5700	7500-7700

Polyvinylidene dihydride fluoride is a kind of polymer having the chemical formula that (CH<sub>2</sub>-CF<sub>2</sub>)<sub>n</sub> has the structure as in Figure 2.8 which is a piezoelectric polymer, with PVDF having a lower  $k_p$  and  $d_{33}$  than PZT as in Table 1. However, PVDF has many advantages; having a high piezoelectric voltage

constant (g). PZT is more resistant to pollution, has higher dielectric strength than PZT, and has an acoustic impedance that is compatible with water and the human body. PVDF may be used as composite and ceramic. Composite compositions will improve the composite properties due to the combined benefits of the two materials.

## CARBON NANOTUBES

The carbon nanotubes are materials[6] that are shaped in a nanometer diameter tube. The pipe wall may have only one layer. (Single-walled) or multi-layer (Multi-walled) made up of atoms of a single carbon element. It was first discovered in 1991 by a Japanese scientist named Sumioliijima. At present, it has properties that can be applied to various uses, such as making fibers reinforced in composite materials. Make an electrode to increase power and battery life. And capacitors, etc. Carbon nanotubes have various structures and properties, depending on the method used for synthesis. Carbon nanotubes have a graphite sheet structure, rolled into a seamless tube. It can have many diameters. There are 3 types of hexagons about the perimeter of the pipe. Therefore, there are

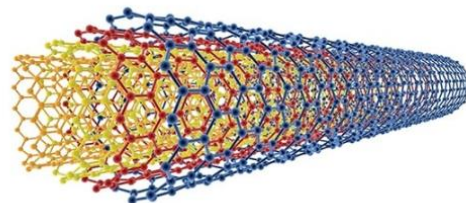


Figure 13 Multi-walled carbon nanotubes (MWCNTs)[6].

Single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWCNTs) are similar in certain respects, but they also have striking differences. SWNTs are an allotrope of  $sp^2$  hybridized carbon similar to fullerenes. The structure is a cylindrical tube, including six-membered carbon rings similar to graphite. Analogous MWCNTs have several tubes in concentric cylinders. The number of these concentric walls may vary from 6 to 25 or more. The diameter of MWCNTs maybe 30 nm when compared to 0.7–2.0 nm for typical SWNTs. The unique properties of carbon nanotubes enable a wide range of novel applications and improvements in the performance of existing ones. This article offers a brief overview of the physics-chemical nature and characterization

of MWCNTs, with specific emphasis on recently introduced materials that signify the most recent advancement of the technology and the level of its commercialization.

## PROPERTIES OF MWCNTs

MWCNTs have excellent properties and are being employed in a large number of commercial applications. The properties of MWCNTs are:

Electrical: MWCNTs are highly conductive when properly integrated into a composite structure, however, the outer wall alone has conductive properties, but the inner walls are not instrumental to conductivity.

Morphology: MWCNTs have a high aspect ratio with lengths typically more than 100 times the diameter, and in certain cases, much higher. Their performance and application are based not just on their aspect ratio but also on the degree of entanglement and the straightness of the tubes, which in turn is a function of both the degree and dimension of defects in the tubes.

Physical: Defect-free, individual, MWCNTs have excellent tensile strength, and when integrated into a composite, such as a thermoplastic or a thermoset compound can significantly increase its strength.

Thermal: MWCNTs have thermal stability above 600 °C, as a result of the level of defects - and to a certain extent on the purity, as a residual catalyst in the product can also accelerate decomposition.

Chemical: MWCNTs are an allotrope of sp<sup>2</sup> hybridized carbon similar to graphite and fullerenes, and therefore have high chemical stability. However, the nanotubes can be functionalized to enhance both the strength and dispersibility of composites.

### Challenges in Commercialization of MWCNTs

The challenges in commercializing MWCNTs include:

Dispersion: This property in MWCNTs is better in solutions or polymers than SWNTs. However, the quality of the dispersion is a critical factor in the performance of the final product.

Purity: Many MWCNTs processes cause a considerable residual metallic catalyst, which can be detrimental to performance.

Defects: The number of defects is dependent on the number of layers within MWCNTs. The high aspect ratio of MWCNTs contributes significantly to its use.

Characterization of MWCNTs and Quality Assurance Parameters  
Observational techniques such as SEM, TEM, and AFM are used for characterizing MWCNTs and can be used to obtain data such as length, diameter, and the number of walls. In addition, thermogravimetric analysis (TGA) is used to measure the residual mass, the temperature at the onset of oxidation, and the temperature of the maximum oxidation rate.

The shape of the derivative curve provides qualitative information with respect to the uniformity of the sample with reference to the polydispersity of the material. A high, narrow peak indicates a narrow distribution of diameters and minimal tube defects.

Applications of MWCNTs There are a large number of present and evolving applications for MWCNTs. These include. Electrically Conductive Polymers: MWCNTs are suitable for these applications – in particular, as a result of their high fabrication, antistatic elastomeric and plastic components for automobile fuel line components, plastics rendered conductive to enable electrostatic spray painting of automobile body parts, RFI shielding materials, and more.

Battery Cathodes: Novel MWNT materials from South West Nano Technologies (SWeNT®) have shown considerable improvements when integrated into cathodes.

Improved Structural Composites: MWCNTs in the form of non-woven or woven fabrics or resin infused buckypaper, when saturated with thermoset resins have shown considerable increases in the stiffness and strength of composite structures, such as structural laminates, golf club shafts and aerospace applications.

conductivity and high aspect ratio. The required conductivity level can be achieved with much lesser loadings than for conventional solutions such as metal particulates or carbon black. Applications include electrostatic discharge protection in wafer processing.

Water filtration membranes: High aspect ratio, high mechanical strength and large specific surface enable very efficient filtration media.



Other development applications include spray-coatable heater elements; thermal interface and other heat conduction materials and enhanced carbon fiber. A new group of MWCNTs has been developed by SWeNT, and are called specialty multi-walled CNT (SMW). In these, the number of walls is controlled to vary between three to eight walls while CNT lengths are maintained above 3  $\mu\text{m}$ , which yields an aspect ratio of between 350 – 550 $\mu\text{m}$ . The lower number of walls results in higher purity, less structural defects, and reduced carbon material waste, while longer and straighter tubes provide better overall CNT morphology. Certain features of the SMW product are The SMW product has a considerably higher aspect ratio (length/diameter) when compared to either of the other grades, and an increased aspect ratio is needed in order to develop a conductive network in the polymer matrix at a low loading of additive. The SMW tubes are straight, which is beneficial in establishing a conducting network. Competitive materials show defects and impurities. Tubes may fracture during dispersion at defect sites, bringing down the number of electrical pathways and the resulting conductivity.

## RELATED RESEARCH

C. Tsonoset al.,(2015)[7] Multifunctional nanocomposites of Poly(vinylidene fluoride) reinforced by carbon nanotubes and magnetite nanoparticles In the present study, the effect of nano magnetite ( $\text{Fe}_3\text{O}_4$ ) content on structural, dielectric/electrical, magnetic and thermal properties of poly(vinylidene fluoride)/carbon nanotubes matrix, is investigated. Anocomposite films of polyvinylidene fluoride, carbon nanotubes, and  $\text{Fe}_3\text{O}_4$  nanoparticles were prepared by the twin-screw compounding method.  $\text{Fe}_3\text{O}_4$ , as magnetic inclusions were incorporated into the composites with carbon nanotubes loadings well above the percolation threshold, where conductive networks were formed. Magnetic characterization revealed the ferrimagnetic behavior of nanocomposites, with saturation magnetization values depending on magnetite content. Results obtained from the analysis of Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), and Differential Scanning Calorimetry (DSC) techniques were very informative for the study of the polymorphism and crystallinity in PVDF. The incorporation of  $\text{Fe}_3\text{O}_4$  inclusions in PVDF/CNT matrix, gradually increases both electrical conductivity and dielectric permittivity up to 10 wt%

$\text{Fe}_3\text{O}_4$  content, while at the higher  $\text{Fe}_3\text{O}_4$  content (15 wt%) reduced values were obtained. This behavior, at higher  $\text{Fe}_3\text{O}_4$  content, should be possible related to the insulating and barrier role of  $\text{Fe}_3\text{O}_4$  nanoparticles. By XRD analysis Figure 3a shows X-ray diffractograms of pristine PVDF and PVDF/CNT nanocomposites with 5, 10, and 15 wt%  $\text{Fe}_3\text{O}_4$  in the 2 $\theta$  range between 5–40°. The well-known diffraction peaks of  $\alpha$  phase of PVDF appearing at 2 $\theta$  = 17.8, 18.5, 20, and 26.8°, are assigned to the lattice planes of (100), (020), (110) and (021) respectively [30]. Furthermore, for samples containing  $\text{Fe}_3\text{O}_4$ , the diffraction peak at 30.6° is assigned to  $\text{Fe}_3\text{O}_4$  crystalline plane of (220) [13]. In fact, with the increase in the addition of  $\text{Fe}_3\text{O}_4$ , the peak becomes increasingly prominent. Interestingly, when CNT are incorporated in the PVDF.

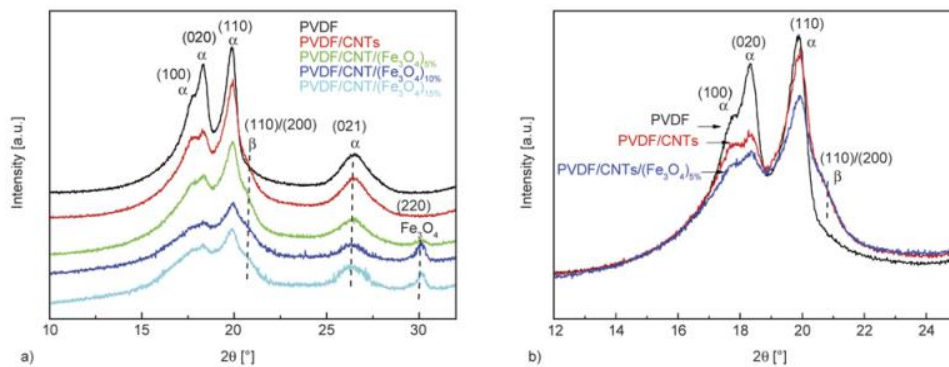


Figure 14 (a) XRD patterns of pure PVDF and PVDF nanocomposites with CNT and  $\text{Fe}_3\text{O}_4$ , (b) zoom of XRD patterns of pure PVDF and nanocomposites showing the existence of ( $\beta$  phase for the nanocomposites containing CNT)[7].

Lee, S., & Lim, Y. (2018). Generating Power Enhancement of Flexible PVDF Generator by Incorporation of CNTs and Surface Treatment of Electrodes Two approaches are proposed for enhancing the generating power of polyvinylidene fluoride (PVDF) flexible generator by incorporating carbon nanotubes (CNTs) and ethylene glycol (EG) treatment of the Poly(3,4-ethylene polythiophene):polystyrene sulfonate (PEDOT: PSS) electrodes. By incorporating CNTs into the PVDF polymer, a higher portion of  $\beta$ -phase PVDF can be obtained, which shows higher piezoelectricity resulting in higher electric charge generating performance. Higher conductivity is also obtained by surface treatment of the PEDOT:PSS electrodes using EG solvent due to the removal of excess PSS in the electrodes. A highly conductive electrode makes effective mobility of charges generated from the CNT/PVDF film, resulting in higher generating performance.

onsequently, higher generating performance can be achieved by collaborating with the above two approaches.

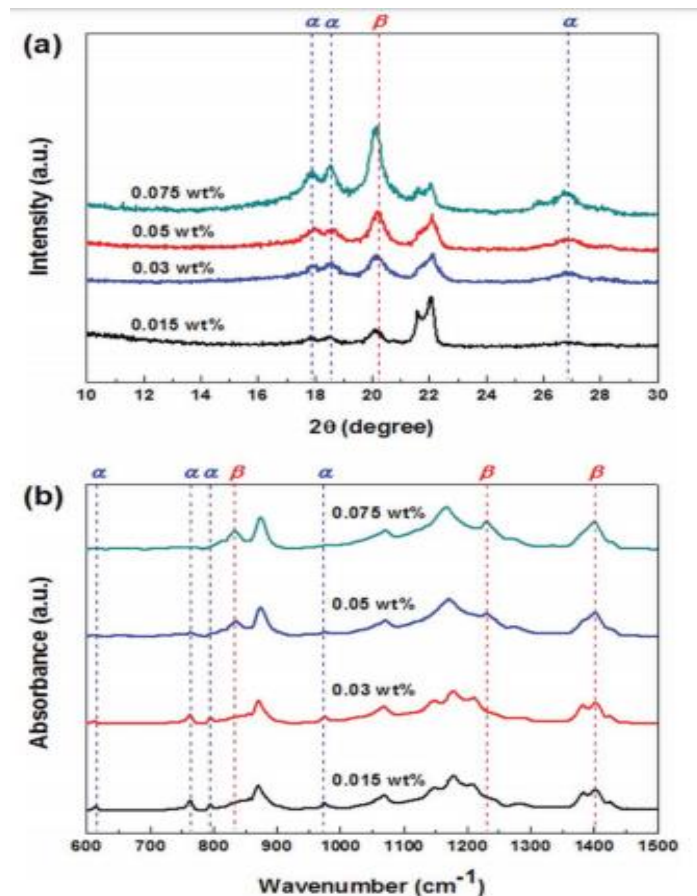


Figure 15 (a) XRD patterns and b) FT-IR spectra of the CNT/PVDF composite films[7].

As the first approach, the dispersed CNT solution was introduced into the PVDF solution to fabricate a higher portion of the  $\beta$ -phase PVDF film showing the most vigorous intensity of the piezoelectricity. XRD patterns and FT-IT spectra were measured

BHOOPESH MAHALE et al.,(2017)[8]. Study of  $\beta$ -phase development in spin-coated PVDF thick films. SEM images of the PVDF films spin-coated at different spinspeeds are shown in figure 10. Figure 18 a, shows SEM images of films baked at 60°C and spin-coated at 1000 and 000rpm, respectively. Microscopic pores oriented fibrils between spherulites can be seen in image (b), which is because of higher spin speed.

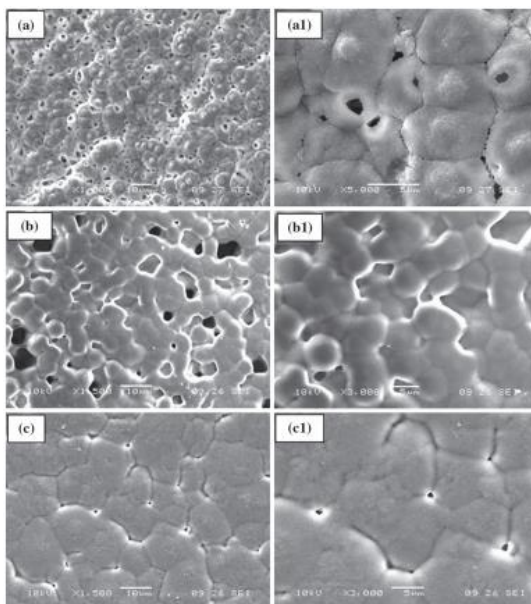


Figure 16 PVDF films crystallized at: (a, a1) room temperature, (b, b1) 60°C and (c, c1) 90°C[8].

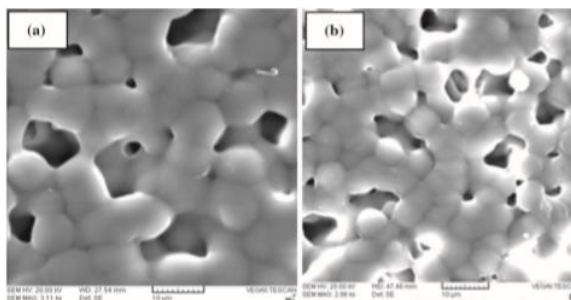


Figure 17 Scanning electron microscopy images of films baked at 60°C and spun at: (a) 1000 rpm and (b) 3000 rpm[8].

## CHAPTER 3

### MATERIALS AND METHODS

In this chapter are presented the Piezoelectric PVDF/CNT preparation, The schematic diagram of the methodology, Preparation of substances, Materials preparation of Piezoelectric samples, Prepare the solution, Rolled cast tape, Structure measurement, Module, Piezoelectric devices design, Crystal structure analysis, Microstructure analysis.

#### THE SCHEMATIC DIAGRAM OF THE METHODOLOGY

Prepare polyvinylidene fluoride (PVDF,  $(C_2H_2F_2)_x$ ), white powder, weigh 1 gram of 6 samples in a test glass tube, sealed with aluminum foil, then carbon nanotubes. (MWCNT) multi-walled black powder, weighing 0.001 grams, 0.002g, 0.003g, 0.004g, 0.005g respectively, stored in 5 test tubes. Next, measure the N-Methyl-2-pyrrolidone solution. [ NMP ( $C_5H_9NO$ )] White clear liquid Get a volume of 20 ml., Amount 6 samples respectively Figure 18.

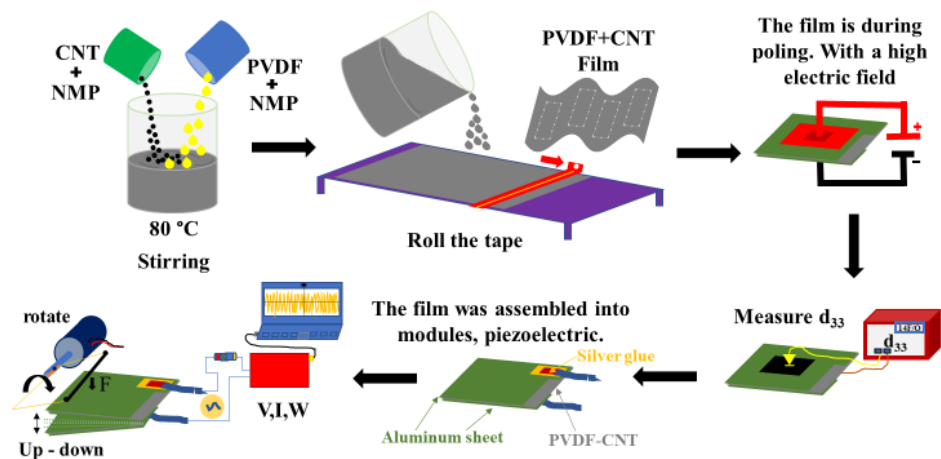


Figure 18 Simulation of the process of invention of the piezoelectric coefficient measurement and electrical measurement.

The schematic diagram of the piezoelectric material step.

