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Pyroelectric Parameters Measurement of Infrared Sensor Based on PANI- CSA/PVDF/BaTiO₃ Composite Films

By

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Abstract:

An infrared sensor based on composite of polyaniline/polyvinylidene fluoride (PANI/PVDF)/barium titanate (BaTiO₃) with different weight percentages (25, 50, 70 and 100) of BaTiO₃ has been fabricated. PANI doped with camphor sulfonic acid (CSA) was prepared chemically. Electrical measurements such as electrical conductivity and pyroelectric current and coefficient of these composites were performed. It was found that the pyroelectric coefficient increases with increasing of the weight percentage of BaTiO₃. The behavior of electrical conductivity of PANI-CSA/PVDF/BaTiO₃ composite films with different weight percentages of BaTiO₃ was followed up the percolation theory. The percolation threshold value of PANI-CSA/PVDF/BaTiO₃ composite films was found at 25 wt.% of BaTiO₃. The conductivity of the composite films was increased from 4.08×10^{-8} S/cm 0 wt.% of BaTiO₃ to 8.84×10^{-6} S/cm at 100 wt.% of BaTiO₃. The pyroelectric coefficient values were enhanced from 2.35×10^{-5} to 1.27×10^{-3} C/m²°C at 0 wt.% and 100 wt.% of BaTiO₃, respectively.

Keywords:

Infrared sensor, Pyroelectric coefficient, electrical conductivity, Percolation threshold.

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1. Introduction:

Pyroelectric sensors are widely used in applications like Radiation Thermometer, Fire Detectors, Thermal Imaging, Medicine, Industry, Communications [1,2]. For many applications a high pyroelectric parameters are required. In order to get maximum pyroelectric parameters, several approaches were already investigated, for example the appropriate choice of pyroelectric parameters, special construction techniques to reduce the heat conduction away from the sensitive element or the use of thermal absorber layers [3,4]. Pyroelectric materials are polar and respond to thermal energy by a change in spontaneous polarisation. This process is dependent on the change in temperature induced in the material. A number of pyroelectric materials are available. Some of these are single crystal (LiTaO₃), Triglycine Sulphate: TGS, or ceramic (PbTiO₃, BaTiO₃). Ceramic materials such as BaTiO₃ has very good pyroelectric properties and used in a variety of applications. But their brittle nature and inflexibility limit their use in some applications. Recently polymers like polyvinylidene fluoride and its co-polymers such as vinylidene fluoride have been used in pyroelectric sensors. However, the low pyroelectric coefficients of such materials and the difficulties involved in poling the thick films restrict their use. Therefore, a composite consisting of highly pyroelectric ceramic material combined with a polymer would be the ideal replacement for obtaining the properties of both these classes. Such a composite would exhibit the pyroelectric coefficient of the ceramic material and the flexibility and strength of the polymer [5]. The aim of this work is to examine the electrical conductivity and pyroelectric coefficient) of the composite films prepared by casting technique as a pyroelectric infrared sensors.

2. Experimental Work:

2.1 Synthesis of Polyaniline:

Polyaniline emeraldine salt PANI-ES doped form was prepared by chemical oxidative polymerization with hydrogen peroxide as an oxidant. Typically 8 g (6.57 ml) of aniline was dissolved in 900 ml hydrochloric acid 1 M (doping agent), and then 0.02 g of ferrous chloride (FeCl₂) was dissolved in 225 ml deionized water. The two solutions were then mixed in beaker and stirred with a magnetic stirring bar. During stirring 100 ml of hydrogen peroxide (H₂O₂) (6 %) was drop wise added to the solution to initiate the polymerization. The stirring was continued for 48 hr to ensure the completion of polymerization. The green powder (PANI-ES) was collected on a filter paper using vacuum filtration and washed with water until filtrate became colorless, then dried at 50 ° C for 24 hr. The PANI was undoped with ammonia solution (5 %) and stirred for 3 hr. The blue powder was collected on a filter paper using vacuum filtration and washed with water until filtrate became neutral, then dried at 50 ° C for 24 hr.

2.2 Preparation of Barium Titanate

Barium titanate powder is synthesized using the standard solid state reaction technique. The raw materials used were BaCO₃, TiO₂. The powders are weighted in stoichiometric proportion and grinding in wet mixed in acetone medium using a ball mill for durations up to 6 hr, in an agate jar with agate balls. The ball/sample mass ratio was 20:1. This power mixture is thermally treated at 1000 °C for 4 h at room temperature to obtain the perovskite phase. Heat treated powder is finally ground and sieved through a mesh to obtain particle of size less than 50 μm.

