

Study of Pyroelectric Activity of PZT/PVDF-HFP Composite

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Flexible, free-standing piezo and pyroelectric composite with 0 to 3 connectivity was made up from Lead Zirconate Titanate (PZT) powder and poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) copolymer. The pyroelectric and the piezoelectric longitudinal (d_{33}) coefficients were measured. A 50/50 vol.% PZT/PVDF-HFP composite resulted in piezo and pyroelectric coefficients of $d_{33} = 25.0$ pC/N and $p = 4.5 \times 10^{-4}$ C/m²K at 70 °C, respectively. Analysis of the complex permittivity in a wide range of frequency was carried out indicating lower permittivity of the composite in comparison with a permittivity of the PZT ceramic. The low value of the permittivity gives a high pyroelectric figure of merit indicating that this material can be used to build a temperature sensor in spite of the lower pyroelectric coefficient compared with PZT.

Keywords: *composite piezoelectric, permittivity, thermally stimulated current, thermal sensors*

1. Introduction

The discovery of ferroelectric effect and its application brings progress in materials science with a growth in search of new materials, which have best properties for specific application. PZT has been the best transducer material for a long time period, however, for some applications, PZT offers some limitations. That is the reason why researchers are still searching for a new single-phase material, or heterogeneous systems satisfying the required conditions. In opposition to heavy and rigid ceramics they found ferroelectric polymers, specially the poly(vinylidene fluoride) (PVDF)¹. Light and flexible, ferroelectric polymers show many advantages over ceramics for several applications. A great impact in the electronic industry was observed with the progress on ferroelectric polymer research.

The continuous progress and ceaseless search for new materials lead to the study of heterogeneous materials. Copolymers of PVDF^{2,3} and composites^{4,5} became the target. The present paper reports some results obtained in electromechanical characterization of a ceramic/copolymer composite prepared mixing lead zirconate titanate and poly(vinylidene fluoride-hexafluoropropylene) - PZT/PVDF-HFP.

2. Experimental

2.1. Sample Preparation

PZT/PVDF-HFP composite was prepared with 50/50 vol.% by mixing ceramic powder and copolymer in powder form. The copolymer PVDF-HFP (90/10 composition) Kynar 2821 in powder form was obtained from Atofina do Brazil. The mixture was pressed (15 MPa) at 180 °C and the composite films were obtained in the range of 100 μm thickness. Aluminum electrodes (1 cm of diameter) were deposited on both sides of the samples for electrical measurements. Samples were poled applying the electric field of 20 MV/m for 1 h at 90 °C.

2.2. Measurements

The longitudinal piezoelectric coefficient d_{33} of the composite film poled as early described was measured using the d_{33} piezo tester model 8000 from American Piezo Ceramics (APC). The measurement is based in the comparison of the piezo activity of a standard piezo-ceramic. The dielectric data was taken in a frequency range from 10⁻⁵ Hz to 10⁶ Hz. In the 100 to 10⁶ Hz range an impedance analyzer (HP model LF 4192A) was used. A setup with a lock-in

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amplifier (PAR model 5210) was used in the medium frequency range (10^{-1} to 100 Hz) and for low-frequencies (10^{-5} to 10^{-2} Hz) the time domain technique was used⁶.

The ϵ'' values in the (10^{-5} to 10^{-2} Hz) frequency range were obtained from the discharge current measured during 3.0 h after charging the sample with an electric field of 10^5 V/m for 27 h. As showed by Hamon ϵ'' can be written as a function of the discharge current, $I(t)$, as:

$$\epsilon'' = \frac{I(t)}{2\pi f C_o V} \quad (1)$$

where C_o is the geometric capacitance of the sample, V the applied voltage and $f = 0.1/t$ is the Hamon frequency⁶.

In the 10^{-1} to 100 Hz frequency range values of the complex permittivity, i. e., real (ϵ') and imaginary (ϵ'') parts, were obtained using the following equations⁷:

$$\epsilon' = \frac{dI_y}{\omega \epsilon_o AV} \quad (2)$$

$$\epsilon'' = \frac{dI_x}{\omega \epsilon_o AV} \quad (3)$$

where d is the sample thickness, A is the electrode area, $\epsilon_o = 8.85 \times 10^{-12}$ F/m is the vacuum permittivity, $f (= \omega/2\pi)$ the frequency, V is the applied voltage and I_y, I_x are the in phase and quadrature current, respectively.