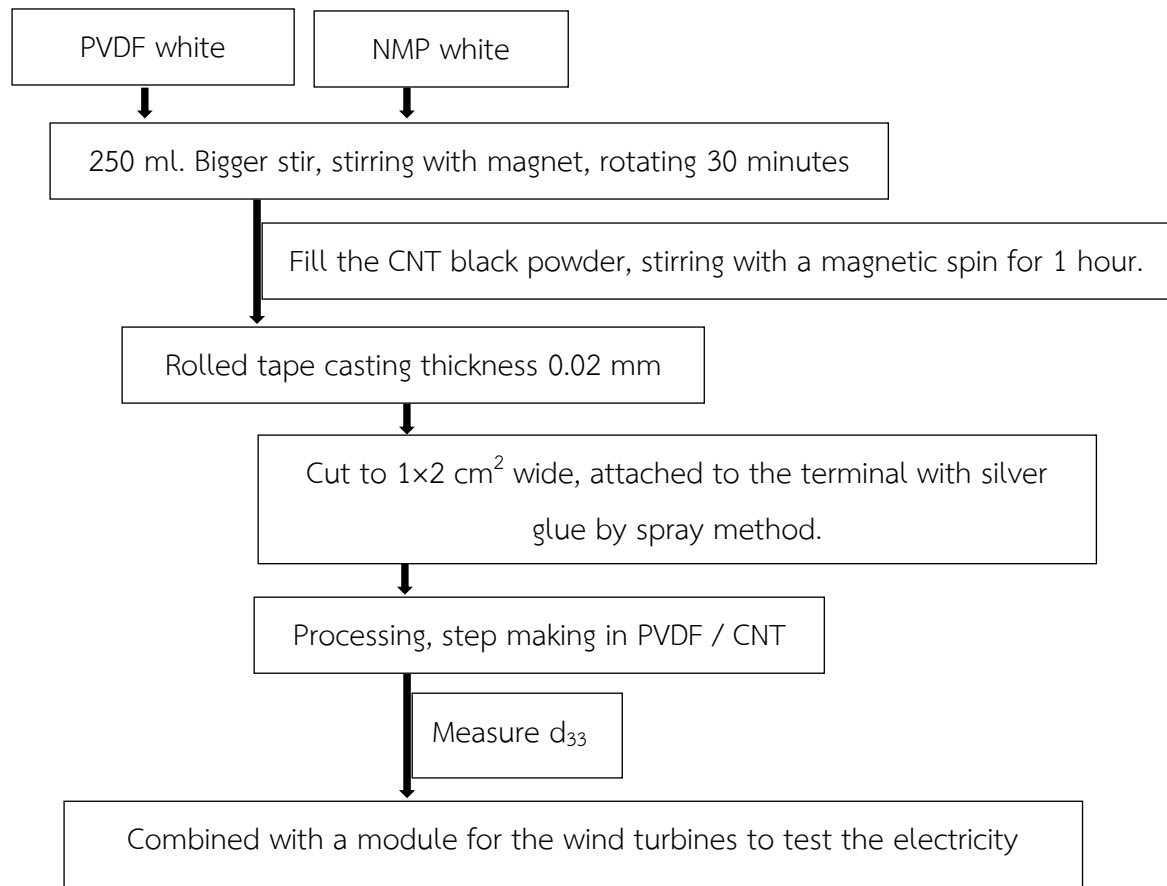


Figure 19 The schematic diagram of the methodology.

## PREPARATION OF SUBSTANCES

Prepare polyvinylidene fluoride (PVDF,  $(C_2H_2F_2)_x$ ), white powder, weigh 1 gram of 6 samples in a test glass tube, sealed with aluminum foil, then carbon nanotubes. (MWCNT) multi-walled black powder, weighing 0.001 grams, 0.002g, 0.003g, 0.004g, 0.005g respectively, stored in 5 test tubes. Next, measure the N-Methyl-2-pyrrolidone solution. [ NMP ( $C_5H_9NO$ )] White clear liquid Get a volume of 20 ml., Amount 6 samples respectively.

## MATERIALS PREPARATION OF PIEZOELECTRIC SAMPLES

PVDF, CNT, and NMP were used raw materials, as shown in Figure 20. (a-b), respectively.

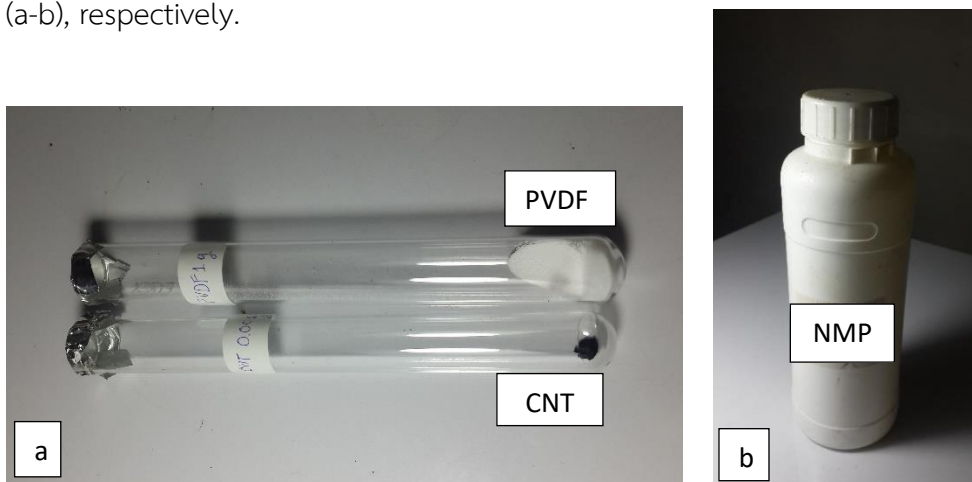


Figure 20 Show the substrate of Piezoelectric (a) PVDF CNT (b) NMP.

## PREPARE THE SOLUTION

The next step is to prepare an unused carbon PVDF solution. Take 20 ml of NMP solution and pour it into a 250 ml bigger, then place it on an electric stove that was set to a temperature of 80°C after that. Pour 1 g of PVDF powder into a Bigger containing patterned material, then stirred with a magnetic spin for 1 hour. Example 1 is a solution that dissolves into white, bright, carbon-nanotube PVDF. The next step is to prepare the PVDF-CNT solution with carbon-nanotubes. By pouring 20 ml of NMP solution into 250 ml of the bigger, then place on the electric stove with temperature setting at 80°C, then pour the 1 g PVDF powder into the big containing the substance is then stirred and stirred by a magnet to spin autism. Take 30 minutes and then mix the carbon nanotubes into the solution. Example 2 is a solution that dissolves into a thin black color. After spinning for 1 hour, PVDF-CNT with carbon nanotube 0.001g was obtained. Example 2 The next step is to prepare the sample at 3,4,5,6 like the 2nd sample, respectively.

## ROLLED CAST TAPE

Next, take the solution 1-6 to roll the tape. By bringing each sample solution to be poured onto a sheet of tape extruder containing heat, adjust the temperature to 80 °C and then extrude the PVDF solution to a thickness of 0.02 mm. After that, wait for the PVDF solution to evaporate the solvent. After 30 minutes, it will turn into a solid film tape. After letting it cool down, you will get a film tape. Piezo Electric PVDF Example 1 and Example 2-6 perform the casting of the same type of film tape, respectively.

## STRUCTURE MEASUREMENT

Measurement of  $d_{33}$  / hysteresis / XRD / FTIR / SEM-EDX The synthesized samples were analyzed with  $d_{33}$  YE2730- $d_{33}$  Meter / Fourier Transform Infrared Spectroscopy (FT-IR) using VERTEX 70 using 532nm lasers in the wavelength of 400–1,400  $\text{cm}^{-1}$  / X- analysis. Ray diffraction (XRD) is achieved by SHIMADZU-LABX-XRD-6100 / TREK dielectric meter MODEL20 / 20c-Hs HIGH VOLTAGE AMPLIFIER / morphological examination of the above samples using a shining electron microscope. Gunships (SEM) JSM-7610F Plus and X-ray spectroscopy (EDX) analysis For power distribution.

## MODULE

Take the PVDF, and PVDF-CNT film tapes Example 1-6 to cut to  $1 \times 2 \text{ cm}^2$  in width to do a module. At this stage, prepare a Silver glue solution mixed with 1 to 10 distilled water in a spray bottle. Prepare two screens that are strung with a frame that has a screen size of  $0.9 \times 1.9 \text{ cm}^2$  in length. Next, take the PVDF film tape to place between the polar screen and spray the prepared silver glue on the screen on both sides, then iron with the screen and remove the PVDF from Wait for the screen to dry for 30 minutes and continue for 2-6 samples respectively.



## PIEZOELECTRIC DEVICES DESIGN

The process of fabricating modules PVDF-CNT and electrical measurement results. Prepare the Piezoelectric PVDF-CNT plate after rolling the tape into the sheet. Cut to 1 cm wide, 2 cm wide, with silver glue on both sides. Top-bottom By not allowing the edges of the electrode to match the top and bottom. After that, dry the silver glue. Lamp with heat to wipe the silver glue. Take it for 1 hour. When the silver glue is dry, check the electrical conductivity of the polarity. Piezoelectric PVDF-CNT then leads the pole after the pole was finished to coat the Piezoelectric sheet PVDF-CNT with hot-rolled plastic, size 1.2 cm wide and 2.2 cm long, then puncture the poles made alternately. Take copper to create a connector. Clamp it to the silver adhesive pad and PVDF-CNT. Tightly closed together.

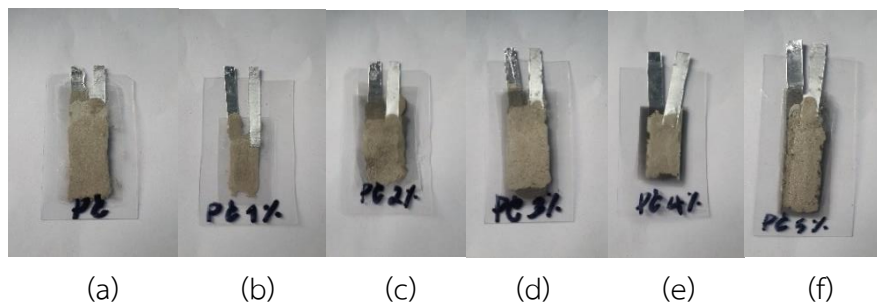


Figure 21 The model of P/C piezoelectric device design (a) PVDF (b) PVDF-CNT1% (c) PVDF-CNT2% (d) PVDF-CNT3% (e) PVDF-CNT4% (f) PVDF-CNT5%.

## CRYSTAL STRUCTURE ANALYSIS

All electromagnetic radiation is characterized by its wave character  $\lambda$  or by means of photon energy  $E$ . The relationship between these quantities can be presented by:

$$\nu = \frac{c}{\lambda} \quad (5)$$

$$E = h\nu \quad (6)$$

$$E = \frac{hc}{\lambda} \quad (7)$$

Where  $c$  is the speed of light,  $\nu$  is frequency  $h$  is Planck's constant.

$$E = \frac{12.398}{\lambda} \quad (8)$$

For  $\text{CuK}\alpha_1$  doublet has an energy of 8.046 keV, the wavelength will be equal to  $12.398/8.046 = 1.541 \text{ \AA}$ . The oscillating electric field of a light wave will interact with the electrons in the matter to cause coherent scattering knowing since Christian Huygens (1629-1695) that each scattering point may be treated as a new source of spherical waves. If a periodic array of objects each scatter radiation coherently, the mutual constructive interference at specifies angles is called diffraction. Max von Laue first developed the description of the diffraction of X-ray by a crystal. William Henry Bragg and William Lawrence Bragg developed a much simpler way of understanding and predicting diffraction.

$$2d \sin \theta = n\lambda \quad (9)$$

Where  $n$  is a positive integer,  $\lambda$  is the wavelength of the incident wave and  $d$  is the interplanar distance.

The crystal structure was analyzed by X-ray diffractometer (Shimadzu, XRD-6100) in scan rang 20-80 degree of  $2\theta$  for 2 deg/min of scan speed with 0.02 of sampling pitch in Figure 22.

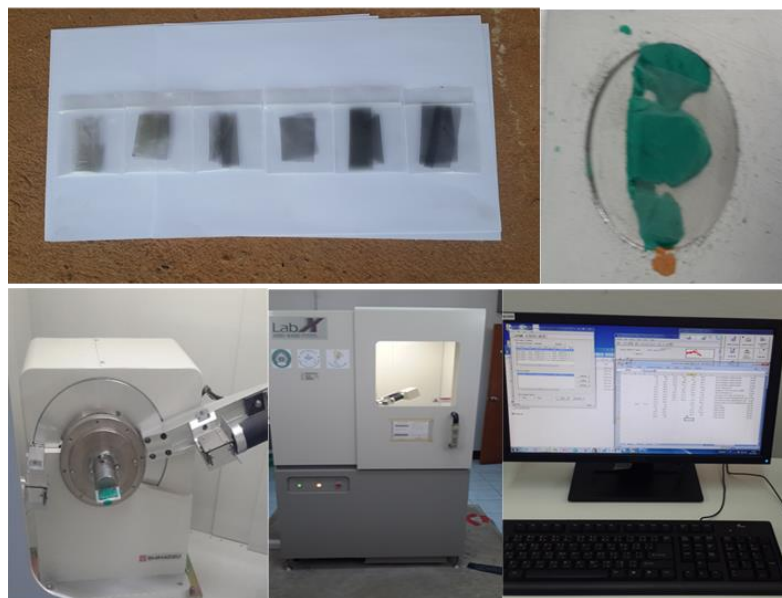


Figure 22 The XRD instrument is an X-ray diffraction analyzer in a sample crystal. Based on the principle of Bragg's law or  $2d \sin\theta = n\lambda$ .

The density of bulk samples was determined by density kit (Mettler Toledo, MS-DNY-54) with deionization water for the auxiliary liquid. Density determinations are frequently performed by Archimedes' principle, which is also used with the densitydetermination kit for the balances. This principle states that every solid body immersed in a fluid losesweight by an amount equal to that of the fluid it displaces.The procedure for the density determination by Archimedes' principle depends on whether the density of solidsor liquids has to be determined.

The density of a solid is determined with the aid of a liquid whose density  $\rho_0$  is known (water or ethanol areusually used as auxiliary liquids). The solid is weighed in air (A) and then in the auxiliary liquid (B). The density ( $\rho$ ) can be calculated from the two weightings.

$$\rho = \frac{A}{A - B}(\rho_0 - \rho_L) + \rho_L \quad (10)$$

$$V = \alpha \frac{A - B}{\rho_0 - \rho_L} \quad (11)$$

Where A is the weight of the sample in air, B is the weight of the sample in the auxiliary liquid, V is the volume of sample,  $\rho_0$  is the density of the auxiliary liquid,  $\rho_L$  is the density of air (0.0012 g/cm<sup>3</sup>) and  $\alpha$  is weight correction factor (0.99985), totake the atmospheric buoyancy of theadjustment weight into account.

## MICROSTRUCTURE ANALYSIS

### Scanning Electron Microscope (SEM) and EDX

The microstructure of bulk samples was analyzed by scanning electron microscope (JEOL, JSM-7600F Prime). The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample, including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas

ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, the spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS) in Figure 23.



Figure 23 Scanning Electron Microscope (SEM) is an electron microscope. Imaging is performed by measuring the electrons reflected from the surface of the surveyed samples.

#### **Fourier Transform InfraRed Spectrometer(FT-IR)**

It is a tool used for the analysis of the functional groups of organic compounds. This is based on the principle of absorption of the middle infrared region of about  $400\text{-}4000\text{ cm}^{-1}$  when the molecules receive energy from infrared waves. With a frequency corresponding to the frequency of vibration (Stretching) or rotation (Bending) of the covalent bond in the molecule. This causes the molecules to undergo IR absorption and changes the molecule's dipole moment. The light intensity per frequency or wavelength (Wave number) has a spectrum called "Interferogram" in which each bond of the class will show a different wavelength, for example C = O of  $\sim 1,800\text{ cm}^{-1}$ , OH stretching very broad at  $3,300\text{-}2,500\text{ cm}^{-1}$ , NH stretching  $\sim 3500\text{-}3300\text{ cm}^{-1}$ , -C = C- Stretching  $\sim 1667\text{-}1613\text{ cm}^{-1}$ , CH Stretching  $\sim 3,000\text{-}2,840\text{ cm}^{-1}$  in Figure 24.



Figure 24 Fourier Transform InfraRed Spectrometer(FT-IR) is an instrument used for the analysis of the functional group of organic compounds. Based on the principle of absorption of the middle infrared region, about  $400\text{-}4000\text{ cm}^{-1}$ .

#### UV-VIS Spectrophotometer

Working principle: UV-VIS Spectrophotometer It is an instrument used to analyze substances based on the radiation absorption principle of substances in the Ultra violet (UV) and Visible (VIS) range of about  $190\text{-}1000\text{ nm}$  wavelength as shown in Figure 1. The amount and type of substance present in the sample When measuring the amount of light transmitted or reflected by the sample relative to light from a source at different wavelengths, according to Beer-Lambert's law, the absorbance of the substance is It is proportional to the number of molecules that carry light absorption. Therefore, this technique can be used to identify different types and quantities of substances. That exist in the example in Figure 25.



Figure 25 UV-VIS Spectrophotometer It is an instrument used in the analysis of substances based on the radiation absorption principle of substances in the range of Ultra violet (UV) and Visible (VIS) wavelength about 190-1000 nm.

### polling

The piezoelectric material obtained by extruding PVDF and PVDF-CNT tape with a thickness of 0.02 mm tape was made by cutting into a 1×1 cm<sup>2</sup> wide sheet and applied with silver glue. In the area of the top-bottom surface of the piezoelectric and leave the edge of the 0.5 mm piezoelectric surface with masking tape and let the silver glue dry, take 2 hours and check the polarity. by testing the completely dry silver glue conductivity, and checking the electrodes above and below the PVDF plate, the piezoelectric was not short-circuited. After that, the polling tool was polled. In which the device has two parts the first part is the Hi-Volt generator set. The second part of the refrigeration unit, the pole, the upper copper plate head, connected to the PVDF plate, the piezoelectric, prepared to glue silver, size 1×1 cm. A polling quantity of 6 kV per 1 mm thickness of PVDF, which must be polled at least 0.12 kV potential difference. In the experiment, the polls at 1.5 kV with PVDF-CNT poles ranged from 0% to 5%, in Figure 26.



Figure 26 A polling quantity of 6 kV per 1 mm thickness of PVDF, which must be polled at least 0.12 kV potential difference. In the experiment, the polls at 1.5 kV with PVDF-CNT poles ranged from 0% to 5%.

### Dielectric properties and dielectric loss

All materials have electrical characteristics that depend on their dielectric properties. Correct and accurate determination of dielectric properties is essential in the application of those materials. Dielectric properties are applied to many processes such as rubber, plastics, ceramics.