2.3 Preparation of PANI-CSA/PVDF/BaTiO₃ Composite Films

Composites of PANI-CSA/PVDF/BaTiO₃ are prepared by mixing of solution of PANI-CSA and PVDF which are soluble in DMF with BaTiO₃. Two grams of PVDF granules are dissolved in 20 ml of DMF for 2 hours and the polyaniline doped with CSA is prepared by adding 0.25 gms of polyaniline to 0.605 gm of CSA in 20 ml of DMF with continuous stirring for 48 hours at room temperature. Composites of PANI-CSA/PVDF/BaTiO₃ having 0, 25, 50, 75, and 100 % by weight are prepared by introducing 0, 0.2118, 0.4236, 0.6355, and 0.8473 gm of BaTiO₃ respectively to 4 ml of PANI-CSA/PVDF. After stirring for 4hr, the resulting solutions are cast.

2.4 Electrical Measurements

The pyroelectric detector is essentially a capacitor that can be charged by an influx of heat. The detector does not require any external electrical bias. It needs only an appropriate electronic interface circuit to measure the charge [6]. Figure 1 shows a pyroelectric detector connected to a resistor R_G that represents either the internal leakage resistance or a combined input resistance of the interface circuit connected to the sensor. The equivalent electrical circuit of the sensor is shown on the right. It consists of three components: (1) the current source generating a heat induced current, I_p, (2) the sensor's internal capacitance, C_A, (3) the internal resistance, R_A.

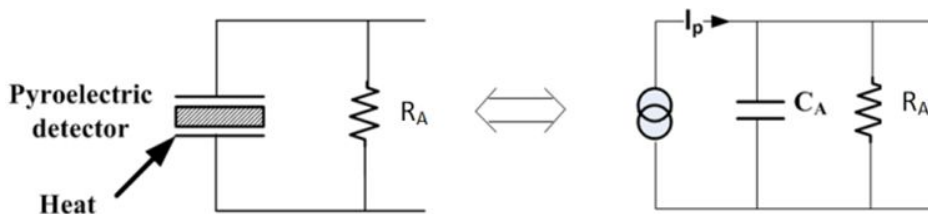


Figure (1): Pyroelectric detector and its equivalent circuit.

The electrical conductivity of the blend films is measured by the two probe method. The thin film samples are coated with silver paste onto the two both sides and mounted on the two probe holder designed on the printed circuit board (PCB) as shown in Figure 2.



Figure (2): Two probe holder designed on the PCB.

2.4.1 Conductivity Measurements

The electrical conductivity of PANI-CSA/PVDF/BaTiO₃ composite films is measured at different temperatures by using the system shown in Figure 3a. A bias voltage V in the range from 0.2 to 4 V was applied by using Kiethley power supply instruments 240A. The temperature is varied from 20 °C to 100 °C. The measured current pass across the sample is measured by Kiethley 616 digital electrometer with the increase of temperature with a rate of 5 °C/min inside a GPC-TZN4M Autonics furnace. The electrical resistance R is calculated from the I-V characteristics at a constant voltage and the resistivity “ ” is then calculated at different temperatures using the definition:

$$= R A/d \tag{1}$$

where A is the area of the electrodes and d is the thickness of the sample. The electrical conductivity “ ” can be computed by using the definition:

$$= 1/ \tag{2}$$

2.4.2 Pyroelectric Current and Voltage Measurement

The pyroelectric detector, as shown in Figure 3b, is a capacitor formed by depositing metal electrodes on both surface of the thin slice of pyroelectric material. The pyroelectric specimen is heated at a variable temperature chamber. The change in the value of dT , which causes a polarization change, and, consequently, results in

displacement of electric charges in the pyroelectric material, hence the pyroelectric current I_p takes place [7,8].

