Investigational study of Material Morphology, Structure and Conductivity characteristics of Rochelle salt based PVDF composites.

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Abstract – *The Rochelle salt which is also familiarly known as Potassium Sodium Tartrate also commonly called as Seignette salt. This material has good piezoelectric properties and effects; it is obtained from natural crystal which is basically obtained inside the surface of barrels at the cellar. It is used in electroplating in electronics field. The present paper work describes the structure which is composed of Rochelle salt which is easily developed with polymer composite to obtain add on advantages of piezo effect also it is environmentally friendly, the product is biocompatible in nature. In the view of a cleaner energy harvesting technology, active sensor response, this material is developed to study its properties.*

The major methods of processing such as polymerization, and other important material characteristics have been studied such as Morphological, microcrytallinity parameters of Rochelle salt have depicted that it consists of pure form of Rochelle salt through EDS analysis, it shows that it moderately aligned peaks in X ray diffraction analysis. FTIR testing showed satisfactory absorption behavior which is illustrated. The Rochelle salt based PVDF polymer composite also exhibited to Electrical good conductivity behavior is briefed to uplift the potential of this green piezoelectric material.

Key words: Rochelle salt, PVDF, XRD, SEM, EDX, Dielectric.

1. INTRODUCTION.

In past few decades, a large funding has been invested in the domain of biomedical sectors and related industries as a result many innovation in the light of biosensors are been developed [1]. This innovations has lead to numerous current prospects for the use of biosensors in the detection, monitoring, and medicinal diagnosis of biological molecules and diseases such as sugar (diabetes), dangerous death deceases such as cancer cell detection, and so on [2-5]. The "electrical activity" of many materials has been known to a mankind for several decades. In 1880 Jacques and Pierre Curie discovered that the compression of single crystal samples tourmaline along certain directions yielded have the presence of electrical charge on the sample surface [6].In the early years of research, the sonar systems two both important materials such as quartz and Rochelle salt were used for electrical investigational study. Quartz had better mechanical properties, which was advantageous in the fabrication process.

On the other hand, Rochelle salt had better piezoelectric response; also it is very sensitive acoustic and vibration mechanical application material. The sodium potassium tartrate tetrahydrate ($NaKC_4H_4O_6{\bullet}4H_2O$)which also called Rochelle salt, is one of the ferroelectric and piezoelectric materials which include no rare element in its composition, very usefully in food industries, preparation of silver mirrors and it is good environmental compatibility. Rochelle salt is the oldest and has been for a long time the only known ferroelectric and piezoelectric material [11, 12].

Polyvinylidene fluoride or most familiarly known as PVDF which is highly not responding thermoplastic fluoropolymer material which is synthesized by the polymerization of diflouride. PVDF has four crystalline phases such as alpha (α), beta (β), gama(γ) and delta (δ) which strongly depends on chain confirmation [7][8]. PVDF is most favorably used in piezoelectric energy harvesting, sensors, transducers applications etc. The PVDF polymer has several properties such as biocompatible, it is resistance towards the chemicals, excellent thin films development quality, it is cost effectiveness compared to other materials [9][10]. Among all four crystalline phases, it is observed that β spontaneous polarization capability and piezoelectric sensitivity, due to this characterization it exhibits electro active phase in PVDF polymers, where in this property can be utilized to form nanogenerator.

2. EXPERIMENTAL DETAILS.

2.1 Materials and methods: The Rochelle salt is a type of crystalline solid material, which is also known by other name Potassium sodium tartrate tetrahydrate. The double salt of Rochelle salt and mono potassium phosphate were the piezoelectric initial materials which were found out. David Brewster was the first time demonstrated the piezoelectric properties from Rochelle salts [13].

These material characteristics led to transducers development had an exceptionally high output rate with typical pick-up cartridge outputs as much as two volts or more. Rochelle salt is deliquescent so any transducers based on the material deteriorated if stored in damp conditions. The important physical properties of Rochelle salt are tabulated in the table-1, as this Rochelle salt was purchased from Aldrich company private ltd.

Table: -1: Physical properties of Rochelle salt

Sl. No.	Properties	Rochelle salt
1	Chemical empirical formula	$KNaC_4H_4O_6 \cdot 4H_2O$
2	Molar mass	282.1 g/mol
3	Outward form	It is colourless in nature
4	Smell(Odor)	It has no smell
5	Density	1.78 g/cm^3
6	Melting point	It has the property to melt at 75˚C
7	Its steaming point or Boiling	It can withstand heat up to 220˚C
8	Solubility in water	26 g / 100 mL (0 °C); 66 g / 100 mL (26 °C)
9	Solubility in ethanol	It is insoluble.