Any substance is referred to as a dielectric only if it has the ability to accumulate energy. When under the power of the electric field If the voltage source is fed across the parallel plate capacitors, the charge will accumulate inside the dielectric rather than when leaving the space between the plates to vacuum. The dielectric material increases the electrical capacitance by neutralizing the charge at the dielectric terminal, thus creating an external electric field. The resulting capacitance is directly related to the dielectric constant as equation.

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (12)$$

Where  $\epsilon^*$  = the complex relative permittivity

$\epsilon'$  = Real dielectric constant

$\epsilon''$  = Dielectric constant, imaginary part

Complex dielectric constant ( $\epsilon^*$ ) Real part That ( $\epsilon'$ ) the ability

Energy storage and imaginary ( $\epsilon''$ ) part That represents the energy loss

Dielectric constant ( $\epsilon^*$ ) It is equal to the salad council or the salad council of the substance compared to the salad council cost. (permittivity in free space, ( $\epsilon^*$ )) where ( $\epsilon_0$ ) =  $8.854 \times 10^{-12}$  F/m The equation that (12) and the equation (13)

$$\epsilon_r = \frac{\epsilon}{\epsilon_0} \quad (13)$$

$$\epsilon_r^* = \frac{\epsilon^*}{\epsilon_0} = (\epsilon' / \epsilon_0) - j(\epsilon'' / \epsilon_0) \quad (14)$$

The real part of the condition ( $\epsilon'_r$ ) Council Indicates the amount of energy from an external electric field that can be held in a solid case. Or general liquid Will always be more than one The imaginary part of the condition ( $\epsilon''_r$ ) Council This is called loss tangent,  $\tan(\delta)$ , which has meaning in vector analysis as illustrated (14).The complex image in the form of a vector where the imaginary part is angled  $90^\circ$  to the real part. The result vector is ( $\epsilon_r^*$ ) going to be an angle  $\delta$  with the real ( $\epsilon'_r$ ) part. The relative loss of any substance is the ratio between the lost energy to the stored energy.

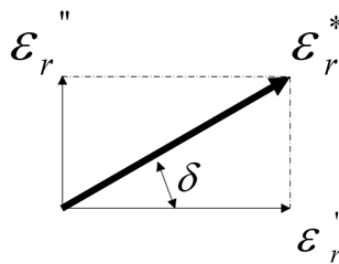


Figure 27 Vector diagram illustration of loss tangent.

$$\tan \delta = \frac{\epsilon''_r}{\epsilon'_r} = \frac{\epsilon''}{\epsilon'} \quad (15)$$

In practice, dielectric constants is related to the electric capacity as equation.

$$r_r = \frac{\epsilon_r}{\epsilon_0} = \frac{tC}{\epsilon_0 A} \quad (16)$$

Where  $\epsilon_r$  is the relative electrical tolerance or the dielectric constant is The real part in the equation (12)  
 $\epsilon_0$  is the electrically acceptable condition of a vacuum ( $8.854 \times 10^{-12}$  F/m)  
 $C$  is the electrical capacitance in F  
 $t$  is the thickness of the sample in m



$A$  is the surface area of the electrode in  $m^2$

Likewise, the dielectric loss can be measured in terms of Dissipation factor,  $D$ . Which means the imaginary part of the equation (16)



Figure 28 Meter of dielectric properties and dielectric loss.

### Electrical measurement of the piezoelectric

piezoelectric measurement of a piezoelectric with a piezoelectric measuring instrument consists of a probe that exerts pressure in the manner of rotation through a piezoelectric disc with a variable frequency of 1 to 20 Hz, when the probe is operated, it puts pressure on the piezoelectric plate and the piezoelectric converts mechanical energy into electrical energy into the electrical circuit with adjustable resistance. 1-100  $M\Omega$ , rectifier and electrolytic capacitor 0.1, 1, 10  $\mu F$  From the electric circuit to the oscilloscope, show the electrical measurement results of the piezoelectric device in the figure 29, 30.

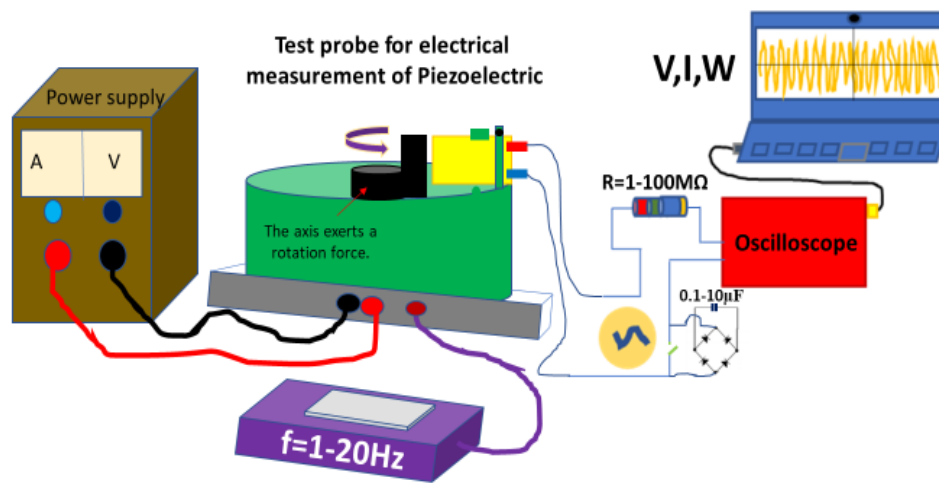


Figure 29 Shows the design of the electric meter of Piezoelectric.

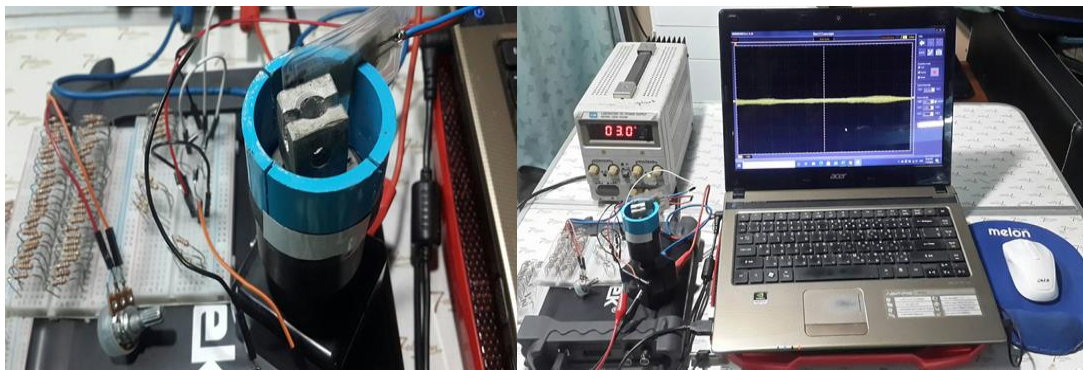


Figure 30 Electrical measurement of the piezoelectric device

## CHAPTER 4

### RESULTS AND DISCUSSION

This chapter represents five topics viz, results of piezoelectric materials synthesis, crystal structure analysis, microstructure analysis, piezoelectric properties, and power generation of piezoelectric of wind turbine devices.

#### MATERIALS PREPARATION

##### Piezoelectric PVDF/CNTs samples

Piezoelectric samples of PVDF, PVDF/CNT1%, PVDF/CNT2%, PVDF/CNT3%, PVDF/CNT4% and PVDF/CNT5% show in Figure 22 (a), (b), (c), (d), (e) and (f), respectively. All samples have the same color and outward appearance.

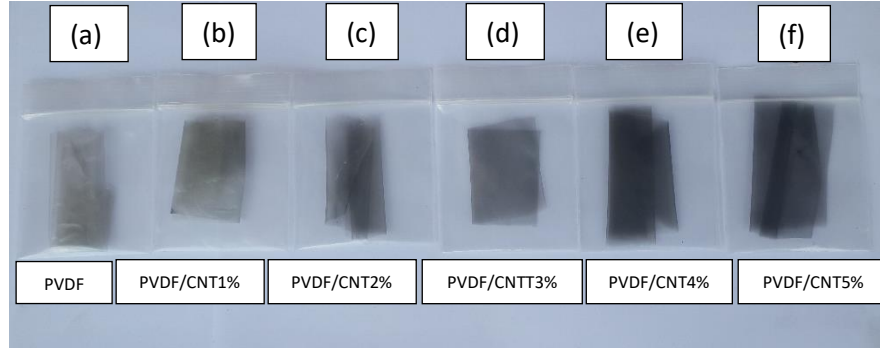


Figure 31 Piezoelectric PVDF/CNT samples of (a)PVDF, (b)PVDF/CNT1%, (c)PVDF/CNT2%, (d)PVDF/CNT3%, (e)PVDF/CNT4% and (f)PVDF/CNT5%.

#### CRYSTAL STRUCTURE

The XRD patterns showing characteristic peaks originating from different planes of the samples are shown in Figure 32. Examples are pure PVDF and PVDF/CNT composite films with 0.1 wt.% to 0.5 wt.% CNT. As peaks of P/C 0 found from the figure at  $2\theta = 17.88^\circ, 18.42^\circ, 20.08^\circ, 26.62^\circ, \text{ and } 38.96^\circ$  are

assigned to crystal plane (100), (020), (110), (120), (101), and (131), respectively, corresponding to the monoclinic structure of  $\alpha$  phase plane. The XRD patterns of PC-1 (black line), PC-2 (red line), PC-3 (green line), PC-4 (purple line) and PC-5 (brown line) show in figure 32. All samples agree with PVDF film added CNT 0.1 – 0.4 wt.% (P/C 1 – P/C 4) show decreasing of the  $\alpha$ -phase presented in figure 32. It is expected to contain peaks corresponding to both  $\alpha$  and  $\gamma$  phases. Indeed, it is observed that the plane (101) of P/C 3 shifted to  $20.3^\circ$  and shifted back to  $20.14^\circ$  of P/C 4 and P/C 5, as well as the decreasing intensity of  $\alpha$  phase at  $26.62^\circ$ , and gradually shifting to  $26.34^\circ$  (P/C 4) for the plane (022) that rather shows characteristics of the  $\gamma$  phase. A more intense peak can also be seen at  $18.5^\circ$  at the plane (020) and  $20.14^\circ$  at the plane (110), resulting in the mixed-phase of the  $\gamma$ -phase and  $\beta$ -phase, i. e.,  $20.98^\circ$  (P/C 5) plane (200) is characteristic of the  $\beta$  phase, which attributes a reflection of the  $\gamma$ - $\beta$ -phase PVDF composite films. The results show that PVDF phase transitions to  $\gamma$ - $\beta$ -phase PVDF of the film are because of adding CNT proper contents

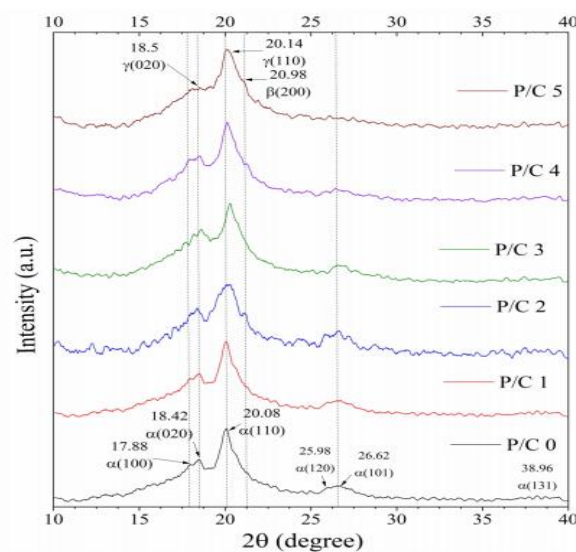


Figure 32 X-ray diffraction patterns of PVDF (P/C 0) and PVDF as a function of adding CNT 0.1% (P/C 1), 0.2% (P/C 2), 0.3% (P/C 3), 0.4% (P/C 4), and 0.5% (P/C 5).

Fourier Transform Infrared Spectroscopy (FT-IR) is a technique that infrared radiation is used to excite molecules into a higher vibrational state to identify the different functionalities present on the PVDF/CNT surface. The functional group of CNT-added PVDF 0 – 0.5 wt.% spectra, as shown in figure 33. FT-IR spectra of PVDF is shown in P/C 0 curve, and CNT-added PVDF of 0.1, 0.2, 0.3, 0.4, and 0.5 wt.% represent P/C 1, P/C 2, P/C 3, P/C 4, and P/C 5, respectively. The main broad peaks of all spectra samples are observed at 613, 763, 871, 1176, and 1400  $\text{cm}^{-1}$  for C-H bend, C-C Aliphatic vibration, C-F stretch, C-N stretch, and C-C stretch, respectively. The  $\beta$  phase of PVDF also exhibited with a CH<sub>2</sub> rocking peak in order of 836  $\text{cm}^{-1}$  [8]. Meanwhile, the functional groups of CNT are normally identified on molecule vibration of C-O stretching in 1608  $\text{cm}^{-1}$  and C–C bending in 613  $\text{cm}^{-1}$ . On the contrary, P/C 1 spectra are different from the other curves of which 613, 763, and 975  $\text{cm}^{-1}$  change to bending vibration mode, the intense high peaks at 1176  $\text{cm}^{-1}$  of C-N stretch and 1400  $\text{cm}^{-1}$  of C-C stretch. The decrease in bonding vibration show that neighbor molecules are closely located with them lead to low vibration. 431, 443, and 520  $\text{cm}^{-1}$  are regarded as characteristic of the  $\beta$  phase. While the CH<sub>2</sub> rocking peak at 836, and 1230  $\text{cm}^{-1}$  not only is common to the mixed phases of  $\gamma$ -  $\beta$ -phase [13] but 439  $\text{cm}^{-1}$  exhibited stretching vibration of found in P/C 1 sample. It is believed that they may be superior electroactive properties.

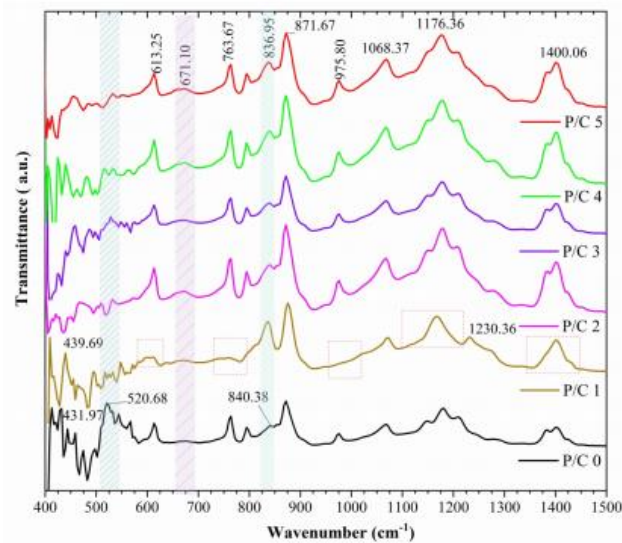


Figure 33 FT-IR spectrum for functional group analysis of PVDF (P/C 0), PVDF/CNT 0.1 wt.% (P/C 1), PVDF/CNT 0.2 wt.% (P/C 2), PVDF/CNT 0.3 wt.% (P/C 3), PVDF/CNT 0.4 wt.% (P/C 4), and PVDF/CNT 0.5 wt.% (P/C).

## MICROSTRUCTURE ANALYSIS

Morphologies of the  $\alpha$ -phase PVDF and  $\alpha$ - $\gamma$ -phase PVDF/CNT surface samples were systematically examined using a Scanning Electron Microscope (SEM) and Energy Dispersive Xray Spectrometer (EDX) analysis illustrated in figure 34. The PVDF/CNT film polymer exhibits the dense homogeneous structure, with fractured surface and some small cracks observed on the surface of all samples due to the evaporation of solvent during the heating film process without external force. PVDF added CNT composites have voids on the surface, as shown in Figure 34 (b–f). Also, the fracture surface with folded lines leads to an elongated corrugated surface that increases with increasing CNT contents into the PVDF matrix [15]. This is seen at 0.5 wt.% CNT shown in Figure 34(f). It attributes the nucleation effect of carbonyl groups of CNT in PVDF crystallization with faster crystallization, which resulted in a large concentration of smaller particles in the film samples [16].

To analyze the homogeneous distribution of elements in the PVDF/CNT films. The EDX mapping and weight ratio in the reaction product of the PVDF/CNT are shown in Figure 34 (a – f) (inset). The elemental mapping exhibits the distribution of oxygen, carbon, and fluorine into the PVDF film seen in

Figure 34 (a) (inset). The elements composition shows that fluorine disperses around carbonyl groups when adding CNT content into PVDF as shown in Figure 34 (b – f) (inset). Furthermore, it is found that fluorine (F) content changes when adding CNT into PVDF, i. e., 36.86 wt.% of F in the PVDF decreases to 27.11 wt.% of F in PVDF/CNT 0.5 wt.%. This shows that strong interaction of molecules between carbonyl groups and fluorine-containing fluorine groups in the casting process will inevitably lead to weakly fluorine bonding is replaced by carbonyl groups by CNT in the PVDF matrix [14]. The results show that the carbonyl groups profoundly affect the mechanism of surface and microstructure of PVDF, which may further tune the ferroelectric properties of PVDF film with CNT-added.

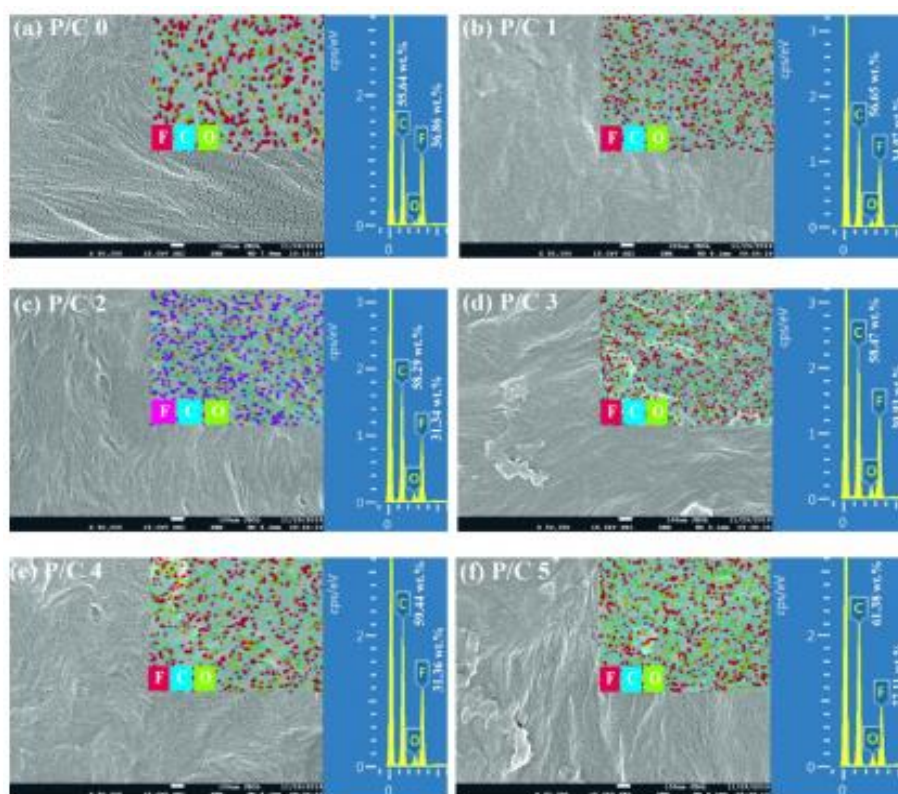


Figure 34 Morphologies of the  $\alpha$ -phase PVDF and  $\alpha$ - $\gamma$ -phase PVDF/CNT surface samples were systematically examined using a Scanning Electron Microscope (SEM) and Energy Dispersive Xray Spectrometer (EDX) analysis illustrated (PVDF) a, PVDF/CNT 0.1 wt.% (PVDF/CNT 1) b, PVDF/CNT 0.2 wt.% (PVDF/CNT 2) c, PVDF/CNT 0.3 wt.% (PVDF/CNT 3) d, PVDF/CNT 0.4 wt.% (PVDF/CNT 4)e, and PVDF/CNT 0.5 wt.%.