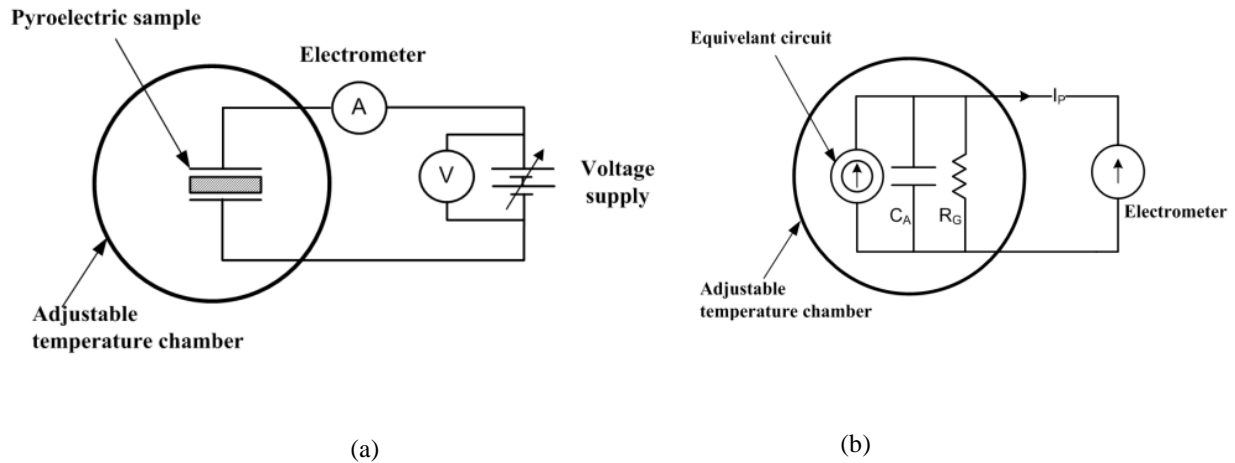


Figure (3): Measurement setup of a) I-V characteristics, b) the pyroelectric current.

The pyroelectric current depends on the temperature change with time. Therefore, pyroelectric devices are considered to be alternating current (AC) coupled devices. The pyroelectric current is proportional to the area (A) and the rate of change of temperature (dT/dt) of the detecting element according to the following equation [3]:

$$I_p = A \cdot p \cdot \frac{dT}{dt}, p = \frac{I_p}{A \cdot \frac{dT}{dt}} \quad (3)$$

When, the detector is heated by incident radiation, the polarization changes by the amount of incident radiation determined by the temperature change and the pyroelectric coefficient of the material [4].

3. Result and Discussion:

3.1 Electrical Conductivity of PANI-CSA/PVDF/BaTiO₃ Composite:

Figure 4 presents the electrical conductivity of the PANI-CSA/PVDF/BaTiO₃ composite films as function of BaTiO₃ loading. It shows that the conductivity increases slightly from 0 wt.% to 25 wt.% of BaTiO₃ this is attributed to doping effect of CSA which maximizes the number of carriers the highest number of carriers can be connected with the delocalization effect of doping process and formation of the polarons or bipolarons in the composite structure as discussed by [9]. According to electron transport mechanism adding BaTiO₃ with lower wt.% to PANI increase the crystallinity of PANI, and the charge transport is limited, which indicates a stronger localization of charge carriers and

thus represents a lower electrical conductivity [10]. The electrical conductivity of the mixture of two the materials with different conductivities can be predicted by the percolation theory. The conductivity of pure PANI-CSA/PVDF composite film is 4.08×10^{-8} S/cm and its increased to 7.64×10^{-8} S/cm at 25 wt.% of BaTiO₃. At 50 wt.% loading of BaTiO₃ the conductivity of the composites jumps drastically to 1.57×10^{-6} S/cm. From Figure 4, we can conclude that percolation threshold is 25 wt.% of BaTiO₃. At higher loading of BaTiO₃ over the 50 wt.%, the conductivity is saturated in the range of 4.54×10^{-6} S/cm and 8.84×10^{-6} S/cm for 75 wt.% and 100 wt.% of BaTiO₃ respectively. The slightly increase in electrical conductivity which is due to the particles blockage of conduction path by the BaTiO₃ nano-particles embedded in the PANI matrix, which indicates a weaker localization [9].

