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Preparation And Characterization Of PTCa/PEEK Pyroelectric Composite For Temperature Sensing

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ABSTRACT

Ferroelectric ceramic/polymer composites were fabricated in the film form hot pressing Calcium modified lead titanate (PTCa) powder and poly(ether-ether-ketone) (PEEK) as polymer matrix. Different ceramic contents such as 40, 50 and 60 volume percent were used and composites films were obtained in the thickness range of 100 to 300μm. To display pyroelectric activity the samples were poled by appropriated electric field. Using this composite as temperature sensors, a fire alarm was constructed. The alarm turn on when the sensor detects a signal variation corresponding to the frequency oscillation of fire light in the range of 5 Hz to 40Hz. Low density, mechanical resistance and high pyroelectric figure of merit(FOM) are some interesting characteristic of this composite, which allow to state that it can be used in photo-thermal spectroscopy.

KEYWORDS

Ferroelectric composite;
Pyroelectric sensors;
Thermally stimulated-discharge current;
Dielectric constant;
Poly(ether-ether-ketone).

INTRODUCTION

Although pyroelectricity have been observed long time ago the development of pyroelectric detectors is more recent and single crystals and ceramics[1] were the common used materials. The discovery of piezo and pyroelectric activities in poly(vinylidene fluoride) (PVDF) in 1969[2,3] brings a new perspective for the applications of pyroelectric effect. Flexibility, formability and mechanical resistance are some of interesting properties, which make ferroelectric polymers an attractive material to electronic industry. PVDF and its various copolymers and ceramics have found a large number of applications such as thermal imaging, fire detection, remote temperature measurements, medical diagnostics and most recently as gate dielectrics in organic field effect transistors and in non-valatile ferroelectric field effect memories[4-6].

In recent years, the research in the field of pyroelectricity has been concentrated on developing materials with high figures of merit (FOM). Composite materials made of ferroelectric ceramics particles embedded in polymer host gained significant interest because of their mechanical flexibility, formability and excellent pyroelectric activity. Also is an advantage the possibility to change the dielectric constant by varying the volume fraction of ceramic particles. Many works have been done on the pyroelectric properties of ferroelectric composites[7–10] and there are several theoretical studies to derive expressions for the effective pyroelectric coefficients[11–14] but the main target for the experimental work is to find a good material that can display better sensing property.

In this work composites made of calcium modified lead titanate ceramic powder and poly(ether-ether-ketone) polymer matrix were fabricated and the pyroelectric property of the composite films with different ceramic content is reported. Furthermore, the composite sensors was used to construct a fire alarm, which turn on when the sensor detect a signal variation corresponding to the frequency oscillation of the fire in the range of 5 to 40 Hz.

EXPERIMENTAL

Polymer matrix

Poly(ether-ether-ketone)(PEEK) is an aromatic polyether developed by imperial chemical industries (I.C.I.), petrochemicals and plastic division as a high-temperature engineering thermoplastic[15]. PEEK offers mechanical strength, resistance to a large range of chemicals and low emission of toxic fumes when exposed to a flame[16].The considerable applications of PEEK as an engineering material is also due to its low dielectric loss, insulating properties, high working temperature(~400°C) and glass transition temperature around 150°C.

Ceramic powder

Calcium modified lead titanate(PTCa) has high anisotropic piezoelectric property and exhibit lower dielectric constant than most of lead zirconate titanate(PZT) materials, which results in a higher voltage sensitivity[17]. Its piezoelectric coefficient (d_{33} =68 pC/N) and its density (ρ=6.8 g/cm^3) are lower than those of PZT but the electromechanical coupling factor is high (k_t=0.47) making PTCa a good piezoelectric receiver[18].