The absorption spectra of PVDF film and PVDF/CNT nanocomposite films in the wavelength range 100 nm to 1100 nm are given in Fig. 35, with the absorption peak in the inset. It can be observed that an additional absorption peak is seen in the nanocomposite film at 260 nm, other than that of PVDF at 196 nm. The origin of this peak and the absorbance measurements showed that when the percentage of CNT increased, the absorption effect increased, respectively, in Figure 35.

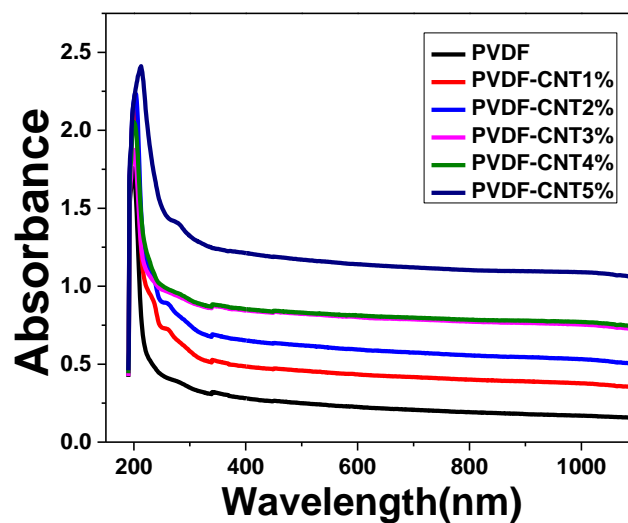


Figure 35 UV-vis absorption spectra of PVDF-CNT films.

## PIEZOELECTRIC PROPERTIES

The dielectric properties of PVDF films can be adjusted by adding CNT of which dielectric constant ( $\epsilon_r$ ) and dielectric loss ( $\tan\delta$ ) are studied as a function of temperature and variation frequencies, as illustrated in Figure 36. The dielectric constant of PVDF decreased with adding CNT at 40 °C, i. e., 29.8, 22.3, 8.5, and 4.3 of P/C 0, P/C 1, P/C 2, and P/C 3, respectively. Alternately, dielectric constant increases to 13.1, and 17.2 of P/C 4, and P/C 5, respectively. The  $\epsilon_r$  at a high temperature with increasing frequency appears as broadening of dielectric peak showing relaxor ferroelectrics behavior due to dipolar freezing transition effect at different temperatures and frequency components. Meanwhile, the  $\epsilon_r$  of the film decreases with increasing the frequency. A significant  $\epsilon_r$  at frequency 100 kHz gradually drops, and then anomaly increases are observed when heating more



than 230 °C. An increase of CNT content in PVDF film has enormous  $\epsilon_r$  that reveals the presence of thermally activated transport properties in the polymer film. It is believed that the PVDF film at higher temperatures is a result of atom vacancies (C, H, F), which are major phase transitions of PVDF/CNT film. Though  $\alpha$ -phase PVDF shows a strong dipole moment due to the presence of vibration fluorine atoms in its molecular bonding found in FTIR results. The addition of CNT (0.1, 0.2, and 0.3 wt.%) is an obstruction domain movement that induces decreasing the dipolar polarization in PVDF film. The dielectric constant is raised by adding 0.4, and 0.5 wt.% of CNT (P/C 4 and P/C 5). Since sufficient CNT can catch with hydrogen bonds with fluorine atoms of C-H group in PVDF, it is expected to enhance the interfacial polarization [14] further. Moreover, an increase of the  $\epsilon_r$  with the addition of CNT (P/C 4 and P/C 5) should attribute to the Maxwell-Wagner-Sillars polarization (MWS) arising from charge carriers accumulated at the interphase between CNT and PVDF. Since the  $\alpha$ - $\gamma$ -phase PVDF polymer composite and the inorganic show the  $\epsilon_r$  difference, charge carriers accumulate on interfaces of C-H and C-F groups, and CNT leads to developing MWS polarization.

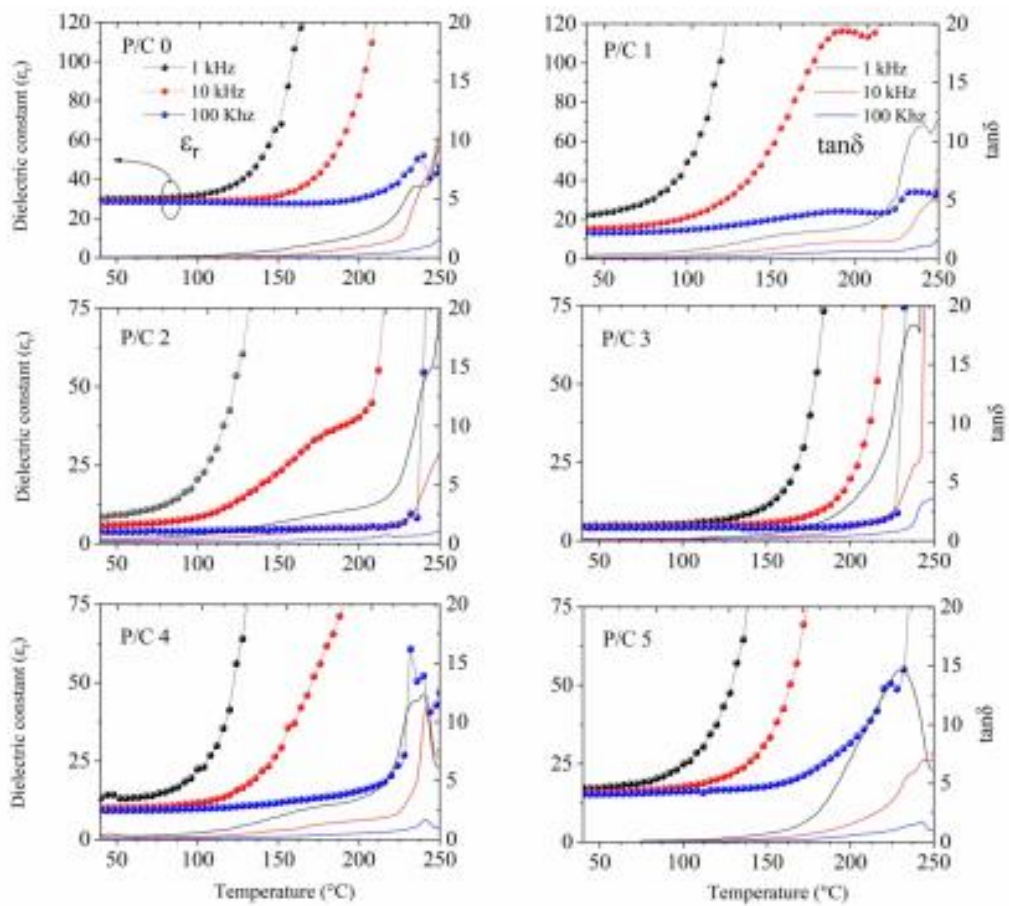


Figure 36 Temperature dependence of dielectric constant and dielectric loss of the PVDF added CNT 0, 0.1, 0.2, 0.3, 0.4 and 0.5 wt.% (P/C 0, P/C 1, P/C 2, P/C 3, P/C 4, and P/C 5) at 1, 10, and 100 kHz frequency and temperature in the range from 40-250 $^{\circ}\text{C}$ .

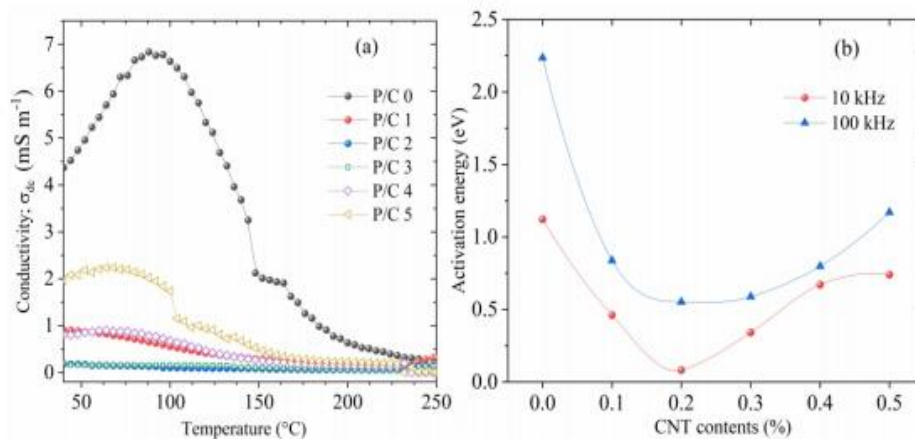


Figure 37 Electrical properties of PVDF/CNT (a) dc conductivity as a function of temperature at 100 kHz and (b) activation energy of PVDF added-CNT at 10, and 100 kHz frequencies.

Ferroelectric behavior of the PVDF/CNT films was studied via polarization electric field hysteresis loop (P-E loop), as shown in Figure 38. Normally, the mechanism of domain switching in the molecule is a ferroelectric nature of the PVDF film. Remnant polarization ( $P_r$ ) and coercive field ( $E_c$ ) is directly proportional to the piezoelectric response of the PVDF films illustrated in Figure 38 (inset). The domain movement primarily shows the presence of fluorine atoms, which shows higher strength of electronegative than the other atoms in PVDF film. The ferroelectricity P-E loop shows that  $P_r$  value of P/C 0 is  $8.4 \mu\text{C cm}^{-2}$ , while  $P_r$  of P/C 1 gradually increases with increasing 0.1 wt.% CNT content as  $8.7 \mu\text{C cm}^{-2}$ , and sharply decreases to  $4.6 \mu\text{C cm}^{-2}$  with adding 0.2 wt.% CNT (P/C 2). Alternatively, the  $P_r$  of PVDF escalates with adding CNT 0.3, 0.4, and 0.5 wt.% (P/C 3, P/C 4, and P/C 5) to be 5.6, 5, and  $6.4 \mu\text{C cm}^{-2}$ , respectively. In contrast, the  $E_c$  value of PVDF increases (decreasing  $P_r$ ) with increasing CNT contents, particularly P/C 4, and P/C 5 values are higher than the others. Furthermore, it is also found that for P/C 4 and P/C 5 samples, the  $P_r$  is close to saturation polarization ( $P_s$ ). This means that the availability of switching dipoles increases with an increase in  $\gamma$ - $\beta$ -phase fraction, which causes an increase in by XRD results. Also, phase transition such that  $\alpha$  to  $\alpha$ - $\gamma$ -phase of PVDF is obtained at low temperature at 80  $^{\circ}\text{C}$  by adding CNT. The results indicate that doping with CNT could also be a useful way to improve domain switching in the PVDF film.

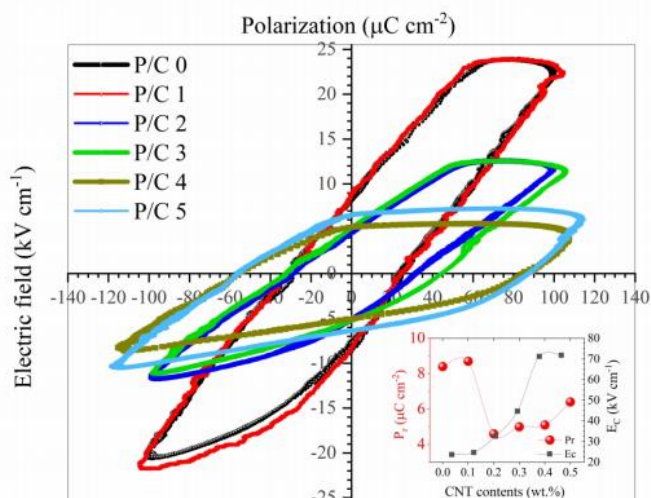


Figure 38 Polarize-electric field hysteresis loops; remnant polarization and electric coercive field (inset) of PVDF/CNT films at 0.1, 0.2, 0.3, 0.4 and 0.5 wt.%.

The piezoelectric property of PVDF/CNT film is analyzed from the piezoelectric charge coefficient ( $d_{33}$ ) and piezoelectric voltage coefficient ( $g_{33}$ ) with the formation of a mixture of  $\alpha$ - $\gamma$  phase in the film composite. Figure 30 illustrates the piezoelectric  $d_{33}$  and  $g_{33}$  coefficients of CNT added PVDF films. The  $d_{33}$  values of the films exhibit a similar trend to  $g_{33}$  values. The PVDF/CNT 0.3 wt.% (P/C 3) shows maxima of  $d_{33}$  and  $g_{33}$  as  $9.77 \text{ pC N}^{-1}$  and  $0.23 \text{ Vm N}^{-1}$ , respectively, while the obtained polarization result of P/C 3 figure 31 is not a maximum  $P_r$  value. The increasing  $d_{33}$  and  $g_{33}$  of P/C 3 show that molecules originated from random orientation in the  $\alpha$ - $\gamma$  phase of the polymer could be aligned in the same direction. Furthermore,  $(\text{CH}_2\text{-CF}_2)_x$  is the molecular structure of the PVDF structure. When they are applied with high voltage, the  $\text{CF}_2$  dipoles are aligned parallel as electric field direction.

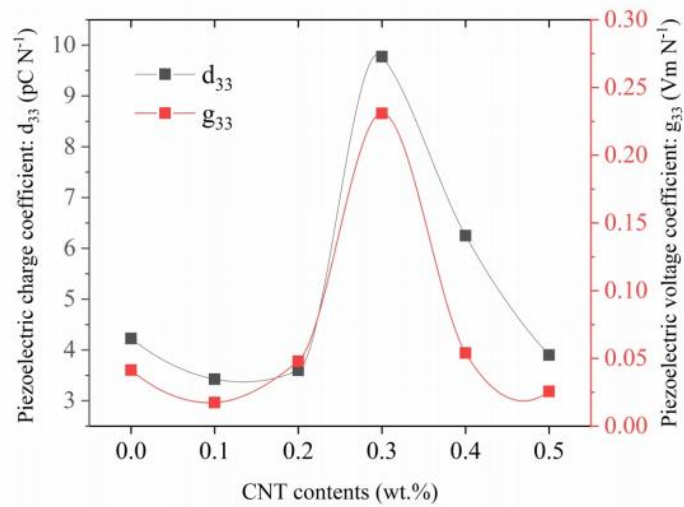


Figure 39 Piezoelectric properties with piezoelectric charge coefficient ( $d_{33}$ ) and piezoelectric voltage coefficient ( $g_{33}$ ) of PVDF/CNT film composite.

## POWER GENERATION OF PIEZOELECTRIC DEVICES

The results from the measurement of the voltage difference and the PVDF piezoelectric current measurements yielded a mean voltage of 3.8V, an average current of  $0.13 \mu\text{A}$  in Figure 40.

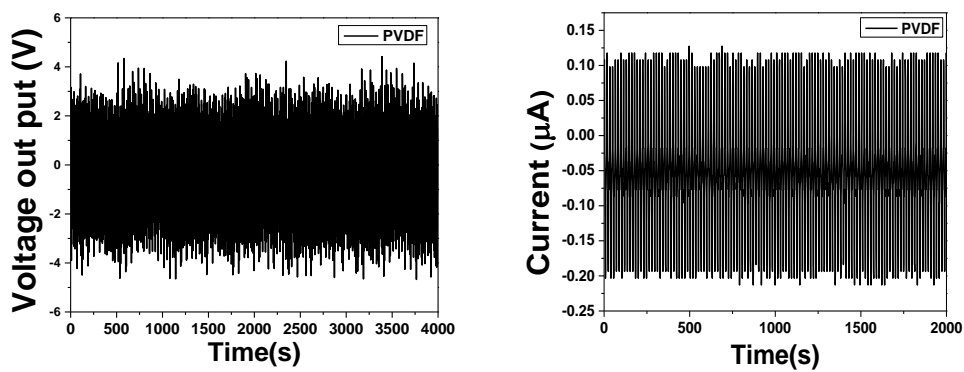


Figure 40 Show measurement of the voltage difference and the PVDF piezoelectric current.

The results from the measurement of the voltage difference and the PVDF/CNT 1% piezoelectric current measurements yielded a mean voltage of 5.1V, an average current of  $0.18\mu\text{A}$  in Figure 41.

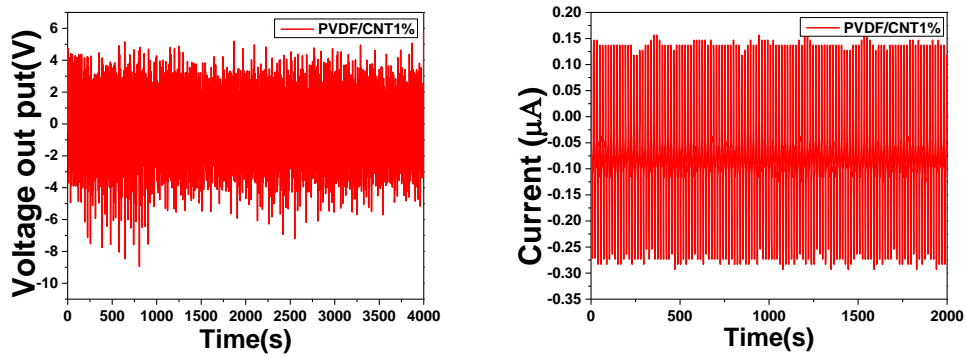


Figure 41 Show measurement of the voltage difference and the PVDF/CNT 1% piezoelectric current.

The results from the measurement of the voltage difference and the PVDF/CNT 2% piezoelectric current measurements yielded a mean voltage of 8.1V, an average current of  $0.47\mu\text{A}$  in Figure 42.