The pyroelectric current was measured using the direct method⁸. In this method a pre-polarized sample is heated with its electrodes shorted and the short-circuit current is monitored with an electrometer. The sample was poled at 90 °C and was heated till 70 °C in all TSDC runs were to avoid its depolarization. Three runs were carried out to obtain the pyroelectric current (reversible) because some charge were released during the first and second runs. The presence of space charges in the first run gives an unreal pyroelectric current.

Scanning electron microscopy (SEM) was performed in a ZEISS DSM 960 computerized microscope operated between 10 to 20 kV on a PVDF-HFP copolymer film and PVDF-HFP/PZT composite. A thin layer of gold was sputtered on the sample surface. Phase transitions were studied using a differential scanning calorimetry (DSC) (TA Instruments model MDSC 2920) at a scan rate of 10 °C/min in nitrogen atmosphere.

3. Results and Discussion

Figures 1 and 2 show the behavior of real (ϵ') and imaginary (ϵ'') parts of permittivity for copolymer PVDF-HFP (90/10 composition) and for the 50/50 vol.%

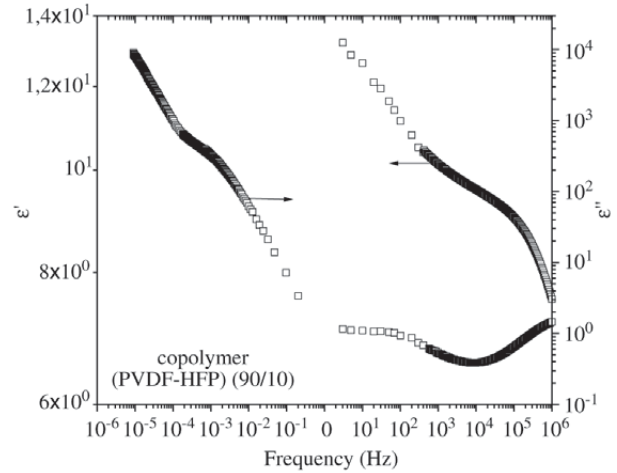


Figure 1. Real and imaginary parts of the complex permittivity for the copolymer PVDF-HFP (90/10).

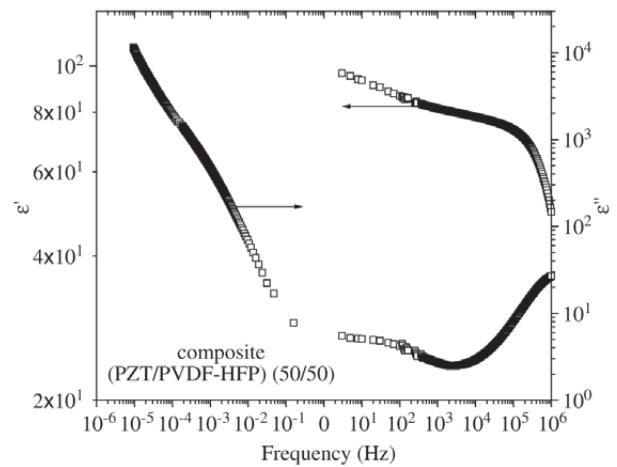


Figure 2. Real and imaginary parts of the complex permittivity for the PZT/PVDF-HFP composite (50/50 vol.%).

PZT/PVDF-HFP composite. ϵ'' was experimentally obtained in the frequency range of 10^{-5} to 10^6 Hz while ϵ' was experimentally obtained in the range of 0.5 to 10^6 Hz. The ϵ' value in low-frequency range (10^{-5} to 10^{-2} Hz) can be calculated using the Kramers-Kronig⁹ relationship

$$\epsilon' = \epsilon_\infty + \frac{P}{\pi} \int_{-\infty}^{\infty} \frac{\epsilon''(\omega)}{x - \omega} dx \quad (4)$$

where P is the Cauchy principal value of the integral and ϵ_∞ is the permittivity in the highest frequency value.