The PVDF is a mixture of both crystalline and amorphous structure that has been extensively considered for its prime piezoelectric properties, high chemical resistance in nature, strength, and it is also thermal resistance [14]. Among them, the beta (β) phase has the largest spontaneous polarization per unit cell and therefore presents the highest electro active properties [15]. The contents in PVDF was found to increase by about 8% with a silver nanoparticle ,AgNPs content of 0.4%, which is most vital and useful silver nano particle which has good piezoelectric characteristics for engineering applications [16]. This chemical is also purchased from Aldrich company private ltd.

The service temperature up to 150˚C exhibit good combination of properties such as

•Good chemical resistance.

•High mechanical toughness.

•Good Piezoelectric and pyroelectric properties.

•As well as good process ability.

2.2 Overall Methodology of the work.

2.2.1 Preparation of Rochelle salt based with PVDF Polymers.

In detail, the polymerization process is carried out as follows. For a polymer of PVDF, 0.5%,1% and 2% of Rochelle salt is mixed, for 1gram of PVDF,0.01gram, 0.02gram of Rochelle salt which gives rise to 0.5%,1% and 2% of polymers, is processed. Then the homogenous solution of polymer composites of Rochelle salt with PVDF polymer based solution was poured in to a clean glass mould and the solvent is dried by using hot air oven at 60˚C in the absence of water for 3-4 hours. After 3 hours the polymer films were carefully peeled from the glass tray. In this present method, the calculated amount of PVDF was considered and diffused in suitable solvent amalgam i.e, dimethyl formamide and dimethyl acetamide in the definite proportion by keeping it hot plate. The process also involves Laser ablation is a method of breaking down one part of material to create a micro feature using a laser beam.

Later the chemical precipitation solution is heated with high temperature. In further stage, magnetic steer procedure is carried out and set the temperature up to 70˚-100˚C or even above. Hence the PVDF based Rochelle salt composite with different percentages is carried out. To fabricate the electrode (silver paste), the as-prepared Rochelle salt based PVDF composite film initially it was carefully cut into 7 cm x 3 cm dimensions and the silver gel was uniformly coated using the doctor blade method. A small piece of conductive adhesive copper tape was attached over the composite, which behaves like positive and negative terminals as shown in the fig-1.

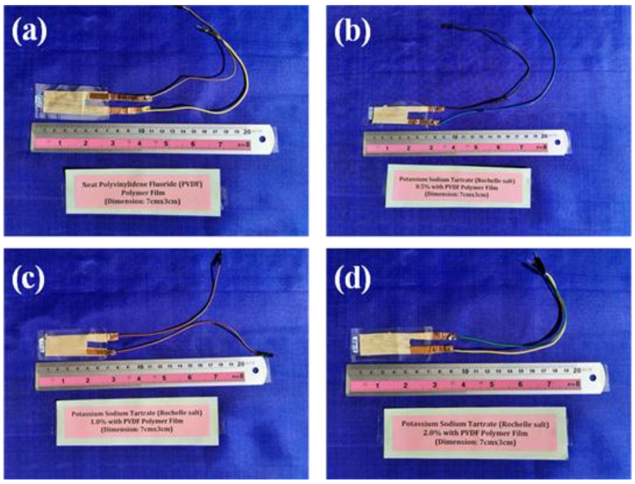

Fig-1: Actual view of (a) Neat PVDF and (b-d) Rochelle salt powder-PVDF polymer electrode films with 0.5, 1 and 2 wt % of Rochelle salt powder compositions.

2.2.2 Palletization of Plain Rochelle salt.

The Rochelle salt powder sample is weighed of 0.1 gram, individual samples are grinded the by using pestle and mortar. Transfer the grinded sample to the pallet setup. The setup was assembled tightly with instrument. The pressure of 15 Kg/cm^2 is applied to pallet equipment. The applied pressure is maintained for 2-4 minutes. Finally the pressure was released manually and circular pallets are collected from pallet set as shown in the Fig-2.The pallets of Rochelle salt elements is prepared in order to perform morphological studies, electrical behavior studies.