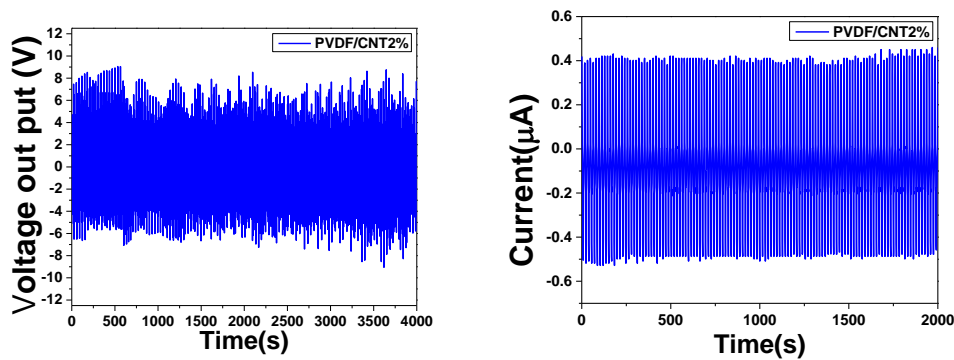


Figure 42 Show measurement of the voltage difference and the PVDF/CNT 2% piezoelectric current.

The results from the measurement of the voltage difference and the PVDF/CNT 3% piezoelectric current measurements yielded a mean voltage of 21V, an average current of  $7.1\mu\text{A}$  in Figure 43.

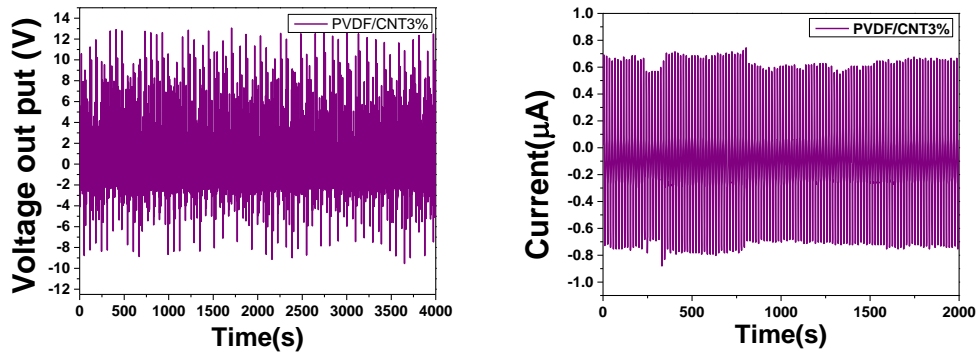


Figure 43 Show measurement of the voltage difference and the PVDF/CNT 3% piezoelectric current.

The results from the measurement of the voltage difference and the PVDF/CNT 4% piezoelectric current measurements yielded a mean voltage of 6.9V, an average current of  $0.52\mu\text{A}$  in Figure 44.

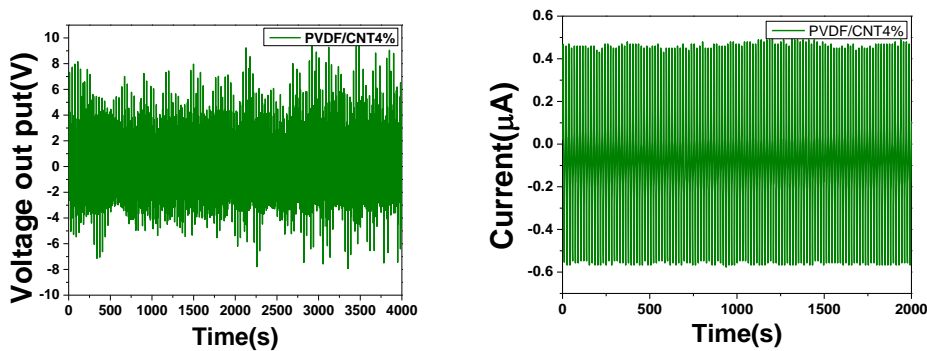


Figure 44 Show measurement of the voltage difference and the PVDF/CNT 4% piezoelectric current.

The results from the measurement of the voltage difference and the PVDF/CNT 5% piezoelectric current measurements yielded a mean voltage of 5.8V, an average current of  $0.33\mu\text{A}$  in Figure 45.

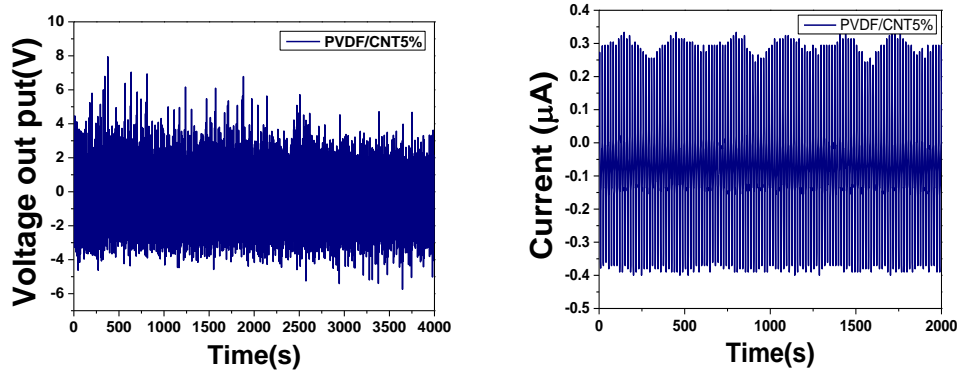


Figure 45 Show measurement of the voltage difference and the PVDF/CNT 5% piezoelectric current.

The results from the measurement of the voltage difference and the PVDF / CNT 1% to 5% piezoelectric, 3.8V, 5.1V, 8.1V, 21V, 6.9V, 5.8V respectively in Figure 46.

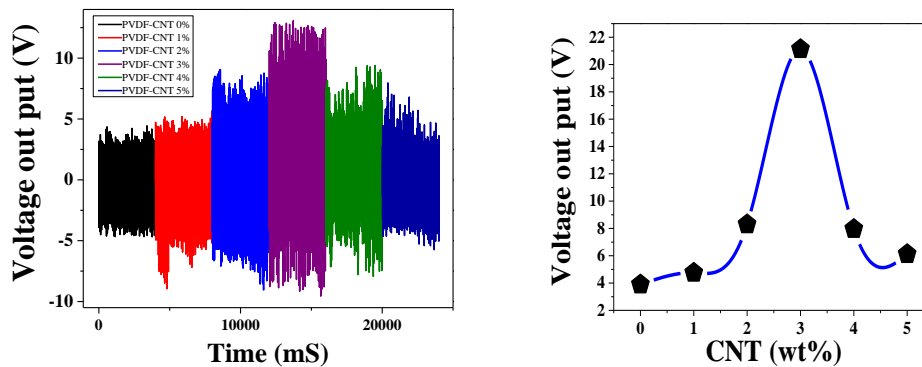


Figure 46 Show measurement of the voltage difference PVDF/CNT 0% to 5%.



The results from the measurement of PVDF/CNT 0% to 5% piezoelectric current measurements yielded a mean current of, 0.13 $\mu$ A, 0.18 $\mu$ A, 0.47 $\mu$ A, 7.1 $\mu$ A, 0.52 $\mu$ A, 0.33 $\mu$ A respectively in Figure 47.

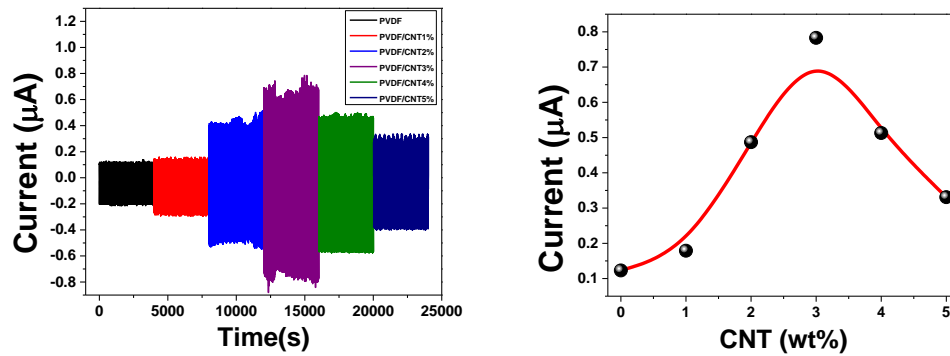


Figure 47 Show measurement of the current PVDF/CNT 0% to 5%.

Show results from the measurement of 0% to 5% PVDF / CNT piezoelectric display is the relationship between current and power obtained from 1 $\Omega$  to 1000 M $\Omega$  resistance in Figure 48., A Power 13.1.  $\mu$ W, Power Figure 48. B 14.9  $\mu$ W, Power Figure 48. C 28.9  $\mu$ W, Power Figure 48. D 59.2  $\mu$ W, Power Figure 48. E 1.3  $\mu$ W, and Power Figure 48. F 31.9  $\mu$ W, respectively.

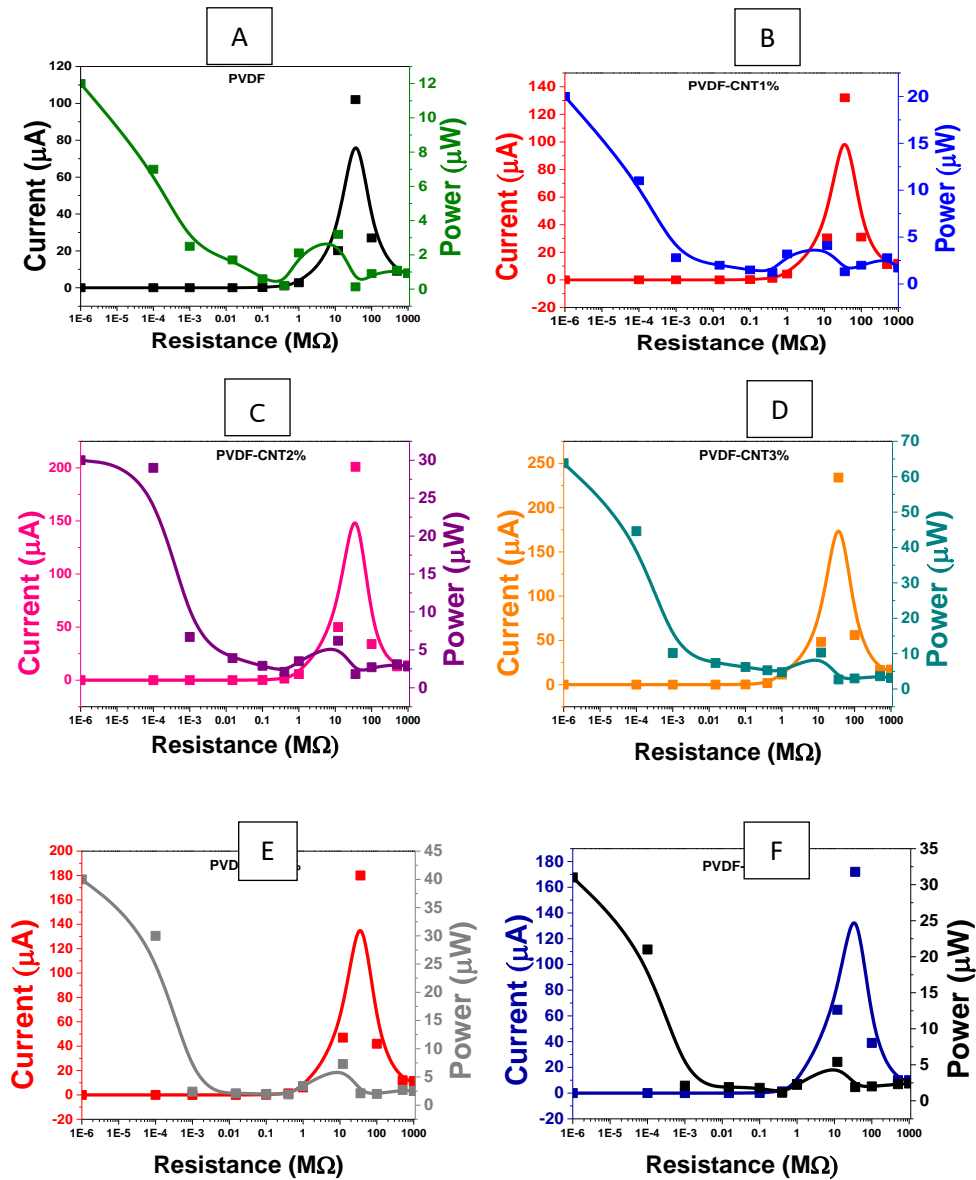


Figure 48 Show results from the measurement of 0% to 5% PVDF / CNT piezoelectric display is the relationship between current and power obtained from  $1\Omega$  to  $1000 \text{ M}\Omega$ .

Display the maximum electrical value of a PVDF / CNT piezoelectric with a percentage of CNT 3% on resistance at  $36M\Omega$ , power  $220\mu W$ , current  $24.1\mu A$  in Figure 51. G, electric potential at  $15.2\text{ mV}$  in Figure 49. H.

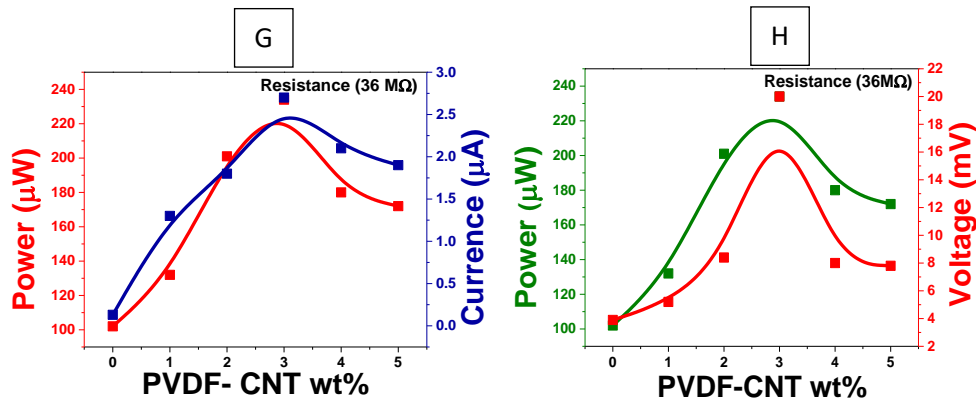


Figure 49 Display the maximum electrical value of a PVDF/CNT piezoelectric with a percentage of CNT 3%.

The wind turbine vertical axis with a height of  $1.5\text{m}$ , a radius of  $1.2\text{m}$  wide, with 6 air receipts. Take the module with the piezoelectric attached to the vertical axis of the wind turbine. Then when the branches of the wind turbine rotates at a speed of  $0.1\text{Hz}$ ,  $1\text{Hz}$ ,  $5\text{Hz}$ ,  $10\text{Hz}$ ,  $15\text{Hz}$  with mechanical energy causing the branches to touch pushing the module piezoelectric to bend which is attached to the center axis and therefore diverting electricity and measure the electric voltage with an oscilloscope. The electrical output comes in a periodic ripple which results from the turbine branches which has a gap of 6 branches per rotation and the potential difference average at  $1.1\text{V}$ ,  $1.8\text{V}$ ,  $3.5\text{V}$ ,  $4.8\text{V}$ ,  $5.3\text{V}$  as in Figure 50.

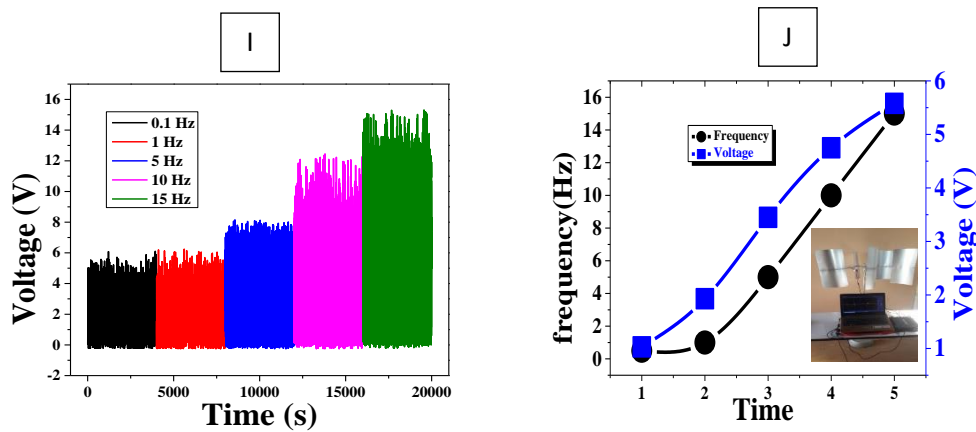


Figure 50 Shows the electric potential difference piezoelectric obtained from the rotation of the wind turbine at a speed of 0.1-15Hz(I) and the potential difference average at 1.1V,1.8V,3.5V,4.8V,5.3V (J).

Electrical measurement procedure PVDF-CNT 3% from the PVDF-CNT adulpisoelectric module is applied to a mechanical force device that is made into a device that can be applied to the surface of the adulpisoelectric surface. Rick connect the piso electrode to the probe of the oscilloscope. Connect it to the notebook, display on the screen and adjust the PVDF-CNT piezoelectric voltage measurement value from 3%. The result of the average voltage measurement of 3.8V, 4.9V, 8.1V, 21.2V, 7.9V, 6.1V, respectively, as shown in Figure 51(K). The effect of the electric voltage with the greatest percentage of CNT is 3%, as shown in figure 51(L). At 230 $\mu$ W, the effect of the capacitance of 0.1 $\mu$ F, at voltage 2.9 V, 1  $\mu$ F, voltage at 1.5V, 10  $\mu$ F at 1.2 V is shown in Figure 51(L).

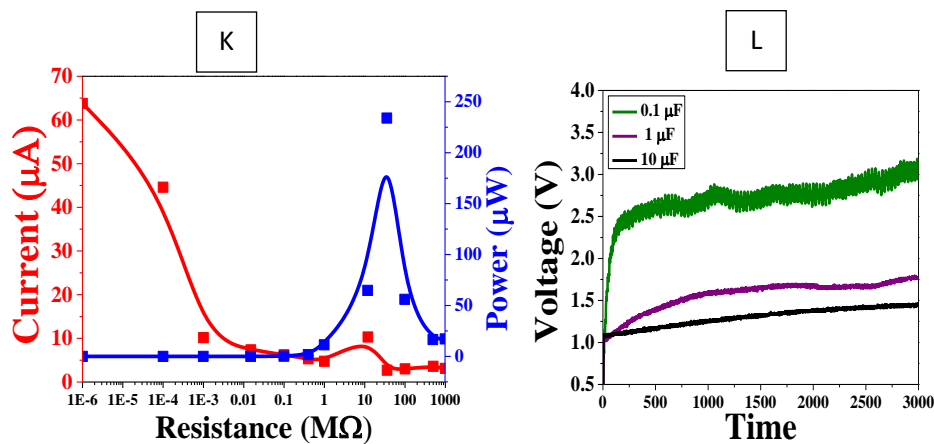


Figure 51 Shows the electric current. Piezoelectric obtained from the rotation of the wind turbine.