Composite films

A perovskite ceramic PT doped with Ca^{+2} with $(Pb_{0.76}Ca_{0.24})[(Co_{0.5}W_{0.5})_{0.05}Ti_{0.95}]O_3$ composition (GEC Marconi–UK) as powder, was mixed with PEEK powder (Goodfellow). The average grain sizes are 2 μm and 80 μm for ceramic and polymer, respectively. PTCa/PEEK composite films in the thickness range of 150 to 300 μm were obtained by pressing the mixture at 370°C during 2 h with 20 MPa pressure. Three different ceramic volume fractions were used to provide 40/60, 50/50 and 60/40 vol. % PTCa/PEEK composite films. The powder quantity were calculated using the equation:

$$M_c = M_p \rho_c \Phi^c/\rho_p \ 1 - \Phi^c \qquad (1)$$

where M is the mass, ρ is the density and the subscripts c and p are related with ceramic and polymer, respectively. ϕ^χ is the volume fraction of ceramic.

Aluminum electrodes with 1.0cm of diameter were vacuum evaporated onto both sides of the samples. The films were poled with an appropriated electric field in silicone oil bath with controlled temperature. A Trek high voltage power supply was used for the dc poling process.

Measurements

1. AC dielectric measurements

The dielectric constant (ε) was measured as a function of frequency (10^3–10^6 Hz) at three different temperatures (30°C, 50°C, 70°C). The measurements were carried out using a HP 4129A impedance analyzer. A two-terminal parallel-plate capacitor dielectric cell with gold-plated electrodes temperature-controlled (Toyo Seiki) was used in association with the analyzer. The composite films were cut in the form of disc with 2.0 cm of diameter.

2. Pyroelectric current measurements

Thermally stimulated depolarization current (TSDC) technique was employed to measure the pyroelectric current. In this method, called direct method [19] a pre-poled sample was placed in a temperature-controlled chamber (Toyo Seiki) and was heated at a constant rate (1 °C/min) with its electrodes short-circuited. The short-circuited current is monitored with an appropriated impedance electrometer.

3. Differential scanning calorimetry (DSC) measurements

DSC measures the temperatures and heat flow associated with transitions in materials as a function of time and temperature. The technique provides qualitative and quantitative information about physical and chemical changes that involve endothermic or exothermic processes or changes in heat capacity. Phase transition of PEEK film and composite film were studied using a DSC (TA instruments model MDSC 2920) at a rate of 10 °C/min in nitrogen atmosphere.

Fire alarm sensor

An aluminum box with 5.0cm width, 3.5cm height and 7.2 cm depth dimensions was constructed for the electrical circuit of the fire alarm device. Figure 1 shows the scheme of the circuit. The alarm turns on when the input signal reaches 99 mV. There is a 10 kΩ potentiometer, which can be adjusted according to the sample sensitivity. A glass window protected the composite film used as sensing element. Two 9.0 V battery are used as power supply.

RESULTS AND DISCUSSION

Figure 2 shows the behavior of the relative dielectric constant (ε) for the composite PTCa/PEEK with 60/40 vol.% compositions. It can be seen the increase of ε as the temperature is increased. There is no significant change in the relative dielectric constant in the frequency range of 1 kHz to 1000 kHz.