Fig-2: Rochelle salt Pallet disc form Samples

2.2.3 Polymerization technique to obtain Rochelle salt based PVDF Polymer thin films.

The weight ratio of polymer PVDF based Rochelle salt is first taken to carryout the polymerization process. In this method calculated amount PVDF was weighed and is dissolved with suitable solvent mixture of Dimethyl formide (DMA) in a define proportion by keeping it in hot plate with steering at 55˚C-60˚C for one hour duration in a beaker. After complete dissolution of the PVDF then add the calculated amount of rochelle salt filler and homogenous solution was obtained by using ultrasonication[17][18].

3. MATERIAL CHARACTERIZATION STUDIES.

3.1 X-ray diffraction (XRD).

The XRD equipment specifications as follows Rigaku smart lab diffractometer with radiation Cuk α Consisting the wavelength 1.5406 Å spec. The equipment can scan the particles with the range span of 6°– 80° with the scan speed of 5˚/min in steps of 0.02°. The system execution of process voltage and its current values are as follows were 30 kV and 15 mA respectively. Material structure performance study of Rochelle salt/Quartz/PZT/BZT and other nanohybrid was performed by using X-ray Diffracto meter at room Temperature [18].

3.2 Scanning Electron Microscopy (SEM).

The Scanning Electron Microscopy (SEM) Make., HITACHI, S3400N (Japan) , it has an voltage acceleration of about 5-15KV, basically this technique is used in studying of surface conducting. The device was further developed by improving the design of S3000N, which was well accepted in the global market. It take 6 minutes of duration for cold start, and less than 100 seconds to exchange specimen, it requires only 2.0KVAof power supply[17][18].

3.3 Energy Dispersive X-Ray Analysis (EDX).

It is also known as EDS or EDAX, which is a basically an X-ray elemental technique used to identify the elemental composition and allocate together with atomic number for the materials such PZT, BZT, SiO_2, Rochelle salt, Polymers etc. The device has typical product research application, reformulation, etc. The equipment maker, is thermo scientific NORON7, it has the capacity to redefine x-ray pulse process efficiently, such as more than 1,000,000 counts per second more than double previously available count rates. It can reduce amount of time required to process and also execute to collect the data required [18].

3.4 Fourier Transform Infrared Spectroscopy (FTIR).

FTIR spectroscopy equipment is utilized used to ensure that raw materials, intermediate compounds and final products are within required specifications. The equipment specifications are as follows, Maker, Perkin Elmer Spectrum Version ,model spectrum 2 series, NIOS2 Main software, which is of standard with high performance DTGS (Deuterated Triglycine Sulfate) MIR detector. Wherein it is most ideal and most suitable for low-light, high throughput applications. The spectral range is from 8,300-350cm^{-1} through the data collection, which has the best data resolution of 0.5cm^{-1}, optional Zn Se windows for exceptionally humid environment conditions.

3.5 Precision Impedance Analyzer.

The impedance analyzer maker is Wayne Kerr, the 6500B series which is the entry level model in the range. This device provides precise and rapid testing of materials up to 120 MHz. It has best in class the frequency range of about ±0.05%. These specifications of the instrument make the process high accuracy, component design which is ideal tasks for many choice of experimentation. Some of the electrical behavior analysis such as conductance, dielectric constant, dielectric loss, capacitance basic accuracy is an excellent ±0.05% can be executed. The instrument will calculate the nearest equivalent circuit parameters for the measurement tracks and revise the results. Alternatively, the parameters of the component may be entered so that instrument will automatically plot the frequency characterization.[16-18].

4. THE OUTCOMES AND DISCUSSIONS.

4.1 X-Ray Diffraction Analysis of Rochelle salt with PVDF based composites.

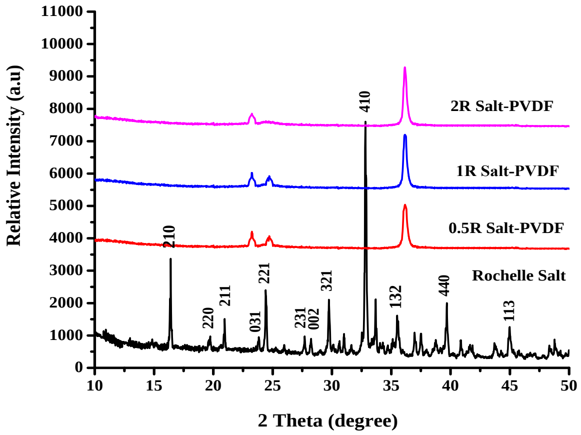

Fig-3. XRD pattern of as prepared Rochelle salt with different % weight PVDF based composites.