## CHAPTER 5

### CONCLUSION AND SUGGESTION

6 samples were prepared from PVDF-CNT piezoelectric material at a ratios of 1 g PVDF per CNT 0wt%, 1wt%, 2wt%, 3wt%, 4wt%, 5wt% dissolved in NMP 20mL solvent at a temperature of 80 °C and tape with a thickness of 200  $\mu\text{m}$  at a temperature of 100 °C. Polarized by an electric field of 1.5kV/200 $\mu\text{m}$  is composed of 6 samples of 1x2  $\text{cm}^2$  piezoelectric device by structural inspection. The microstructure of the PVDF-CNT with XRD, FTIR, measure the photocatalytic coefficient.  $d_{33}$ , measuring electrical values, it was found that the peak angle at XRD at 020,110, the highest value  $d_{33}$  -2.9,9.7 3wt% in 6 samples. 3wt%, maximum current at 0.3 $\mu\text{A}$ , maximum power 230  $\mu\text{W}$ , respectively, the capacitance effect 0.1 $\mu\text{F}$ , the potential difference at 2.9 V, as a result of the application to wind turbines. 3V at a frequency range of 1-15Hz.

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## APPENDIX

Appendix A

Conferences

1. Aphisak Kaeopisan, and H. Wattanasarn, “Fabrication of piezoelectric flexible on PVDF/CNTs”

5<sup>th</sup> Southeast Asia Conference on Thermoelectrics 2018 14-17 December 2018, Empress Angkor Resort & Spa, Siem Reap, Cambodia

2. Aphisak Kaeopisan, Hassakorn Wattanasarn, “Piezoelectric PVDF/CNT Flexible Applied on Motorcycle”

The 4<sup>th</sup> International Conference on Applied Physics and Materials Application (ICAPMA 2019) 18 – 20 September 2019 at Grand Mercure Hotel & Resort Medan, Indonesia.

*5<sup>th</sup> Southeast Asia Conference on Thermoelectrics 2018  
14-17 December 2018, Empress Angkor Resort & Spa, Siem Reap, Cambodia*

**SACT 2018**

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## Fabrication of piezoelectric flexible on PVDF/CNTs

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### Abstract

Fabrication of piezoelectric module Flexible But still, the properties of the piezoelectric. The study was conducted in the form of composite materials called this material. Piezoelectric Composite The piezoelectric composite consists of a piezoelectric polymer. It is flexible and strong because it combines the physical properties of nanosized materials and polymers. One of the fundamental problems for small-scale applications is the design and selection of effective material structures to convert mechanical energy into electrical energy. In this research, composite dielectric materials were prepared by impregnating carbonnanotubes (MCNTs) into polyvinyl fluoride (PVDF). Composite dielectric composites are fabricated. PVDF / MCNTs are polarized by hot-fixing 135 °C Polarizing Piezoelectric Material 1kV and measuring electrical signals by resonant.

*Keywords: PVDF/NMP CNT composites and actuator*



5<sup>th</sup> Southeast Asia Conference on Thermoelectrics 2018  
14-17 December 2018, Empress Angkor Resort & Spa, Siem Reap, Cambodia

**SACT 2018**  
sact.snru.ac.th



# PIEZOELECTRIC Fabrication of piezoelectric flexible on PVDF/CNTs

A. Kaeopisan<sup>a,e1</sup>, H. Wattanasarn<sup>b,e2</sup>

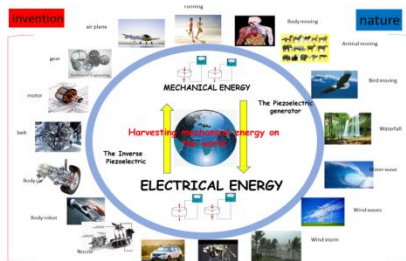
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## 1. Abstract

Fabrication of piezoelectric module Flexible But still, the properties of the piezoelectric. The study was conducted in the form of composite materials called this material. Piezoelectric Composite The piezoelectric composite consists of a piezoelectric polymer. It is flexible and strong because it combines the physical properties of nanosized materials and polymers. One of the fundamental problems for small-scale applications is the design and selection of effective material structures to convert mechanical energy into electrical energy. In this research, composite dielectric materials were prepared by impregnating carbonnanotubes (MCNTs) into polyvinyl fluoride (PVDF). Composite dielectric composites are fabricated. PVDF / MCNTs are polarized by hot-fixing 135 °C Polarizing Piezoelectric Material 1k

## 2. Harvesting mechanical energy



## 3. PIEZOELECTRIC EFFECT

**The direct piezoelectric Effect : Generator**  
 $D = dT + \epsilon^T E$

**The Inverse Piezoelectric Effect**  
 $S = s^E T + dE$

Compression Effect: Decrease in volume and it has a voltage with the same polarity as the material.

Tension Effect: Increase in volume and it has a voltage with opposite polarity as the material.

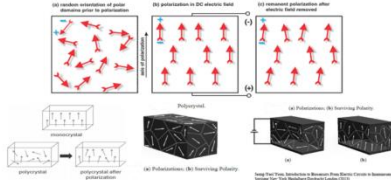
If the applied voltage has the same polarity than the material expands.

If the applied voltage has the opposite polarity than the material contracts.

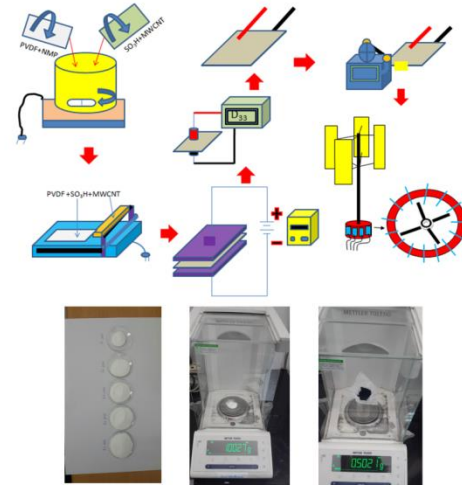
## 4. Polarizing Piezoelectric Material

Adjoining dipoles form regions of local alignment called domains. The alignment gives a net dipole moment to the domain, and thus a net polarization. The direction of polarization among neighboring domains is random, however, so the ceramic element has no overall polarization. The domains in a ceramic element are aligned by exposing the element to a strong, direct current electric field, usually at a temperature slightly below the Curie point.

When the electric field is removed most of the dipoles are locked into a configuration of near alignment



## 5. Chemical preparation steps Piezoelectric flexible on PVDF/CNTs



## 6. Effect of material preparation Piezoelectric D33



## 7. Purpose of the research

- 1) To fabricate flexible poly (vinyl diethyl ether) PVDF with nano-carbon nanotubes. (CNTs)
- 2) To study the microstructure. And electrical properties of PVDF / CNTs.
- 3) To fabricate wind turbine generators from the PVDF / CNTs piezoelectric module.

## 8. Acknowledgement

This work was supported by the Piezoelectric Research Laboratory, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, and Nawa College Nakhophanom University Thailand.

14	ABS-38	Energy and environment materials
<p style="text-align: center;"><b>Piezoelectric PVDF/CNT Flexible Applied on Motorcycle</b>  <i>Aphisak Kaeopisan (1), Hassakorn Wattanasarn (2)*</i></p> <p style="text-align: center;">(1,2) Program of Physics, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, Sakon Nakhon, 47000, Thailand.</p> <p style="text-align: center;"><b>Abstract</b></p> <p>For harvesting energy, mechanical energy converts to electrical energy using piezoelectric devices. In this study, piezoelectric flexible (PF) was synthesized from composite materials of polyvinylidene difluoride adding 1wt.% of carbon nanotube (PVDF-1wt.%CNT). The PVDF-1wt.%CNT size 0.5×30×100 mm<sup>3</sup> and annealed at 60 °C for 1h. A copper tape was compressed for electrode on the top and bottom of the PF, poling at 6 kV mm<sup>-1</sup> for 20 min. The results show that the piezoelectric coefficient (d<sub>33</sub>) maximum was 22 pC N<sup>-1</sup>. The 5 PF modules was fabricated to a device and attachment on a motorcycle coil spring compressor to investigate the generating electricity of the PF from mechanical energy. The motorcycle was tested using velocity at 50 km h<sup>-1</sup> for 5 min run-on various surface road. The electricity from the PF modules were arranged using rectifier circuit installed motorcycle coil spring compressor, the output voltage was 3, 3.3, and 4 V for asphalt, cement, and gravel road, respectively. It expected that the harvesting energy devices using piezoelectric flexible is useful to apply on a motorcycle for generated electricity.</p> <p><b>Keywords:</b> PVDF; CNT; Composites; Harvesting energy; Mechanical energy</p> <p><a href="#">PermaLink</a>   <a href="#">Plain Format</a>   <a href="#">Corresponding Author (Aphisak Kaeopisan)</a></p>		

Appendix B

Publications

## Step Synthesis, Electrical Generator of PVDF/CNTs Piezoelectric

Aphisak Kaepisan (1), Hassakorn Wattanasarn (2)\*

(1,2) Program of Physics, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, Sakon Nakhon, 47000, Thailand.

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### Abstracts:

The piezoelectric is a material that can convert mechanical energy into electrical energy and can convert electrical energy into mechanical energy. It is a device that is fabricated from a piezoelectric material. It may be in the elemental form or composite materials in general. The composite material, or composite material, was one material as the main body and the other was the first dispersed material using polyvinylidene fluoride (PVDF,  $(C_2H_2F_2)_x$ ) powder, PVDF 1% by fill weight. 6 samples were doped with carbon-nanotube CNT powder, 0.001%, 0.002%, 0.003%, 0.004%, and 0.005%. The N-Methyl 1-2-pyrrolidone solution, [NMP  $(C_4H_9NO)$ ] 20 mL, the solution was rolled, casting tape at 80 °C, then extruded and molded to 200  $\mu$ m thick. The film was inspected with XRD to determine the structure from preparation to make the pole with silver glue. Conducted to arrange the electrodes with a 1.5 kV / 200 $\mu$ m field was conducted to arrange, the dielectric coefficient  $d_{31}$  2.90 to 9.77 pC/N, the highest of 3wt% in 6 samples was measured, measure the potential difference 21.2V was also measured, the highest value 3wt%. Maximum current at 0.3 $\mu$ A, maximum power 230  $\mu$ W, respectively, the capacitance of 0.1 $\mu$ F, the potential difference at 2.9V, as a result of the application to wind turbines. 3V at a frequency range of 1-15Hz.

**Keywords:** PVDF materials, synthesis Piezoelectric, Electrical properties.

### I. Introduction

Energy is essential to human beings. There are many forms of energy such as thermal energy, optical energy, electrical energy, mechanical energy which can be transformed from mechanical to electrical energy. The piezoelectric is a material that can convert mechanical energy into electrical energy and can convert electrical energy into mechanical energy as well. May be in elemental form or composite materials in general composites, or composite materials, where one type of material as the main body and the other being the dispersed material of the first material. The combined components differ in form and form. Chemical elements and are not mutually solvent. The original properties of each component will have one of the more prominent properties, resulting in a new material with all the good properties of the substrate [1-3]. The piezoelectric composite material is fabricated. Is polyvinylidene-fluorine and carbon-nanotubes. The prepare polyvinylidene-fluoride (PVDF,  $(C_2H_2F_2)_x$ ), is a material with some outstanding properties such as high flexibility and flexibility[4-6]. Has a smooth finish without the need for polishing. It is lightweight, can be rolled into a thin sheet, and has multiple production processes. The carbon nanotubes are good electrical and thermal materials. When it is fabricated as a composite material [7-11]. A good electrical piezoelectric element is expected to be useful for other electrical and electronic measurement applications.

### II. Material And Methods

#### Preparation of substances.

Prepare polyvinylidene fluoride (PVDF,  $(C_2H_2F_2)_x$ ) white powder, weigh 1 gram of 6 samples in a test glass tube, sealed with aluminum foil, then carbon nanotubes. (MWCNT) multi-walled black powder, weighing 0.001 grams, 0.002g, 0.003g, 0.004g, 0.005g respectively, stored in 5 test tubes. Next, measure the N-Methyl-2-pyrrolidone solution. [NMP  $(C_4H_9NO)$ ] White clear liquid Get a volume of 20 ml, Amount 6 samples respectively figure 1.

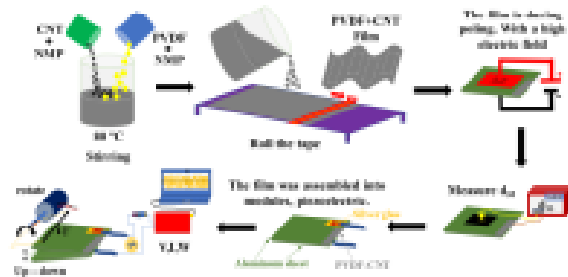


Figure 1. Simulation of the process of invention of the piezoelectric coefficient measurement and electrical measurement.

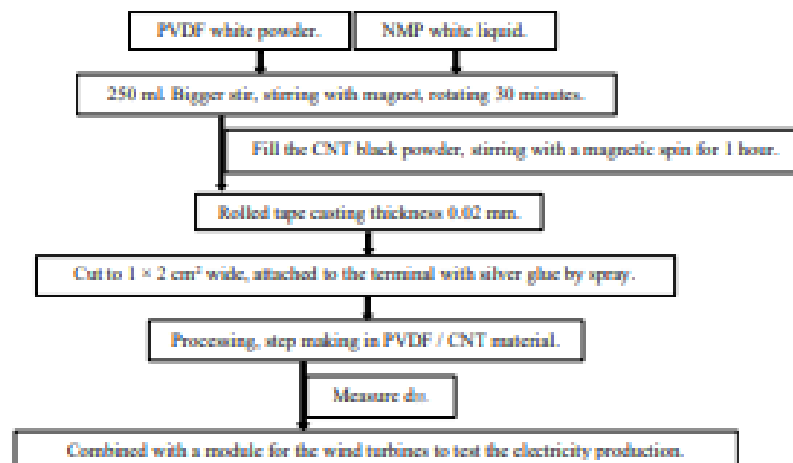


Figure 2. Procedure sequence for the experiment in making a piezoelectric device.

#### Materials preparation of Piezoelectric samples.

##### Prepare the solution.

The next step is to prepare an unswayed carbon PVDF solution. Take 20 ml of NMP solution and pour it into a 250 ml bigger; then place it on an electric stove that was set to a temperature of  $80\text{ }^{\circ}\text{C}$  after that. Pour 1 g of PVDF powder into a bigger containing patterned material, then stir with a magnetic spin for 1 hour. Example 1 is a solution that dissolves into white, bright, carbon-nanotube PVDF. The next step is to prepare the PVDF-CNT solution with carbon-nanotubes. By pouring 20 ml of NMP solution into 250 ml of the bigger, then place on the electric stove with temperature setting at  $80\text{ }^{\circ}\text{C}$ , then pour the 1 g PVDF powder into the bigger containing the substance is then stirred and stirred by a magnet to spin action. Take 30 minutes and then mix the carbon nanotubes into the solution.



Example 2 is a solution that dissolves into a thin black color. After spinning for 1 hour, PVDF-CNT with carbon nanotube 0.001g was obtained. Example 2, the next step is to prepare the sample at 3,4,5,6 like the 2nd sample, respectively.

#### **Rolling casting tape.**

Next, take the solution 1-6 to roll the tape. By bringing each sample solution to be poured onto a sheet of tape extruder containing heat, adjust the temperature to 80 C° and then extrude the PVDF solution to a thickness of 0.02 mm. After that, wait for the PVDF solution to evaporate the solvent. after 30 minutes, it will turn into a solid film tape. After letting it cool down, will get a film tape. Piezoelectric PVDF example 1 and example 2-6 perform the casting of the same type of film tape, respectively.

#### **Measure structure.**

Measurement of  $d_{31}$  / hysteresis / XRD / FTIR

The synthesized samples were analyzed with  $d_{31}$  YE2730- $d_{31}$  Meter / Fourier Transform Infrared Spectroscopy (FT-IR) using VERTEX 70 using 532nm lasers in the wavelength of 400-1,400  $cm^{-1}$  / X- analysis. Ray diffraction (XRD) is achieved by SHIMADZU-LABX-XRD-6100 / TREK dielectric meter MODEL20 / 20k-Hz HIGH VOLTAGE AMPLIFIER / morphological examination of the above samples using a shining electron microscope.

#### **Module.**

Take the PVDF, and PVDF-CNT film tapes, example 1-6 to cut to 1x2  $cm^2$  in width to do a module. At this stage, prepare a silver glue solution mixed with 1 to 10 distilled water in a spray bottle. Prepare two screens that are strong with a frame that has a screen size of 0.9x1.9  $cm^2$  in length. Next, take the PVDF film tape to place between the polar screen and spray the prepared silver glue on the screen on both sides, then iron with the screen and remove the PVDF from wait for the screen to dry for 30 minutes and continue for 2-6 samples respectively.

#### **Piezoelectric device fabrication.**

The process of fabricating modules PVDF-CNT and electrical measurement results.

Prepare the Piezoelectric PVDF-CNT plate after rolling the tape into the sheet. Cut to 1 cm wide, 2 cm wide, with silver glue on both sides. Top-bottom by not allowing the edges of the electrode to match the top and bottom. After that, dry the silver glue. Lamp with heat to wipe the silver glue. Take it for 1 hour. When the silver glue is dry, check the electrical conductivity of the polarity. Piezoelectric PVDF-CNT then leads the pole after the pole was finished to coat the Piezoelectric sheet PVDF-CNT with hot-rolled plastic, size 1.2 cm wide and 2.2 cm long, then puncture the poles made alternately. Take copper to create a connector. Clamp it to the silver adhesive pad and PVDF-CNT. Tightly closed together.

### **III. Result and Discussion**

Table 1. Preparation of PVDF / CNT / NMP dosage for the preparation of PVDF-CNT piezoelectric solution.

EXPT NO	PVDF	Additive	Solvent
1	1g	-	20cc NMP
2	1g	0.001g CNTs	20cc NMP
3	1g	0.002g CNTs	20cc NMP
4	1g	0.003g CNTs	20cc NMP
5	1g	0.004g CNTs	20cc NMP
6	1g	0.005g CNTs	20cc NMP

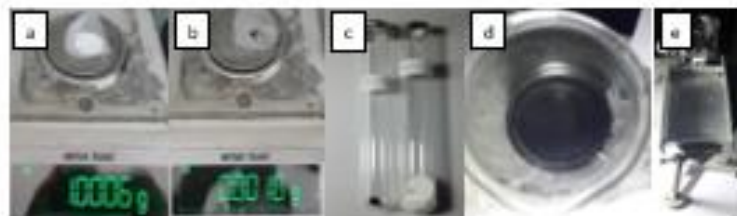


Figure 3. Shows PVDF content (a), CNT content (b), PVDF-CNT preparation in vitro (c), dissolved PVDF-CNT effect in NMP (d), extrusion solution to casting tape (e).

