

## Electroactive Properties of Flexible Piezoelectric Composites

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A flexible piezoelectric composite with 0-3 connectivity, made from Lead Zirconate Titanate (PZT) powder and vegetable-based polyurethane (PU), was doped with small amount of semiconductor powder. As a result a composite with 0-0-3 connectivity was obtained. The nature of absorption and steady state electrical conduction and the dielectric behaviour have been studied for this ceramic/polymer composite. The dielectric loss processes of the composite were observed to be dominated by those the polymer. Adding a semiconductor phase in the composite the electrical conductivity can be controlled and a continuous electric flux path could be created between the PZT grains. This composite may be poled at low voltage and in shorter time compared with composites without a conductive phase.

**Keywords:** *sensors, piezoelectricity, pyroelectricity, composites, complex permittivity, discharge current*

### 1. Introduction

Ceramic-polymer composites have received considerable attention from many researchers during the last 30 years<sup>1,2,3,4</sup>. They were developed to be an alternative material to ferroelectric ceramics and to ferroelectric polymers. Combining properties of two single-phase materials (*i.e.*, ceramic and polymer), the composite appear to possess the mechanical strength, flexibility and formability of the polymer together with high electroactive properties of the ceramic.

There are many ways in producing ceramic-polymer composites, but the most commonly studied are the 0-3 connectivity. This concept was established by Newnham and co-workers<sup>5</sup> to describe the interspatial relationships in a two-phase material. The connectivity has greatest importance in a multiphase material because it controls the mechanical, electrical and thermal fluxes between the phases.

Composites with 0-3 connectivity are obtained by mixing the ceramic powder with polymer matrix when the particles are not in contact with each other and the polymer phase is self connected in all dimensions. That is the easiest fabrication procedure of ceramic/polymer composite.

Although ceramic/polymer composites have some advantages compared with ferroelectric ceramics or ferroelectric polymers, the poling process deserves special attention because the effective electric field is much less than the applied field as described by Yamada<sup>6</sup> and by Furukawa<sup>7</sup> for 0-3 composites. Such composites will exhibit piezo- and pyroelectricity if they are suitably poled. A detailed investigation is still necessary to develop the composite with optimum properties for good poling conditions.

This work shows some results obtained with flexible piezoelectric composite made from lead zirconate titanate (PZT) and vegetable-based polyurethane (PU) doped with a semiconductor phase. Adding small amounts of carbon powder the electrical conductivity of composite can be controlled and a continuous electric flux path between PZT grain can be established and poling can be carried out at low voltages and in shorter time. Furthermore the permittivity and dielectric loss were measured in a wide range of frequency ( $10^{-5}$  Hz to  $10^6$  Hz) using time domain and bridge techniques.

### 2. Experimental

#### 2.1. A: Sample

Commercial PZT powder (American Piezo Ceramics - APC) and castor oil based polyurethane (GQATP - USP/São Carlos) were used as piezo-ceramic and polymer matrix respectively. A fine-grained carbon (C) was used as semiconductor phase. The PZT powder was mixed with carbon by a vibrator (Mod. DDR-GM9456) for 30 min prior to introducing this mixture in the polyurethane matrix. The composite was placed between two-paraffin paper and pressed at room temperature<sup>8</sup>. The applied pressure was about 20 MPa and it was possible to obtain samples in the thickness range of 250  $\mu\text{m}$  to 350  $\mu\text{m}$ . Aluminium electrodes were evaporated onto both sides of the sample after cutting in an appropriated size. The electrodes area were  $3.5 \times 10^{-4} \text{ m}^2$ . Table 1 shows the samples with respective volume percent of carbon used in this work.

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## 2.2. B: Measurement

The Pennebaker Mod. 8000 Piezo  $d_{33}$  Tester (APC) was used for the measurement of  $d_{33}$  piezo coefficient in the thickness direction. A high voltage supply (TREK Mod. 610C) was used for poling the sample that was conditioned in a temperature- controlled chamber. In the charging and discharging procedure the currents were monitored with an electrometer Keithley model 617.