It can be seen from Figs. 1 and 2 that the imaginary part of permittivity of the composite is dominated by that of the

polymer phase. In the low-frequency range both the ionic conduction contribution and low-frequency dispersion (LFD) were observed. According to Jonscher¹⁰ several polymers show similar behavior. For the PZT/PVDF-HFP composite there is an evidence of a peak around 3×10^{-4} Hz, masked by the ionic contribution. That peak is more visible in the copolymer alone. Using the co-relation frequency-temperature due to van Turnhout¹¹ the peak can be observed in TSDC spectra and related with the observed peak in the imaginary part of the permittivity measurements by

$$\omega = \frac{E_a}{bkT^2} \quad (5)$$

where E_a is the activation energy, b is the inverse of heating rate, $k = 1.38 \times 10^{-23}$ J/K is Boltzmann constant and T is the absolute temperature (50 °C) of the maximum in the TSDC curve.

Using 1.0 eV for the activation energy resulted in the corresponding frequency of 3×10^{-4} Hz. The activation energy ($E_a = 1.0$ eV) was calculated by initial rise method¹². The peak observed around 50 °C in the TSDC is related with a phase transition in copolymer according to Jayasuriya¹³.

Figure 3 and 4 show, respectively, the thermally stimulated discharge current and the pyroelectric current in PVDF-HFP copolymer and in PZT/PVDF-HFP composite 50/50 vol.%, respectively. The first run provides irreversible current, which is subsequently reduced in the following runs.

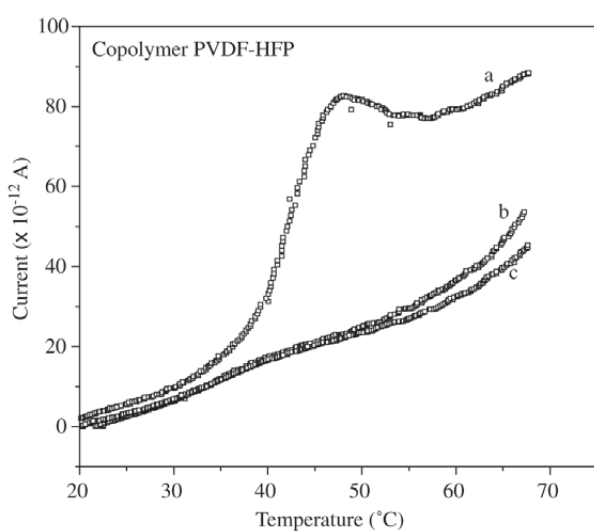


Figure 3. Typical thermally stimulated discharge current and pyroelectric current for the 90/10 PVDF-HFP copolymer: a) first run; b) second run; c) third run.

The second TSDC run shows reduction of current as some charges have been released during the first heating. The third subsequent heating shows no appreciable reduction in the current, thus establishing a reversible pyroelectric current in the sample.

The pyroelectric coefficient $p(T)$ is calculated using the well-known relationship¹⁴:

$$p(T) = \frac{I}{A \frac{dT}{dt}} \quad (6)$$

where I is the pyroelectric current, A is the electroded sample area and dT/dt is the heating rate (1 °C/min).

It can be seen from Fig. 4 that the pyroelectric current, consequently the pyroelectric coefficient (Fig. 5), of the PZT/PVDF-HFP 50/50 vol.% is much higher than that of the copolymer. Furthermore, the composite is very sensitive in the temperature range of 40 to 70 °C, where the pyroelectric coefficient changed from 0.4 to 4.5×10^{-4} C/m²K, i.e., for small temperature variations there is a large change in the pyroelectric current.

The permittivity, pyroelectric coefficient and longitudinal piezoelectric coefficient for some materials are showed in Table 1. It can be seen that although the poling of ceramic is difficult, due to the decrease of the electric field across the polymer phase, very good piezo and pyroelectric activities were obtained in PVDF-HFP/PZT composite, in comparison with the copolymer itself and other composites

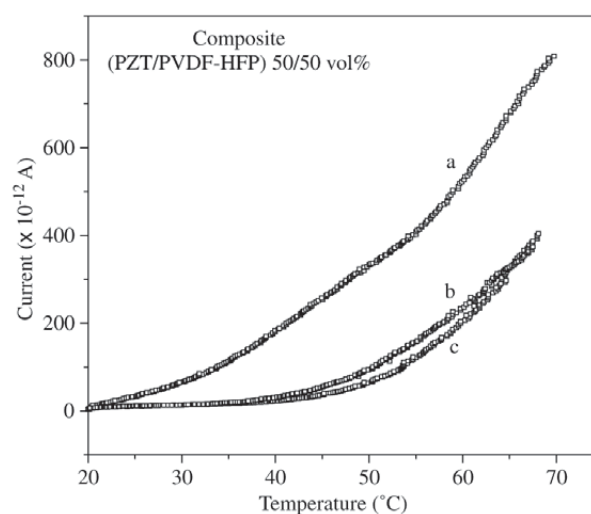


Figure 4. Typical thermally stimulated discharge current and pyroelectric current for the 50/50 vol.% PZT/PVDF-HFP composite: a) first run; b) second run; c) third run.