When analyzing the polymer with X-ray diffraction technique (XRD), it was found that the form of adding carbon nanotubes to 1wt% -5wt% polyvinylidene fluoride had an effect. To the internal structure using the sample, there is a mixed crystal structure  $\alpha$  and  $\beta$ . In every substance, it was also found that the deflection angle shifted to a higher value when the carbon nanotube added percentage shown in figure 4. The addition of carbon nanotubes in polyvinylidene fluoride changes within the internal structure.

When the results were analyzed by Fourier Transform Infrared Spectroscopy of Polymer Materials (PVDF) techniques with the addition of carbon nanotubes (CNT) by percentage weight (1wt%, 2wt%, 3wt%, 4wt%, 5wt%) into the structure of polyvinylidene fluoride by analysis from Fourier Transform Infrared Spectroscopy (FTIR) technique. As shown in figure 5, it was found that (frequency) or wave number (wave number)/PVDF at  $613.01\text{cm}^{-1}$ ,  $871.42\text{cm}^{-1}$ ,  $1179.42\text{cm}^{-1}$ ,  $1401.57\text{cm}^{-1}$  / PVDF-CNTwt1% at  $613.02\text{cm}^{-1}$ ,  $871.53\text{cm}^{-1}$ ,  $1179.55\text{cm}^{-1}$ ,  $1401.54\text{cm}^{-1}$  / PVDF-CNTwt2% at  $613.06\text{cm}^{-1}$ ,  $871.56\text{cm}^{-1}$ ,  $1179.42\text{cm}^{-1}$ ,  $1401.37\text{cm}^{-1}$  / PVDF-CNTwt3% at  $613.12\text{cm}^{-1}$ ,  $871.67\text{cm}^{-1}$ ,  $1179.65\text{cm}^{-1}$ ,  $1401.18\text{cm}^{-1}$  / PVDF-CNTwt4% at  $613.15\text{cm}^{-1}$ ,  $871.66\text{cm}^{-1}$ ,  $1179.65\text{cm}^{-1}$ ,  $1401.18\text{cm}^{-1}$  and PVDF-CNTwt5% at  $613.00\text{cm}^{-1}$ ,  $871.18\text{cm}^{-1}$ ,  $1179.69\text{cm}^{-1}$ ,  $1401.14\text{cm}^{-1}$  were found to have various peaks. As in the PVDF spectrum, there was no chemical interaction between CNT and PVDF. Thermal stability and the nanometer addition in PVDF increased after composite with CNT as a result of quarantine the movement of the polymer chains with CNT according to the theory of inorganic-polymer composite materials as shown in figure 5.

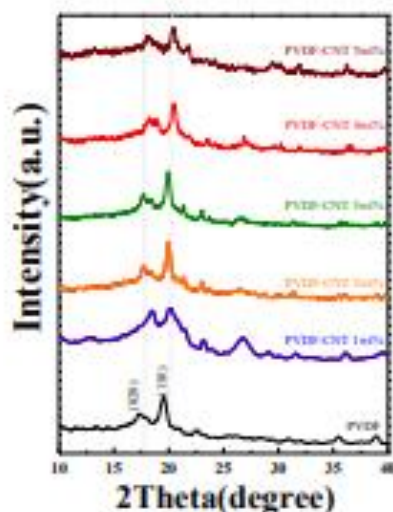


Figure 4. Polymer X-ray diffraction patterns (PVDF-CNT) when conditional nanotubes were added 1wt%, 2wt%, 3wt%, 4wt%, 5wt%, respectively.

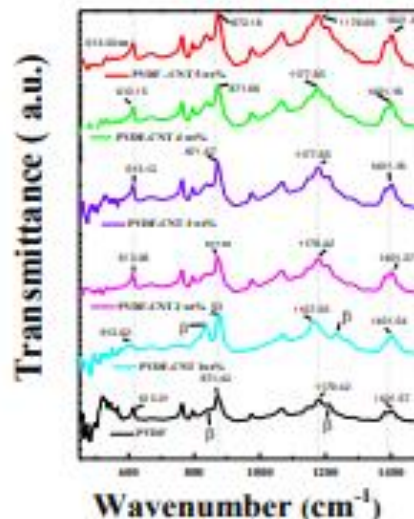


Figure 5. When analyzed by Fourier Transform Infrared spectroscopy of polymer material (PVDF) by adding carbon nanotubes (CNT).

The piezoelectric material obtained by extruding PVDF and PVDF-CNT tape with a thickness of 0.02 mm tape was made by cutting into a  $1 \times 1 \text{ cm}^2$  wide sheet and applied with silver glue. In the area of the top-bottom surface of the piezoelectric and leave the edge of the 0.5 mm piezoelectric surface with masking tape and let the silver glue dry, take 2 hours and check the polarity. By testing the completely dry silver glue conductivity, and checking the electrodes above and below the PVDF plate, the piezoelectric was not short-circuited. After that, the polling tool was polled. In which the device has two parts the first part is the Hi-Volt generator set. The second part of the refrigeration unit, the pole, the upper copper plate head, connected to the PVDF plate, the piezoelectric, prepared to glue silver, size  $1 \times 1 \text{ cm}^2$ . A polling quantity of 6 kV per 1 mm thickness of PVDF, which must be polled at least 0.12 kV potential difference. In the experiment, the polls at 1.5 kV with PVDF-CNT poles ranged from 0% to 5%, respectively, figure 6 and the measurement results of the  $d_{33}$  coefficient are shown in figure 7.



Figure 6. shows the process of poling the PVDF-CNT

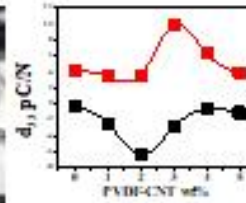


Figure 7. Measurement results of the  $d_{11}$  coefficient

#### The process of fabricating module PVDF-CNT and electrical measurement results

Piezoelectric sheet PVDF-CNT was prepared after the extrusion of the tape. Cut to a size width 1cm, length 2 cm, apply with silver glue on both sides top - bottom by leaving the edges of the electrodes not aligned for the top and bottom. After that, dry the silver glue with heat to dry the silver glue completely, take 1 hour. Once the silver glue dries, check the electrode conductivity. Piezoelectric PVDF-CNT, then pole light, after the pole is finished, apply to coat the plate. Piezoelectric PVDF-CNT with hot rolled plastic, 1.2 cm wide, 2.2 cm long, and then pierce the alternating pole. Bring copper to make a connective clamp to the electrode plate with silver glue and PVDF-CNT in figure 8.

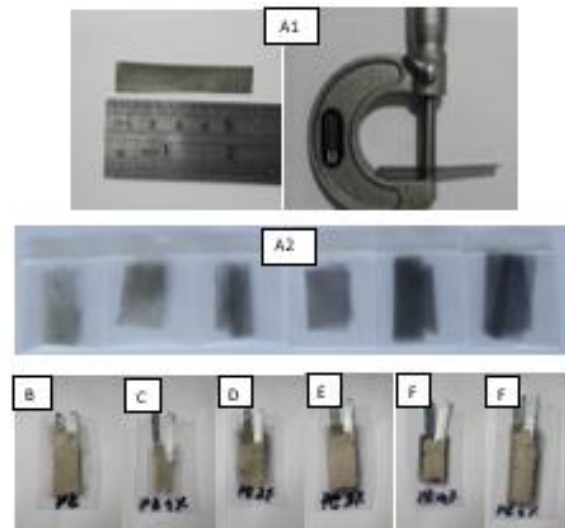


Figure 8. The model of PVC piezoelectric device design (A1,A2) PVDF (B) PVDF-CNT1% (C) PVDF-CNT2% (D) PVDF-CNT3% (E) PVDF-CNT4% (F) PVDF-CNT5%(F).

Electrical measurement procedure PVDF-CNT 0% to5% from the PVDF-CNT ad piezoelectric module is applied to a mechanical force device that is made into a device that can be applied to the surface of the ad piezoelectric surface. Rick connect the pizo electrode to the probe of the oscilloscope. Connect it to the notebook, display on the screen and adjust the PVDF-CNT piezoelectric voltage measurement value from 0% to 5%. The result of the average voltage measurement of 3.8V, 4.9V, 8.1V, 21.2V, 7.9V, 6.1V, respectively, as shown in Figure 9. The effect of the electric voltage with the greatest percentage of CNT is 3%, as shown in figure 10. At 230  $\mu$ W shown in figure 11, the effect of the capacitance of 0.1 $\mu$ F, voltage at 2.9 V, 1  $\mu$ F, voltage at 1.5V, 10  $\mu$ F, voltage at 1.2 V is shown in Figure 12.

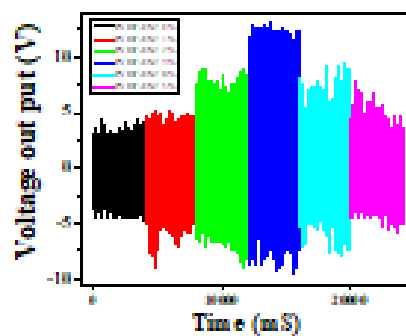


Figure 9. The results of the measurement of average voltage difference (0% to5% at 3.8V, 4.9V, 8.1V, 21.2V.

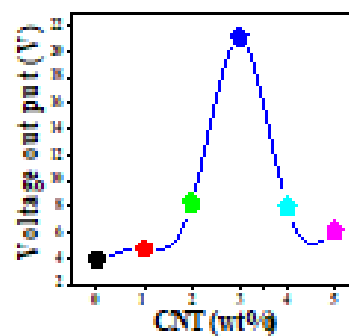


Figure 10. The effect of the electric potential difference with the largest percentage of CNT is 3% .

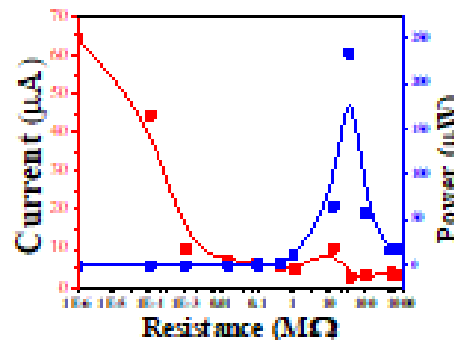


Figure 11. Effect of the maximum power output at 230  $\mu$ W.

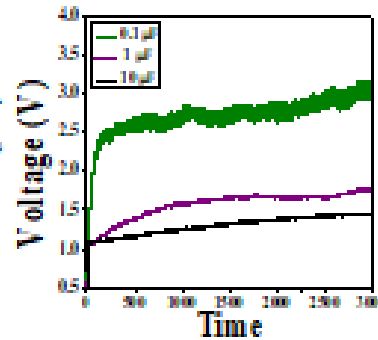


Figure 12. Effect of capacitance 0.1 $\mu$ F voltage at 2.9 V, 1 $\mu$ F voltage at 1.5V, 10 $\mu$ F potential difference of 1.2V.

Measure the electric potential of Piezoelectric electric that is attached to the wind turbine vertical axis with a height of 1.5 meters, a radius of 1.2 meters wide, with 6 air receipts. Take the module with the piezoelectric attached to the vertical axis of the wind turbine. Then when the branches of the wind turbine rotates at a speed of 0.1Hz, 1Hz, 5Hz, 10Hz, 15Hz with mechanical energy causing the branches to touch pushing the module piezoelectric to bend which is attached to the center axis and therefore diverting electricity and measure the electric voltage with an oscilloscope. The electrical output comes in a periodic ripple which results from the turbine branches which has a gap of 6 branches per rotation and the potential difference average at 1.1V, 1.8V, 3.5V, 4.8V, 5.3V as in Figure 13.

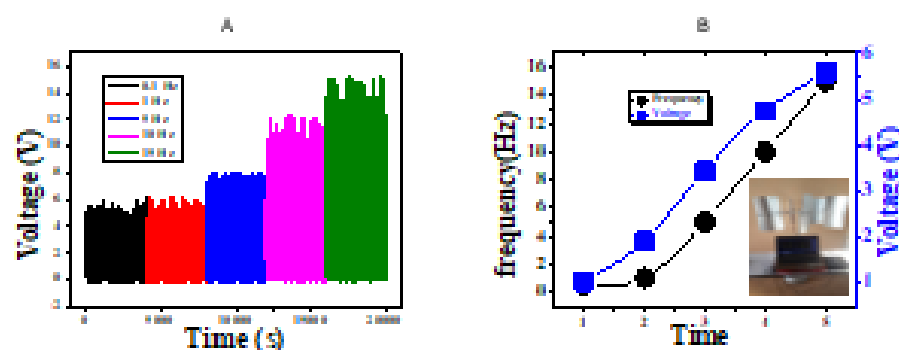


Figure 13. Shows the electric potential difference piezoelectric obtained from the rotation of the wind turbine of a speed of 0.1-15Hz (A) and the potential difference average at 1.1V, 1.8V, 3.5V, 4.8V, 5.3V (B)

#### IV. Conclusion

The 6 samples were prepared from PVDF-CNT piezoelectric material at a ratio of 1 g PVDF per CNT 0wt%, 1wt%, 2wt%, 3wt%, 4wt%, 5wt% dissolved in NMP 20ml. solvent at a temperature of 80°C. Rolled tape with a thickness of 200  $\mu\text{m}$  at a temperature of 100°C. Polarized by an electric field of 1.5kV/cm is composed of 6 samples of 1x2 cm<sup>2</sup> piezoelectric device by structural inspection. The microstructure of the PVDF-CNT with XRD, FTIR, measure the photocatalytic coefficient,  $d_{33}$ , measuring electrical values, it was found that the peak angle at XRD at 001, 110, the highest value  $d_{33}$  -2.9, 0.7 3wt% in 6 samples. 3wt%, maximum current at 0.3  $\mu\text{A}$ , maximum power 250  $\mu\text{W}$ , respectively, the capacitance effect 0.1  $\mu\text{F}$ , the potential difference at 2.9 V, as a result of the application to wind turbines. 3V at a frequency range of 1-15Hz.

#### V. Acknowledgments

This work was supported by the Piezoelectric Research Laboratory, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, and Nong College Nakhosiphansom University Thailand.

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**Dielectric and Ferroelectric Poperties of  $\alpha$ - $\gamma$ -Phase  
Polyvinylidene Fluoride-Carbon Nanotube Films by Low-Cost  
Fabrication**

Journal:	<i>Journal of Materials Science &amp; Technology</i>
Manuscript ID	Draft
Manuscript Type:	Research Article
Date Submitted by the Author:	n/a
Complete List of Authors:	Kaeopisan, Aphisak; Sakon Nakhon Rajabhat University, Faculty of Science and Technology Thanachayanon, Chanchana ; National Science and Technology Development Agency, National Metal and Materials Technology Center Wattanasarn, Hassakorn; Sakon Nakhon Rajabhat University, Sciences and Techonolgy
Keywords:	Poly(vinylidene fluoride), Carbon nanotubes (CNTs), Ferroelectric properties, Dielectric constant, Polymer composite
Speciality:	Piezoelectric Materials, Ferroelectric Materials, solid state reaction process, Tape casting ceramic, Multilayer ceramic

## BIOGRAPHY



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A.D. 2013	- M.Sc. in Science-Physic, Sakon Nakhon Rajabhat University, Sakon Nakhon, Thailand, 2013
A.D. 2020	- Ph.D. in Science-Physic, Sakon Nakhon Rajabhat University, Sakon Nakhon, Thailand, 2020

Appendix B

Publications

## Step Synthesis, Electrical Generator of PVDF/CNTs Piezoelectric

Aphisak Kaepisan (1), Hassakorn Wattanasarn (2)\*

(1,2) Program of Physics, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, Sakon Nakhon, 47000, Thailand.

### Abstracts:

The piezoelectric is a material that can convert mechanical energy into electrical energy and can convert electrical energy into mechanical energy. It is a device that is fabricated from a piezoelectric material. It may be in the elemental form or composite materials in general. The composite material, or composite material, was one material as the main body and the other was the first dispersed material using polyvinylidene fluoride (PVDF,  $(C_2H_2F_2)_x$ ) powder. PVDF 1% by fill weight. 6 samples were doped with carbon-nanotube CNT powder, 0.001%, 0.002%, 0.003%, 0.004%, and 0.005%. The N-Methyl-2-pyrrolidone solution. [ NMP ( $C_4H_7NO$ )] 20 mL, the solution was rolled, casting tape at 80 °C, then extruded and molded to 200  $\mu$ m thick. The film was inspected with XRD to determine the structure from preparation to make the pole with silver glue. Conducted to arrange the electrodes with a 1.5 kV / 200  $\mu$ m field was conducted to arrange, the dielectric coefficient  $d_{33}$  2.90 to 9.77 pC/N, the highest of 3wt% in 6 samples was measured, measure the potential difference 21.2V was also measured, the highest value 3wt%. Maximum current at 0.3  $\mu$ A, maximum power 230  $\mu$ W, respectively, the capacitance of 0.1  $\mu$ F, the potential difference at 2.9V, as a result of the application to wind turbines. 3V at a frequency range of 1-15Hz.

**Keywords:** PVDF materials, synthesis Piezoelectric, Electrical properties.

Date of Submission: 28-10-2020

Date of Acceptance: 09-11-2020

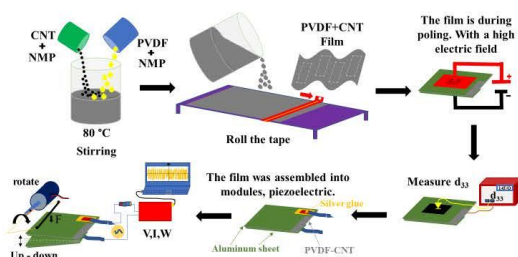
### I. Introduction

Energy is essential to human beings. There are many forms of energy such as thermal energy, optical energy, electrical energy, mechanical energy which can be transformed from mechanical to electrical energy. The piezoelectric is a material that can convert mechanical energy into electrical energy and can convert electrical energy into mechanical energy as well. May be in elemental form or composite materials in general composites, or composite materials, where one type of material as the main body and the other being the dispersed material of the first material. The combined components differ in form and form. Chemical elements and are not mutually solvent. The original properties of each component will have one of the more prominent properties, resulting in a new material with all the good properties of the substrate [1-3]. The piezoelectric composite material is fabricated. Is polyvinylidene-fluorine and carbon-nanotubes. The prepare polyvinylidene-fluoride (PVDF,  $(C_2H_2F_2)_x$ ), is a material with some outstanding properties such as high flexibility and flexibility [4-6]. Has a smooth finish without the need for polishing. It is lightweight, can be rolled into a thin sheet, and has multiple production processes. The carbon nanotubes are good electrical and thermal materials. When it is fabricated as a composite material [7-11]. A good electrical piezoelectric element is expected to be useful for other electrical and electronic measurement applications.