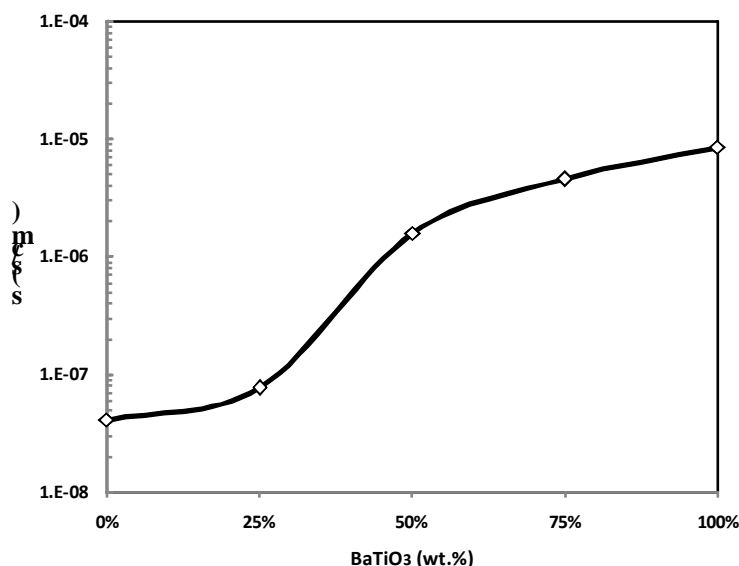


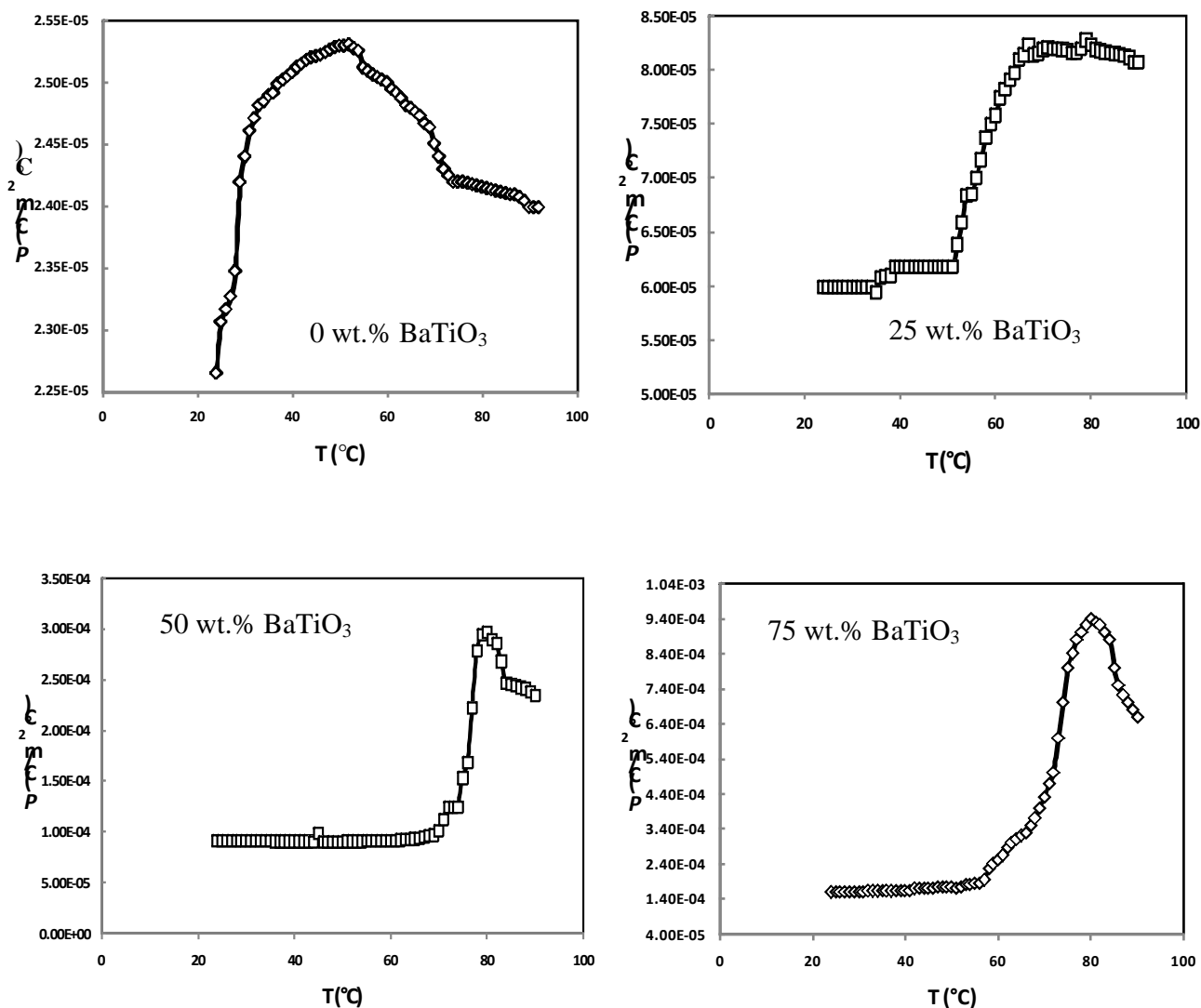
Figure (4): Dependence of electrical conductivity of PANI-CSA/PVDF/BaTiO₃ composite films versus wt.% of BaTiO₃ at room temperature.