The dielectric data were taken using a General Radio Bridge model 1621 and the time domain technique and subsequent Hamon approximation<sup>9</sup> for the low-frequency range.

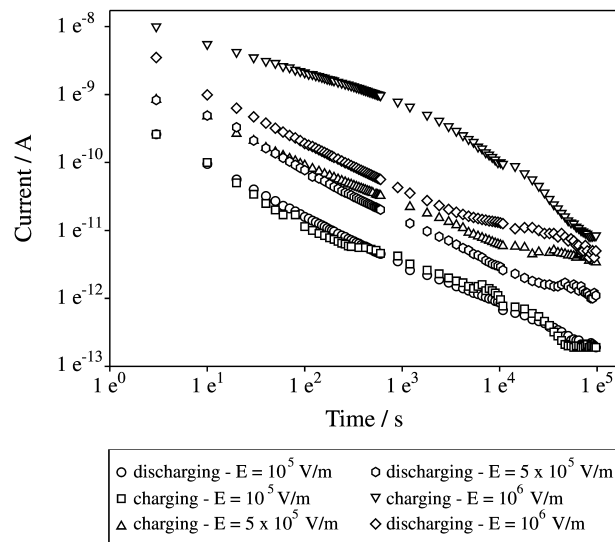
## 3. Results and Discussion

Figure 1 shows the typical nature of field dependence of charging  $I_c(t)$  and discharging  $I_d(t)$  currents at room temperature, for fields  $1 \times 10^5$  V/m to  $1 \times 10^6$  V/m in PZT/C/PU composite with 59/1/40 vol. % composition. For  $E = 1 \times 10^5$  V/m the magnitudes of charge and discharge transients were mirror images of each other. For  $E = 5 \times 10^5$  V/m the mirror image nature was observed at short time and for time above 300 s the charging and discharge transients departed from mirror image nature. At  $E = 1 \times 10^6$  V/m there is no mirror image and the charging transients suggest the beginning of the space charge effect.

The discharge current follows the well-known expression<sup>10</sup>,

$$I_d = A(T)t^{-n} \quad (1)$$

where  $A(T)$  is a temperature dependent factor,  $t$  is the time after removal of the externally applied electric field and  $n \approx 0.6$  for this sample showing that space charge polarisation is not a dominant effect<sup>11</sup>. Similar result was reported by Das-Gupta and Abdullah<sup>12</sup> who found that the quasi-steady state conduction current in PZT5/VDF-TrFE 50/50 vol.% composite is of ionic nature. Although the space charge is not a dominant effect it can be present for

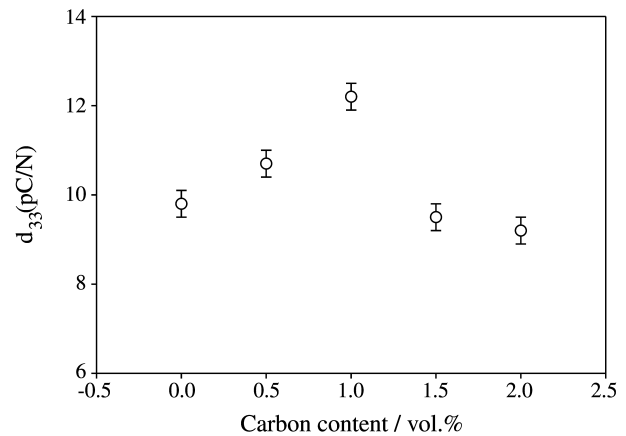


**Figure 1.** Charging and discharging currents in PZT/PU/C with 59/40/1 vol. % at different fields. Room temperature.

electric field over  $10^6$  V/m. The presence of space charge in the polymer matrix can help in stabilising the polarisation and also can contribute to the piezoelectric activity in porous polymers as shown in recent paper<sup>13</sup>. The steady state conduction currents were observed at  $10^5$  s at room temperature and  $10^5$  V/m electric field.