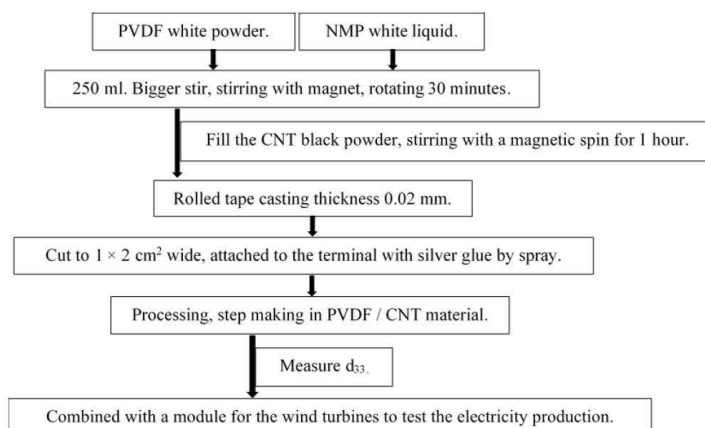
### II. Material And Methods

#### Preparation of substances.

Prepare polyvinylidene fluoride (PVDF,  $(C_2H_2F_2)_x$ ), white powder, weigh 1 gram of 6 samples in a test glass tube, sealed with aluminum foil, then carbon nanotubes. (MWCNT) multi-walled black powder, weighing 0.001 grams, 0.002g, 0.003g, 0.004g, 0.005g respectively, stored in 5 test tubes. Next, measure the N-Methyl-2-pyrrolidone solution. [ NMP ( $C_4H_7NO$ )] White clear liquid Get a volume of 20 ml., Amount 6 samples respectively Figure 1.



**Figure1.** Simulation of the process of invention of the piezoelectric coefficient measurement and electrical measurement.



**Figure2.** Procedure sequence for the experiment in making a piezoelectric device.

#### Materials preparation of Piezoelectric samples.

##### Prepare the solution.

The next step is to prepare an unused carbon PVDF solution. Take 20 ml of NMP solution and pour it into a 250 ml bigger, then place it on an electric stove that was set to a temperature of  $80^{\circ}\text{C}$  after that. Pour 1 g of PVDF powder into a bigger containing patterned material, then stir with a magnetic spin for 1 hour. Example 1 is a solution that dissolves into white, bright, carbon-nanotube PVDF. The next step is to prepare the PVDF-CNT solution with carbon-nanotubes. By pouring 20 ml of NMP solution into 250 ml of the bigger, then place on the electric stove with temperature setting at  $80^{\circ}\text{C}$ , then pour the 1 g PVDF powder into the bigger containing the substance is then stirred and stirred by a magnet to spin autism. Take 30 minutes and then mix the carbon nanotubes into the solution. Example 2 is a solution that dissolves into a thin black color. After spinning for 1 hour, PVDF-CNT with carbon nanotube 0.001g was obtained. Example 2, the next step is to prepare the sample 1, 3, 4, 5, 6 like the 2nd sample, respectively.

##### Rolled casting tape.

Next, take the solution 1-6 to roll the tape. By bringing each sample solution to be poured onto a sheet of tape extruder containing heat, adjust the temperature to  $80^{\circ}\text{C}$  and then extrude the PVDF solution to a thickness of 0.02 mm. After that, wait for the PVDF solution to evaporate the solvent. After 30 minutes, it will turn into a

*Step Synthesis, Electrical Generator of PVDF/CNTs Piezoelectric*

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Measurement of  $d_{33}$  / hysteresis / XRD / FTIR

The synthesized samples were analyzed with  $d_{33}$  YE2730- $d_{33}$ Meter / Fourier Transform Infrared Spectroscopy (FT-IR) using VERTEX 70 using 532nm lasers in the wavelength of 400–1,400  $\text{cm}^{-1}$  / X- analysis. Ray diffraction (XRD) is achieved by SHIMADZU-LABX-XRD-6100 / TREK dielectric meter MODEL20 / 20c-Hs HIGH VOLTAGE AMPLIFIER / morphological examination of the above samples using a shining electron microscope.

**Module.**

Take the PVDF, and PVDF-CNT film tapes, example 1-6 to cut to  $1 \times 2 \text{ cm}^2$  in width to do a module. At this stage, prepare a silver glue solution mixed with 1 to 10 distilled water in a spray bottle. Prepare two screens that are strung with a frame that has a screen size of  $0.9 \times 1.9 \text{ cm}^2$  in length. Next, take the PVDF film tape to place between the polar screen and spray the prepared silver glue on the screen on both sides, then iron with the screen and remove the PVDF from wait for the screen to dry for 30 minutes and continue for 2-6 samples respectively.

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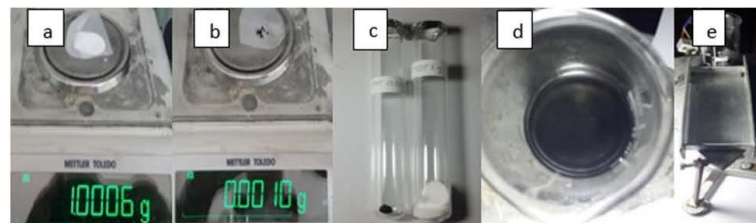


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When analyzing the polymer with X-ray diffraction technique (XRD), it was found that the form of adding carbon nanotubes to 1wt% -5wt% polyvinylidene fluoride had an effect. To the internal structure using the sample, there is a mixed crystal structure  $\alpha$  and  $\beta$ . In every substance, it was also found that the deflection angle shifted to a higher value when the carbon nanotube added percentage shown in figure 4. The addition of carbon nanotubes in polyvinylidene fluoride changes within the internal structure.

When the results were analyzed by Fourier Transform Infrared Spectroscopy of Polymer Materials (PVDF) techniques with the addition of carbon nanotubes (CNT) by percentage weight (1wt%, 2wt%, 3wt%),

4wt%, 5wt%) into the structure of polyvinylidene fluoride by analysis from Fourier Transform Infrared Spectroscopy (FTIR) technique. As shown in figure 5, it was found that (frequency) or wave number (wave number) PVDF at  $613.01\text{ cm}^{-1}$ ,  $871.42\text{ cm}^{-1}$ ,  $1179.42\text{ cm}^{-1}$ ,  $1401.57\text{ cm}^{-1}$  / PVDF-CNTwt1% at  $613.02\text{ cm}^{-1}$ ,  $871.53\text{ cm}^{-1}$ ,  $1179.55\text{ cm}^{-1}$ ,  $1401.54\text{ cm}^{-1}$  PVDF-CNTwt2% at  $613.06\text{ cm}^{-1}$ ,  $871.56\text{ cm}^{-1}$ ,  $1179.42\text{ cm}^{-1}$ ,  $1401.37\text{ cm}^{-1}$  / PVDF-CNTwt3% at  $613.12\text{ cm}^{-1}$ ,  $871.67\text{ cm}^{-1}$ ,  $1179.65\text{ cm}^{-1}$ ,  $1401.18\text{ cm}^{-1}$  / PVDF-CNTwt4% at  $613.15\text{ cm}^{-1}$ ,  $871.66\text{ cm}^{-1}$ ,  $1179.65\text{ cm}^{-1}$ ,  $1401.18\text{ cm}^{-1}$  and PVDF-CNTwt5% at  $613.00\text{ cm}^{-1}$ ,  $871.18\text{ cm}^{-1}$ ,  $1179.69\text{ cm}^{-1}$ ,  $1401.14\text{ cm}^{-1}$  were found to have various peaks. As in the PVDF spectrum, there was no chemical interaction between CNT and PVDF. Thermal stability and the nanometer addition in PVDF increased after composite with CNT as a result of quarantining the movement of the polymer chains with CNT according to the theory of inorganic-polymer composite materials as shown in figure 5.

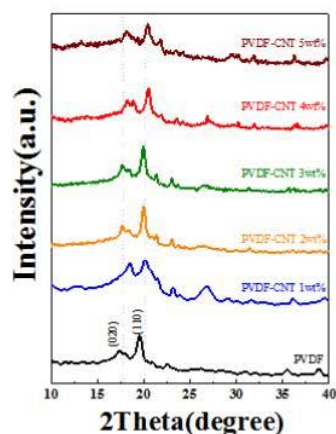


Figure 4. Polymer X-ray diffraction patterns (PVDF-CNT) when conditional nanotubes were added 1wt%, 2wt%, 3wt%, 4wt%, 5wt%, respectively.

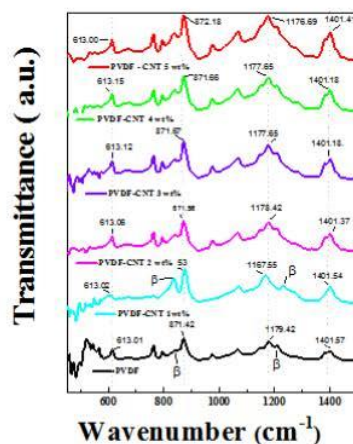


Figure 5. When analyzed by Fourier Transform Infrared spectroscopy of polymer material (PVDF) by adding carbon nanotubes (CNT).

The piezoelectric material obtained by extruding PVDF and PVDF-CNT tape with a thickness of 0.02 mm tape was made by cutting into a  $1 \times 1\text{ cm}^2$  wide sheet and applied with silver glue. In the area of the top-bottom surface of the piezoelectric and leave the edge of the 0.5 mm piezoelectric surface with masking tape and let the silver glue dry, take 2 hours and check the polarity. By testing the completely dry silver glue conductivity, and checking the electrodes above and below the PVDF plate, the piezoelectric was not short-circuited. After that, the polling tool was polled. In which the device has two parts the first part is the Hi-Volt generator set. The second part of the refrigeration unit, the pole, the upper copper plate head, connected to the PVDF plate, the piezoelectric, prepared to glue silver, size  $1 \times 1\text{ cm}^2$ . A polling quantity of 6 kV per 1 mm thickness of PVDF, which must be polled at least 0.12 kV potential difference. In the experiment, the polls at 1.5 kV with PVDF-CNT poles ranged from 0%

to 5%, respectively, figure 6 and the measurement results of the  $d_{33}$  coefficient are shown in Figure 7.



Figure 6. shows the process of polling the PVDF-CNT

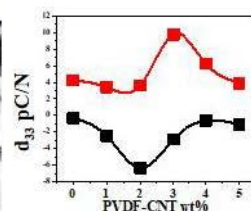


Figure 7. Measurement results of the  $d_{33}$  coefficient

#### The process of fabricating module PVDF-CNT and electrical measurement results

Piezoelectric sheet PVDF-CNT was prepared after the extrusion of the tape. Cut to a size width 1 cm, length 2 cm, apply with silver glue on both sides top - bottom by leaving the edges of the electrodes not aligned for the top and bottom. After that, dry the silver glue with heat to dry the silver glue completely, take 1 hour. Once the silver glue dries, check the electrode conductivity. Piezoelectric PVDF-CNT, then pole light, after the pole is finished, apply to coat the plate. Piezoelectric PVDF-CNT with hot rolled plastic, 1.2 cm wide, 2.2 cm long, and then pierce the alternating pole. Bring copper to make a connector clamp to the electrode plate with silver glue and PVDF-CNT in Figure 8.

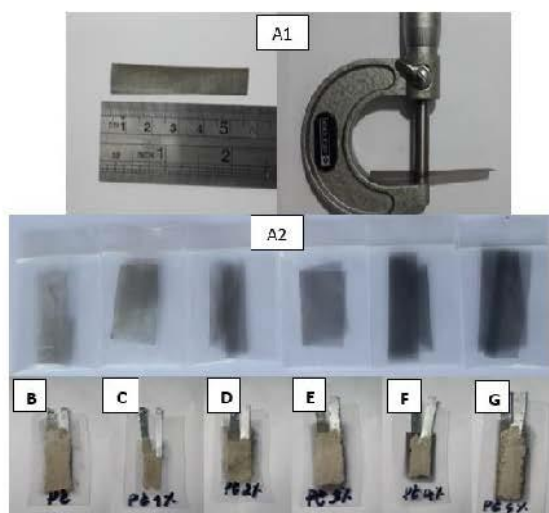


Figure 8. The model of P/C piezoelectric device design (A1,A2) PVDF (B) PVDF-CNT1% (C) PVDF-CNT2% (D) PVDF-CNT3% (E) PVDF-CNT4% (F) PVDF-CNT5%(G).

Electrical measurement procedure PVDF-CNT 0% to 5% from the PVDF-CNT aduipisoelectric module is applied to a mechanical force device that is made into a device that can be applied to the surface of the aduipisoelectric surface. Rick connect the piso electrode to the probe of the oscilloscope. Connect it to the notebook, display on the screen and adjust the PVDF-CNT piezoelectric voltage measurement value from 0% to 5%. The result of the average voltage measurement of 3.8V, 4.9V, 8.1V, 21.2V, 7.9V, 6.1V, respectively, as shown in Figure 9. The effect of the electric voltage with the greatest percentage of CNT is 3%, as shown in Figure

10. At 230  $\mu$ W shown in Figure 11, the effect of the capacitance of 0.1  $\mu$ F, voltage at 2.9 V, 1  $\mu$ F, voltage at 1.5 V, 10  $\mu$ F, voltage at 1.2 V is shown in Figure 12.

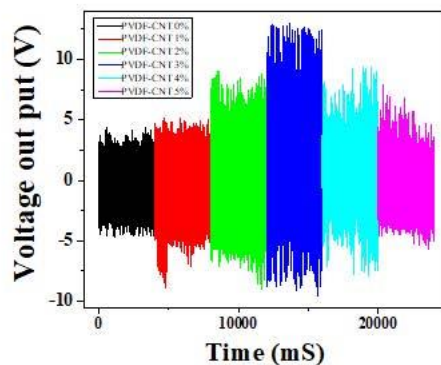


Figure 9. The results of the measurement of average voltage difference 0% to 5% at 3.8V, 4.9V, 8.1V, 21.2V, 7.9V, 6.1V.

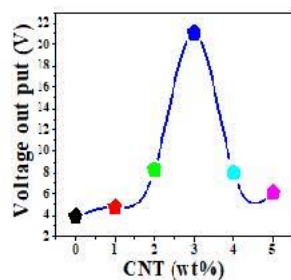


Figure 10. The effect of the electric potential difference with the largest percentage of CNT is 3%.

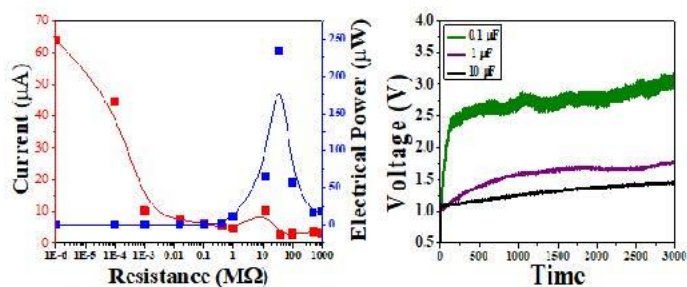


Figure 11. Effect of the maximum power output at 230  $\mu$ W.

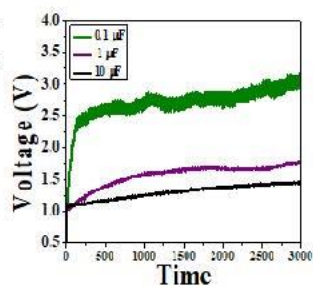
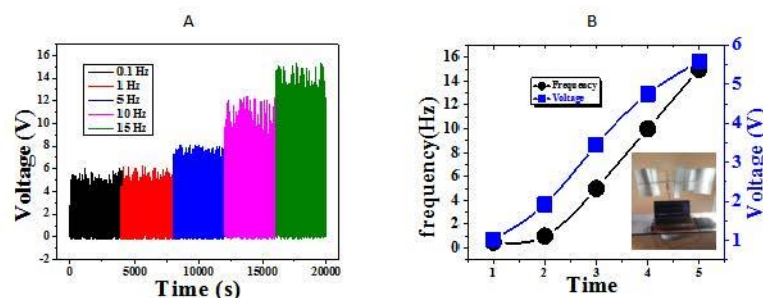


Figure 12. Effect of capacitance 0.1  $\mu$ F voltage at 2.9 V, 1  $\mu$ F voltage at 1.5V, 10  $\mu$ F potential difference at 1.2V.



Measure the electric potential of Piezoelectric electric that is attached to the wind turbine vertical axis with a height of 1.5 meters, a radius of 1.2 meters wide, with 6 air receipts. Take the module with the piezoelectric attached to the vertical axis of the wind turbine. Then when the branches of the wind turbine rotates at a speed of 0.1Hz, 1Hz, 5Hz, 10Hz, 15Hz with mechanical energy causing the branches to touch pushing the module piezoelectric to bend which is attached to the center axis and therefore diverting electricity and measure the electric voltage with an oscilloscope. The electrical output comes in a periodic ripple which results from the turbine branches which has a gap of 6 branches per rotation and the potential difference average at 1.1V, 1.8V, 3.5V, 4.8V, 5.3V as in Figure 13.



**Figure 13.** Shows the electric potential difference piezoelectric obtained from the rotation of the wind turbine at a speed of 0.1-15Hz(A) and the potential difference average at 1.1V, 1.8V, 3.5V, 4.8V, 5.3V (B)

#### IV. Conclusion

The 6 samples were prepared from PVDF-CNT piezoelectric material at a ratio of 1 g PVDF per CNT 0wt%, 1wt%, 2wt%, 3wt%, 4wt%, 5wt% dissolved in NMP 20mL solvent at a temperature of 80 °C. Rolled tape with a thickness of 200 μm at a temperature of 100 °C. Polarized by an electric field of 1.5kV / is composed of 6 samples of 1x2 cm<sup>2</sup> piezoelectric device by structural inspection. The microstructure of the PVDF-CNT with XRD, FTIR, measure the photocatalytic coefficient.  $d_{33}$ , measuring electrical values, it was found that the peak angle at XRD at 020,110, the highest value  $d_{33}$  -2.9,9.7 3wt% in 6 samples. 3wt%, maximum current at 0.3μA, maximum power 230 μW, respectively, the capacitance effect 0.1μF, the potential difference at 2.9 V, as a result of the application to wind turbines. 3V at a frequency range of 1-15Hz.

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**Dielectric and Ferroelectric Poperties of  $\alpha$ - $\gamma$ -Phase Polyvinylidene Fluoride-Carbon Nanotube Films by Low-Cost Fabrication**

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