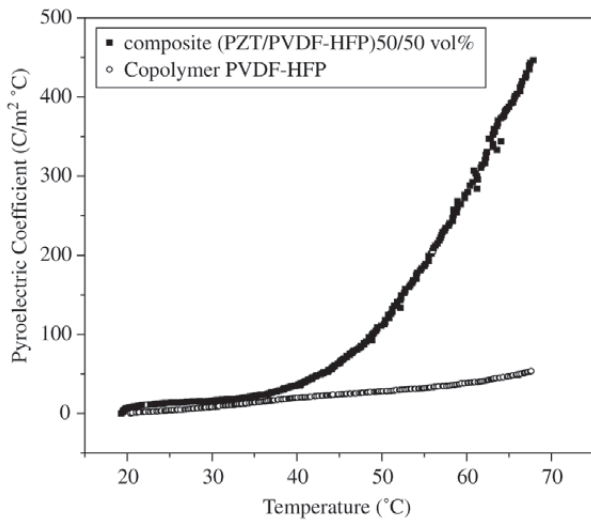


Figure 5. Pyroelectric coefficient as a function of temperature. Sample poled with $E = 20$ MV/m at 90°C for 1.0 h.

Table 1. Values of the permittivity and of the pyroelectric coefficient of some materials.

MATERIAL	ϵ' (1 kHz)	p (C/m ² K)	d_{33} (pC/N)
PZT ^(13,15)	1200	5.0×10^{-4}	110
PVDF ^(13,15)	12	9.0×10^{-6}	20
PZT/PVDF 50/50 vol.% ^(13,15)	95	1.4×10^{-4}	36
PZT/VDF-TrFE 50/50 vol.% ^(13,15)	85	1.4×10^{-4}	20
PVDF-HFP 90:10	12	0.5×10^{-4}	3
PZT/PVDF-HFP 50/50 vol.%	85	4.5×10^{-4}	25

described in literature^{13,15}. The values of $p(T)$ were taken at 70°C for comparison. The high pyroelectric activity and also the high figure of merit ($\text{FOM} = p/\epsilon = 5.3 \times 10^{-6} \text{ C/m}^2\text{K}$) of PZT/PVDF-HFP 50/50 vol.% give a real possible application as temperature sensor, mainly in the temperature range 40 to 70°C . The longitudinal piezoelectric coefficient d_{33} were found to be 3.0 and 25.0 pC/N for PVDF-HFP and PZT/PVDF-HFP, respectively, which also gives to the composite the possibility of being applied as an actuator since those values of d_{33} are comparable with these of PVDF and PZT/VDF-TrFE 50/50 vol.% composite.

Figure 6 shows the PVDF-HFP micrograph. The observed morphology for the copolymer used as matrix for

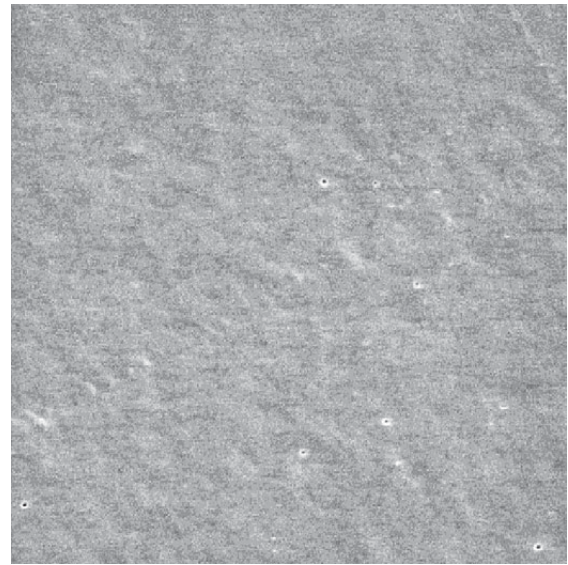


Figure 6. SEM photomicrograph of the PVDF-HFP copolymer film (magnification 5000 \times).