All samples, shown in Table 1, were poled with 3 MV/m electric field at  $100^\circ\text{C}$  for 1 h. After poling, the  $d_{33}$  coefficient was measured and its nature is shown in Fig. 2. It may be observed that the highest value of  $d_{33}$  coefficient was observed with PZT/C/PU sample of 59/1/40 vol. % composition. Adding 1.0 vol.% of carbon the  $d_{33}$  piezo-coefficient increases by 25% in comparison with the composite without the semiconductor phase. The values showed are the average of three measurements in three consecutive days. The piezoelectric activity displayed by this composite is due the ceramic phase. Although the space charges are there when an electric field of  $10^6$  V/m is applied (see figure 1), they just help to stabilise the polarisation and have no contribution to the piezoelectric coefficient unlike in porous and non-polar polymers. The PU used as matrix, is non-polar but has no piezoelectric activity when poled at this range of electric field.

The highest value of  $d_{33}$  for composite, doped with 1.0 vol.% of semiconductor phase, might be because the carbon particles could be trapped between PZT grains, creating a continuous electric flux path, thus making the



**Figure 2.** Piezoelectric activity as a function of semiconductor phase content.

**Table 1.** Composites composition: Volume percent of semiconductor phase, PZT and PU.

Samples	PZT (vol. %)	PU (vol. %)	C (vol. %)
1	60.0	40.0	0.0
2	59.5	40.0	0.5
3	59.0	40.0	1.0
4	58.5	40.0	1.5
5	58.0	40.0	2.0

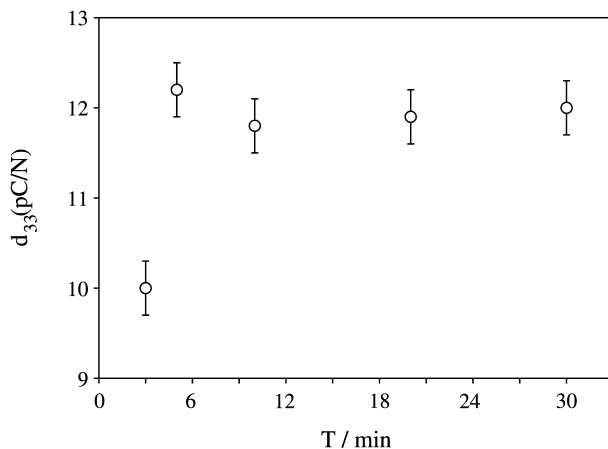
poling process more efficient. Above 1.0 vol. % of carbon content the piezo- activity is reduced, possibly because the electrical conductivity of the composite has increased so much. SA-Gong *et al.*<sup>14</sup> obtained similar results using epoxy-based polymer as matrix.

Figure 3 shows the piezoelectric coefficient of PZT/C/PU (59/1/40 vol. %) as a function of poling time. It appears that a very short poling time of 5 min was enough to polarise this composite while without carbon the composite require almost 1 h to be poled.

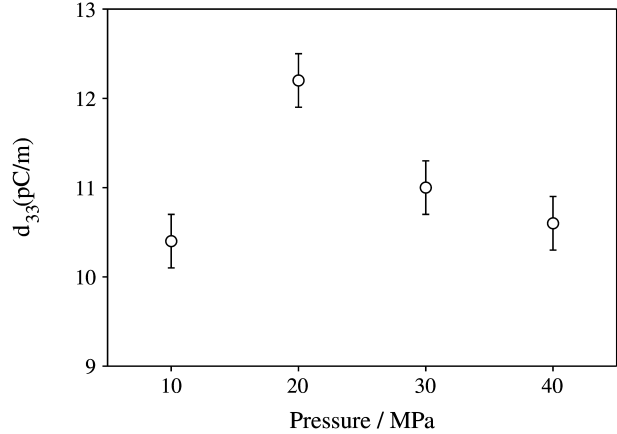
Again these results suggest that a presence of carbon particles in the composite film makes easier the poling process by increasing the electrical conductivity of the polymer phase. According to Maxwell-Wagner model<sup>15</sup> the field acting on the ceramic (PZT) is controlled by the ratio of the electrical conductivity of the polymer to that of the ceramic ( $\sigma_p/\sigma_c$ ).