The representative powder X-ray diffraction pattern of Potassium sodium tartrate tetrahydrate is given in Fig.3. The above plot of the diffraction pattern is represented in the range 2θ between 10˚ to 50˚ where the diffraction peaks at 2θ values of 16.41°, 19.72°, 20.96°, 23.81°, 24.42°, 27.60°, 28.12°, 29.71°, 32.83°, 35.62°, 39.63° and 44.92° which is indexed by (210), (220), (211), (031), (221), (231), (002), (321), (410), (132), (440), and (113) , the reflection planes of Rochelle salt with Orthorhombic crystal with space group P21212 particle structure with lattice parameter α = 11.7859 Å, b = 14.1972 Å, and c = 6.1875 Å.

Due to the polymerization process of Rochelle salt with PVDF polymer, the X-ray diffraction of polymerized materials such as 0.5%RS-PVDF, 1%RS-PVDF and 2%RS-PVDF are not well crystallized and slowly shifted in small range, but plain PVDF as depicted better peaks of crystallized materials [19].

4.2 Fourier Transforms Infrared Spectroscopy (FTIR) study for Rochelle salt and PVDF composite with different percentages.

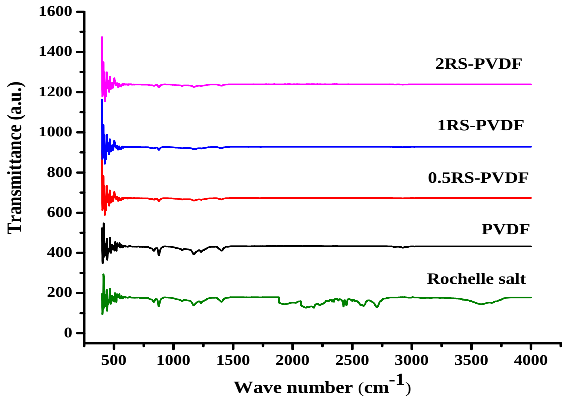

Fig.4. FT-IR spectrums of Rochelle salt and Rochelle salt based PVDF composite films.

The peaks which are related to the elongation and bending of C–C bonds which is obtained in very low frequency band region (i.e. below the value 500cm^{-1}). The broad range of C-C stretching of the bonds is 1200–800 cm^{-1} in the region. The peaks in the above fig.4, with values of 1082, 1118 and 890 cm^{-1} can be assigned vibrations of C–C stretching. The dimers ,Carboxylic acid depicts a very broad intense O–H stretching absorption in the region of 3300–2500 cm^{-1}[20].The crystal lattice consists of carboxylic acid which shows with peaks at 2978, 2924 and 3271 cm^{-1} which has witness.

The absorption bands of infrared spectra has the range of 511 and 840cm^{-1}, this range of values depicts that the PVDF polymer material contains β-phase in the structure. The band range at 764, 795 cm^{-1} has clearly showed that it consists of α phase, while other range of values 778, 795, and 834cm^{-1} have been attributed to γ phase. The 840 cm^{-1}, range of value corresponds to PVDF with β phase [21].

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4.3 SEM and EDS analysis of Rochelle salt material.

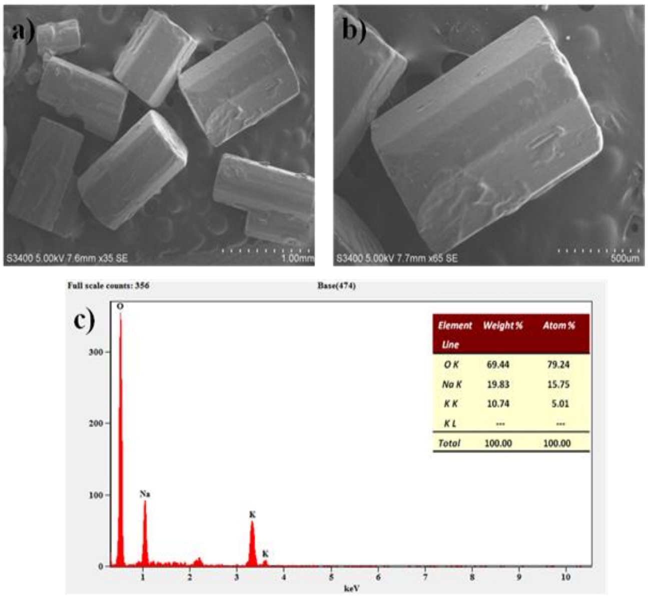

Fig.5 a) & b) are the SEM images of Rochelle salt materials and c) EDS of Rochelle salt with inserted table of different weight and atomic percentage.