3.2 Pyroelectric Properties of PANI-CSA/PVDF/BaTiO₃ Films:

Figure 5 shows the pyroelectric coefficient p of composite films of PANI-CSA/PVDF/BaTiO₃ with different wt.% of BaTiO₃ at different temperature range from 20 to 100 °C with rate of 1 °C/min. For pure PANI-CSA/PVDF with (0 wt.% of BaTiO₃), the pyroelectric coefficient is steeply increased to 2.43×10^{-5} C/m²°C in the range from 20 to 40 °C and has a broad peak at 50 °C. This peak is due to the presence of the dipole moments which are aligned in the -phase resulting in strongest dipole moment per unit cell of the PVDF. Pyroelectric coefficient is decreased beyond 50 °C due to the release of charge trapped at crystalline/amorphous boundaries and a rise of -

phase in PVDF polymer [11]. The movement of ions at side chain form dipoles which are returned to a randomly oriented state which is referred to as dipolar relaxation. This -phase dipoles relaxation is associated with the dipole orientation of the polar side group of the PVDF [5].

By increasing BaTiO₃ in the PANI-CSA/PVDF/BaTiO₃ composite films the pyroelectric coefficients value is increased two orders of magnitude. For 25 wt.%, 50 wt.%, and 75 wt.% of BaTiO₃, the pyroelectric coefficient values are equal to 6.19×10^{-5} C/m²°C, 1.07×10^{-4} C/m²°C and 1.45×10^{-4} C/m²°C respectively at room temperature as shown in Figure 5. Also, the delay increased of pyroelectric coefficient from 20 °C to 60 °C may be due to the existence of the dipoles of BaTiO₃ which are transform -phase to -phase dipoles of the PVDF. From 60 °C to 80 °C the current was increased which reaches to peak at 80 °C due to the transformation from -phase to -phase dipoles [11]. Above 80 °C the pyroelectric coefficient is decreased for 50 wt.% and 75 wt.% of BaTiO₃, this is due to the release of charge trapped at crystalline/amorphous boundaries [12]. At 100 wt.% of BaTiO₃, the pyroelectric coefficient increased in the range of 20 °C to 40 °C and is equal to 1.27×10^{-3} C/m²°C at room temperature.



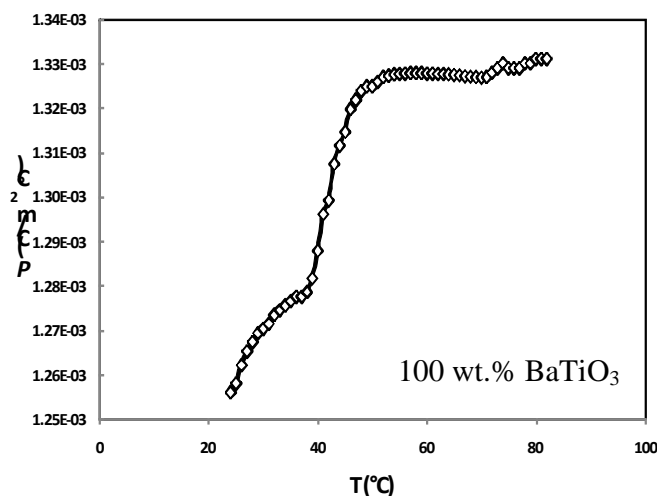


Figure (5): Pyroelectric coefficients of PANI-CSA/PVDF/BaTiO₃ composite films with different wt.% of BaTiO₃.

6. Conclusions:

Composite films of polyaniline doped with camphor sulfonic acid/polyvinylidene fluoride/barium titanate were successfully prepared with different weight percentages of BaTiO₃. Experimentally, it is observed that, the conductivity of the composite films was increased from 4.08×10^{-8} S/cm 0 wt.% of BaTiO₃ to 8.84×10^{-6} S/cm at 100 wt.% of BaTiO₃. The percolation threshold of this composite was found to be 25 wt.% of BaTiO₃. This low percolation threshold will allow the use of the prepared composite film for infrared sensor applications. The pyroelectric current was measured by increasing temperature with rate 1 °C/min and then the pyroelectric coefficients were calculated. The pyroelectric coefficient values were enhanced from 2.35×10^{-5} to 1.27×10^{-3} C/m²°C at 0 wt.% and 100 wt.% of BaTiO₃, respectively.

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