Another parameter considered was the pressure applied to the sample during the preparation and curing of the composite. Figure 4 shows the variation of piezo-activity with the applied pressure. Although the mechanical pressure applied to the composite is not directly related with the piezoelectric coefficient, the result suggest that with 20 MPa the compactness of the ceramic grains together with the carbon grains allows a cohesive flux path between the adjacent PZT particles. SA-Gong and co-workers<sup>14</sup> found that 50 Mpa was the best pressure to be used for their PZT/C/epoxy composite with 68.5/1.5/30 vol. % composition. Here also the values plotted are the average value of 3 measurements. Figure 5 shows the behaviour of the permittivity and dielectric loss of PZT/PU/C composite with 59/40/1- vol. % poled with 3 MV/m for 5 min at 100 °C. The high frequency data were taken with a General Radio Bridge while the low-frequency data were obtained from the time domain discharge current. The discharge current was measured for 3 h after charging for 27 h. Using the Hamon approximation<sup>9</sup>, the loss factor  $\epsilon''$  could be obtained by,

$$\epsilon'' = \frac{I(t)}{2 \pi f C_0 V} \quad (2)$$



**Figure 3.** Variation of piezoelectric coefficient with the poling time for PZT/PU/C composite with 59/40/1 vol. %.



**Figure 4.**  $d_{33}$  coefficient as a function of applied pressure. Composite PZT/PU/C with 59/40/1 vol. % poled for 10 min.

where  $I(t)$  is the magnitude of the transient current at time  $t$ ,  $C_0$  is the geometric capacitance of the electrode area without the sample,  $V$  is the applied voltage for charging the sample and  $f$  is the Hamon frequency given by,

$$f = \frac{0.1}{t} \quad (3)$$

The low-frequency permittivity ( $\epsilon'$ ) was obtained using Kramer-Kronig transformation<sup>16</sup> given by,

$$\epsilon' = \epsilon_\infty + P \int_{-\infty}^{\infty} \frac{\epsilon''}{\omega - \omega_0} d\omega \quad (4)$$

where  $\epsilon_\infty$  is the permittivity at infinitely high frequency and  $P$  is the Cauchy principal value of the integral.

The experimental data were fitted with Havriliak-Negami equation<sup>17,18</sup>, with two parameters that has the form,

$$\chi(\omega) \propto \frac{1}{[1 + i(\frac{\omega}{\omega_p})^{1-\alpha}]^\beta} \quad (5)$$

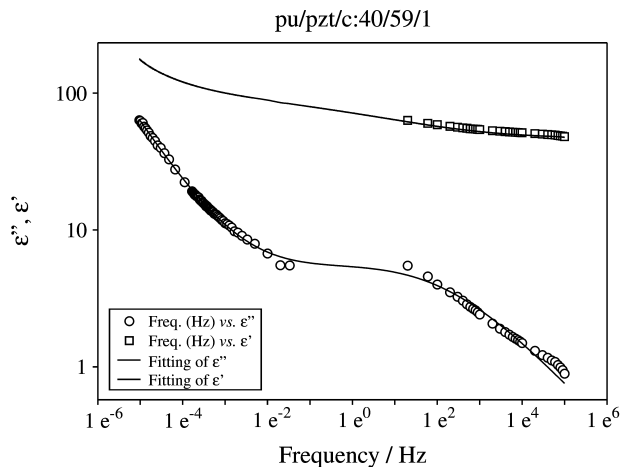
where  $\chi(\omega)$  is the complex dielectric susceptibility and  $\omega_p$  the frequency where occurs the maximum dielectric loss,  $\alpha$  and  $\beta$  are parameters and have no physical significance and  $0 < \alpha < 1$ ;  $0 < \beta < 1$ . The relationship between the permittivity and susceptibility are:

$$\epsilon'(\omega) = \epsilon_\infty + \epsilon_0 \chi'(\omega) \quad (6)$$

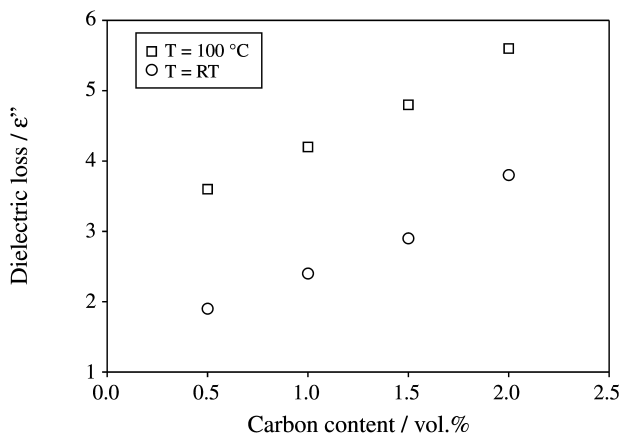
$$\epsilon''(\omega) = \epsilon_0 \chi''(\omega) \quad (7)$$

with  $\epsilon_0 = 8.85 \times 10^{-12}$  F/m being the permittivity of free space.

The peak in the dielectric loss around 10 Hz can be attributed to polymer phase since the dielectric spectroscopy of PZT ceramic shows no relaxation peak in this range of frequency<sup>19</sup>. This peak also was observed in low-density polyethylene (LDPE)<sup>20</sup> and was attributed to the impurities in the polymer matrix. The quasi dc (QDC) conduction, arising from ionic space charge may be observed at low



**Figure 5.** Dielectric behaviour of PZT/PU/C composite. The experimental data were obtained by bridge and time domain techniques.



**Figure 6.** Variation of dielectric loss with the semiconductor phase content in the composite. Frequency = 1 kHz. (□) T = 100 °C, (○) T = RT.

frequency. This phenomenon is also called low-frequency dispersion (LFD)<sup>21</sup>.

The values of permittivity and dielectric loss at 1 kHz for PZT/C/PU with 1.0 vol.% of carbon and PZT/PU 60/40 vol.% are:  $\epsilon' = 54.0$ ,  $\epsilon'' = 2.41$  and  $\epsilon' = 38.4$ ,  $\epsilon'' = 0.82$ , respectively. The influence of the carbon filler in the dielectric loss is evident.

Figure 6 shows the behaviour of dielectric loss of PZT/PU/C composite with 59/40/1 vol.% composition at 1 kHz. It may be observed that the loss factor increases with the increasing of semiconductor phase in the composite, for room temperature and for poling temperature of 100 °C. It is suggested that the enhancement of  $\tan \delta$  may arise from an increasing interfacial polarisation, i.e., Maxwell-Wagner effect. Higher values of dielectric loss create difficulty to apply voltage required for poling and the piezoelectric activity decreases as shown in Fig. 2.

#### 4. Conclusions

An addition of a small amount of semiconductor phase in flexible piezoelectric 0-3 composite allows easy poling at relatively low field and in a short time. With 1.0 vol.%

of carbon the piezoelectric longitudinal  $d_{33}$  coefficient became 25% higher than that obtained with composite without carbon filler, poled at same conditions. The carbon particles located between the PZT grains help to create a continuous electric flux path. By increasing the electrical conductivity of the polymer phase, the applied electric field became more effective on PZT grain.

The applied pressure during the fabrication of the composite appears to be an important parameter to obtain samples with surface and grain distribution quality for good piezoelectric coefficient. Morphological analyses should be done for a consistent conclusion about this question.

Although improved poling conditions of such composites are obtained with carbon doping than for the non-doped composite (PZT/PU), the electrical breakdown observed at relative low field (about 6 MV/m), appears to be a disadvantage. Further studies are in progress to investigate this matter, which might be related with sample preparation.

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