The SEM is very versatile and powerful tool for material characterization study. It basically uses electrons for imaging; it shrinks the material dimensions for obtaining good morphological studies.

The micrographs depicts the 0.5-1.5 mm size of freely distributed crystals are observed in Rochelle salt materials and it is dried at required temperature about 60°C. Each crystal of Rochelle salt materials is well crystallized in orthorhombic phase.

The EDS process is studied of individual crystals, here the results of the testing is tabulated in the above fig-5(c). The elements clearly shows that all are present in the required stoichimetric amount, there is no impurities detected in the EDS spectra of the sample at the suggested temperature, which shows the material is of pure form lattice structure.

4.4 Electrical conductivity behavior of Rochelle salt based PVDF Composite materials.

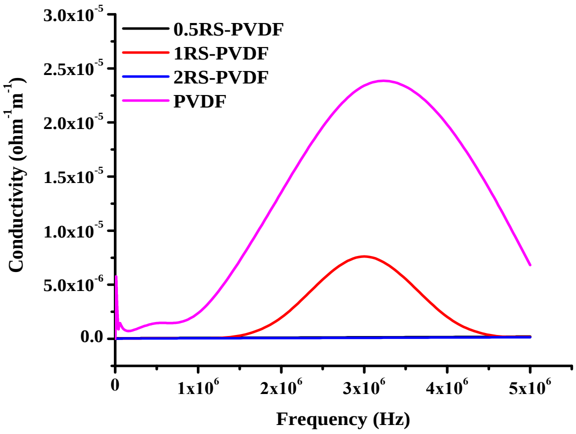

Fig.6. Dielectrical conductivity of PVDF nano-composites with different concentrations of Rochelle salt nanoparticles.

The dielectric conductivity behavior of the neat PVDF film which has compared with the polymers of Rochelle salt with the PVDF with 0.5, 1 and 2 wt % with respect to the frequency along the x axis plot in the fig.6. The Rochelle salt exhibits good dielectric constant and high piezoelectric properties [22]. It was observed that, neat PVDF exhibited good dielectrical conductivity property when compared with the different concentration of RS with PVDF.

From the graph, it is observed that 1 wt% of Rochelle salt-PVDF polymer exhibited maximum dielectric conductivity compared with the 0.5% and 2.0 wt% of Rochelle salt. The dielectric conductivity of 0.5%RS-PVDF and 2%Rochelle Salt-PVDF shows minimum performance.

5. FUTURE SCOPE.

The future scope of the material developed can be enormous used in various fields of engineering such as Energy harvesting, sensor applications can be applied on floor tiles as the vehicle is passed on the floor tiles, weight sensors, and automotive engine control system. Voltage sensors such as applications in wireless sensors.

6. CONCLUSION.

In this chapter, the study explains the ferroelectric phase transition, in Rochelle salt at macroscopic level, microscopic level. The XRD study has confirmed that the crystal system shows the diffraction pattern which is represented in the range 2θ between 10° to 50° where it clearly demonstrates the diffraction peaks. The Appearance of sharp well is not so defined peaks in XRD confirms the crystallinity of the sample is slightly shifted towards sideward. In infrared spectra, absorption bands at 511 and 840 cm^{-1} which basically shows the presence of β-phase of the PVDF. The bands at 764, 795 cm^{-1} have been attributed to the α phase while 778, 795 and 834 cm^{-1} have been assigned to γ phase and 840 cm^{-1} which correlate to the β phase of PVDF films which shows good performance and material characteristics of polymer.

The elements clearly shows that all are present in the required stoichimetric amount, there is no impurities detected in the EDS spectra of the sample. It is observed from the graph, that 1 weight percentage of Rochelle salt-PVDF based polymer exhibited maximum dielectric conductivity with value slightly more than $5.0x10^{-6}$ at a frequency of $3x10^{6}$Hz, when compared with other two composition of Rochelle salt doped with PVDF polymer.

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