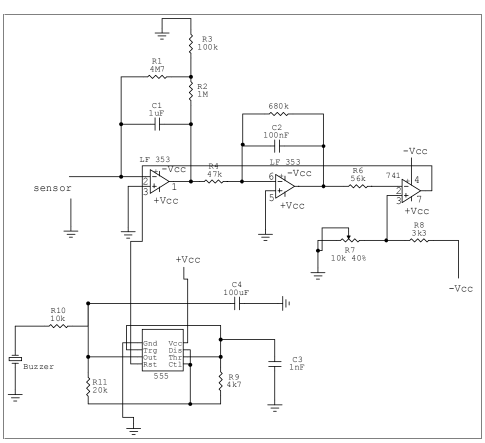

Figure 1: Electrical circuit of the fire alarm

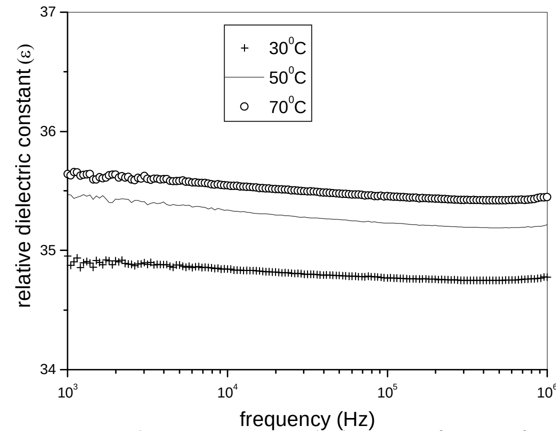

Figure 2 : Dielectric constant behavior of PTCa/PEEK composite for three different temperature

Similar behavior was found for all composite composition (40/60 and 50/50 vol.%).

As expected ε increases with the increasing ceramic contents. This behavior is shown in figure 3 at 70°C and similar result was obtained for others two temperatures used in this work (30°C and 50°C). It is important to know the value of ε because of the pyroelectric figure of merit (FOM), which gives sensing characteristics to the sample.

Figures 4 and 5 show the thermograms of PEEK pure and PTCa/PEEK-40/60 vol.% composite, respectively. No significant change was observed in the glass transition temperature(T_g) with ceramic inclusion. The value of T_g is an indicative of the poling temperature for better poling efficiency. Previous work[20] shown higher piezoelectric coefficient (d_{33}) for composite poled at 160°C. The increase of

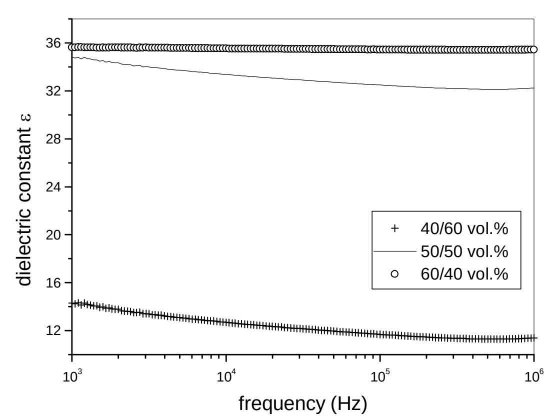

Figure 3 : Variation of relative dielectric constant with ceramic contents

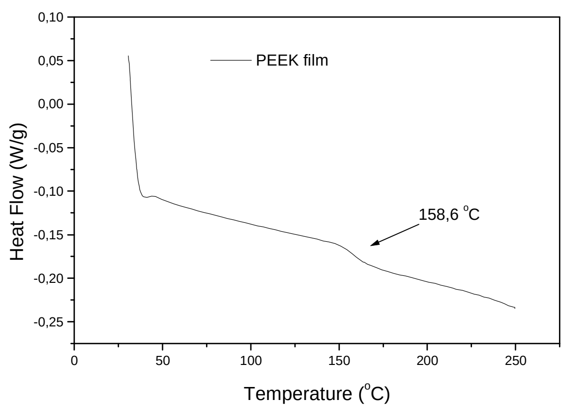

Figure 4 : DSC thermogram for PEEK film Heating rate 10 deg/min

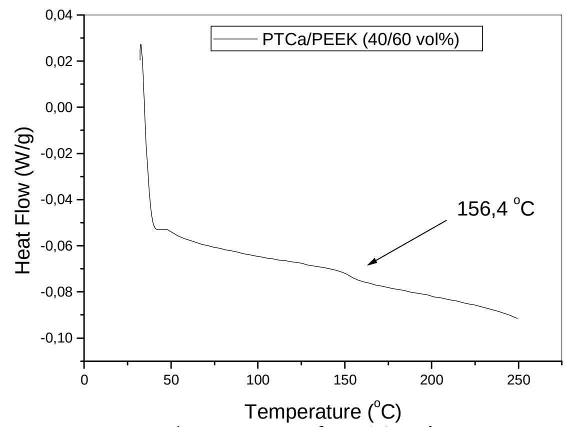

Figure 5 : DSC thermogram for PTCa/PEEK composite. Heating rate 10 deg/min

the dielectric loss with increasing temperature also should take into account because there is an increasing in the conductivity of the polymer matrix, which gives better poling conditions [9].