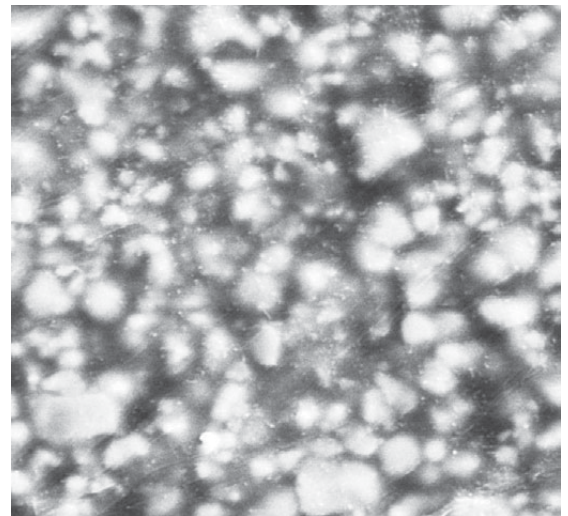


Figure 7. SEM photomicrograph of the (PZT/PVDF-HFP) 50/50 vol.% composite film (magnification 5000 \times).

the composite being so closed and compacted means an undefined morphology, unlike observed in the PVDF film¹⁶. The PVDF-HFP/PZT micrograph showed in Fig. 7 reveals the homogeneity of the PZT grain distribution and also that a 0 to 3 connectivity is predominant in that composite. Besides, the Furukawa's model¹⁷ or Yamada's model¹⁸ for two phase systems could be used for dielectric, elastic and piezoelectric constants.

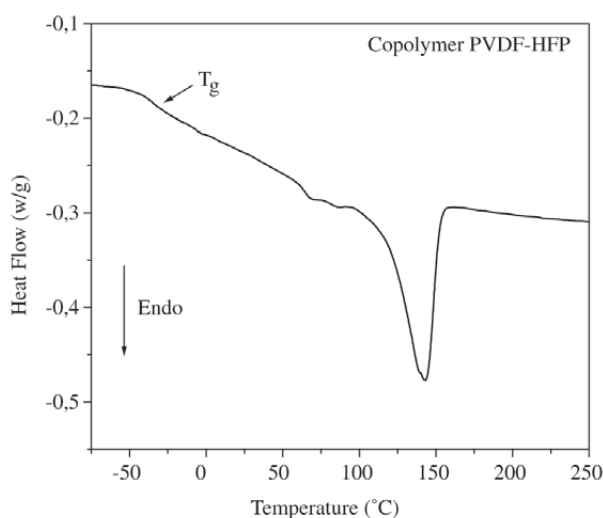


Figure 8. DSC thermogram of the PVDF-HFP copolymer film.

Figure 8 shows the DSC thermograms of the copolymer. The sample was scanned at a heating rate of 10 °C/min within an appropriated temperature range. It can be seen from Fig. 8 that the glass transition temperature (T_g) of the PVDF-HFP copolymer is around -35 °C and the melting point (T_m) is 143 °C. It is shown in the thermogram an evidence of a phase transition around 50 °C, which was also observed in the dielectric and TSDC measurements. For the PVDF-HFP/PZT composite that TSDC peak is less evident due to the ceramic contribution to the intensity of the electric current. Ongoing studies are being taken for a comprehensive characterization of the composite such as the piezo and pyroelectric behavior as a function of the ceramic content and poling field.

4. Conclusions

Composite films of PZT/PVDF-HFP were obtained heating the mixture at 180 °C and with at 15 MPa pressure. A relaxation peak was observed in the imaginary part of the complex permittivity around 3×10^{-4} Hz. This peak is related with that observed at 50 °C using TSDC and DSC, and might be due to a phase transition in the copolymer. The piezo and pyroelectric activities of the composite were considerably enhanced in comparison with the copolymer. Also in relation with other single phase or composite materials the PZT/PVDF-HFP composite shows higher

pyroelectric coefficient and pyroelectric figure of merit. Those results indicate that the new composite might be a good alternative for technological applications.

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