In measuring pyroelectric coefficient a sample is heated at a constant rate with its electrodes shorted and the short-circuit current is monitored with an appropriated impedance electrometer. A typical thermally stimulated discharge current and pyroelectric current is shown in figure 6. The current was obtained for a 60/40 vol.% PTCa/PEEK sample pre-poled at 160°C in electric field of 10MV/m for 1.0h.

The first run provides irreversible current, which may have contribution of charges injected during the polarization process and some storage charge that is released while heating. The current intensity is reduced in the following runs. When there is no appreciable current reduction the reversible pyroelectric current is established. The pyroelectric coefficient

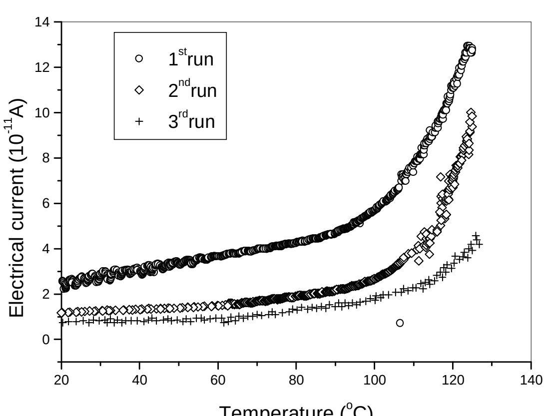

Figure 6 : Typical thermally stimulate discharge current and pyroelectric current in PTCa/PEEK composite. Heating rate 1 deg/min

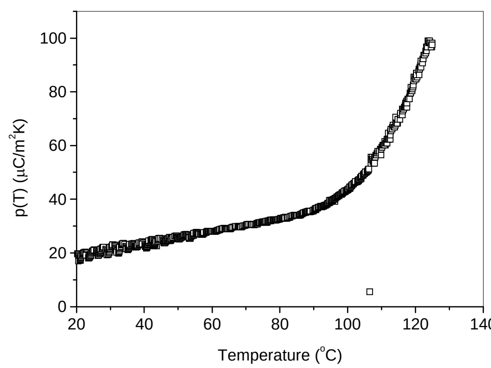

Figure 7 : Pyroelectric coefficient evaluated using equation 2. Sample pre-poled at 160°C in electric field of 10 MV/m

p(T) can be evaluated using the relation:

$$p(T) = \frac{1}{A}\frac{I_P}{dT/dt} \qquad (2)$$

where A is the electroded area, I_P is the short-circuit pyroelectric current and dT/dt is the heating rate (1 deg/min).

Figure 7 shows the pyroelectric coefficient as a function of temperature for 60/40 composite compositions. For comparison, the value of p (70°C) is about 3.0 x 10^{-5}C/m^{2}K and using the dielectric constant at the same temperature the figure of merit (p/ε) is about twice higher than of PZT (taking p(70) = 5×10^{-4} C/m^{2}K, ε(70) = 1250 for PZT)[21]. In the same work the authors have used the value of p(T) for β-PVDF as 1×10^{-5}C/m^{2}K.

CONCLUSIONS

Composite films made of calcium modified lead

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titanate ceramic dispersed in poly(ether-ether-ketone) polymer matrix were fabricated and characterized as pyroelectric material. Electric field of 10 MV/m was enough to polarize the composite, which could display pyroelectric activity. A composite with 60 vol.% of ceramic was used as fire alarm sensor and have worked to detect the variation of the signal corresponding to the frequency oscillation of the fire in the range of 5Hz to 40Hz. The use of a polymer host with high working temperature(~400°C) allows polarizing the sample in high temperature, which gives possibility to use the sensors in environment where the temperature is higher. Some experiments are in course in our lab to show that this material can be used as radiation sensors and to study the behavior of p(T) with the poling electric field.

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