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# PIEZOELECTRIC COEFFICIENT PROPERTIES OF A FLEXIBLE PZT/UPE/C COMPOSITE

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## Abstract

A flexible piezoelectric composite, made from Lead Zirconate Titanate(PZT) powder and Unsaturated polyester (UPE) resin, was doped with small amount of carbon semiconductor powder. The piezoelectric strain coefficient ($d_{33}$) and the dielectric behavior have been studied for this ceramic/polymer composite. The dielectric constant processes of the composite were observed to be dominated by those of undoped ceramic- polymer. The practical results of PZT/UPE/C with ratio 49/50/1 adding a semiconductor phase in the composite showed piezoelectric strain coefficient 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.

## Introduction

Ceramic-polymer composites have received attention from many researchers during the last 30 years [1,2,3,]. They were considerable 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 posses the mechanical strength, flexibility and formability of the polymer together with high electro-active properties of the ceramic. The polymer matrix in a composite consists mainly of a thermoplastic or thermoset resin, it may contain small quantities of additives, inert fillers and adhesives.

Polymer composites are advantageous over other materials for high performance, low cost and simple manufacturing principle. The manufacturing process and molding are greatly influenced by the type of filler being used and the type of polymer being either thermoplastic or thermoset, also influences the process [4].

This concept was established to describe the interspatial relationships in a two-phase material [5]. The connectivity has greatest importance in a multiphase material because it controls the mechanical, electrical and thermal fluxes between the phases.

Composites 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[6] and by Furukawa [7] for 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 Unsaturated polyester (UPE) resin 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 (range from 40 Hz-110MHz) using time domain and bridge techniques.

## Experimental

### *1. A: Sample*

PZT powder (American Piezo Ceramics - APC and - Unsaturated polyester (UPE) this mixture were used as piezo-ceramic and polymer). A fine-grained carbon (C) was used as semiconductor phase. The PZT powder was mixed with carbon by a stirred by Automotive device for 30min prior to introducing and- Unsaturated polyester (UPE) resin was mixing with 0.5 gm accelerator (cobalt napthenate), 0.7 gm hardener (Methyl Ethyl keton peroxide) were added to the mixture and the contents again were mixed thoroughly until a homogeneous state of the mixture was obtained. The slurry of composite was cast into disk mold and it was possible to obtain samples in the thickness range of (100-250)µm. Aluminum electrodes were evaporated onto both sides of the sample after cutting in an appropriated size. The electrodes area were 3.5 x $10^{-4}$ $m^2$. Table (1) shows the samples with respective volume percent of carbon used in this work.

### *2. B: Measurement*

The static Piezoeectric Apparatus Mod. 2011 Piezo d33 Tester (APC) was used for the measurement of d33 piezo coefficient in the thickness direction. A high DC electric field source 6.5kV type Leybold was used for poling the sample that was conditioned in a temperature-controlled chamber.

Capacitance and dielectric loss in the frequency range from 40 Hz-110MHz at room temperature were also measured by using LCR meter type Agilent 42942A terminal Adapter, and the dielectric constant was calculated by equations (1,2).

Microstructural features were observed by using Olympus optical microscope at a magnification of 100X on surfaces of the PZT/UPE film composite. Photomicrographs were shot by using 35mm Olympus camera. The size of the PZT grains were measured at the same magnification on surfaces of the composite films.

## Results and Discussion

All samples, shown in Table 1, were poled with 6.5 kV electric field at 100°C for 7h. After poling, the $d_{33}$ coefficient was measured and its nature is shown in Fig. (1).

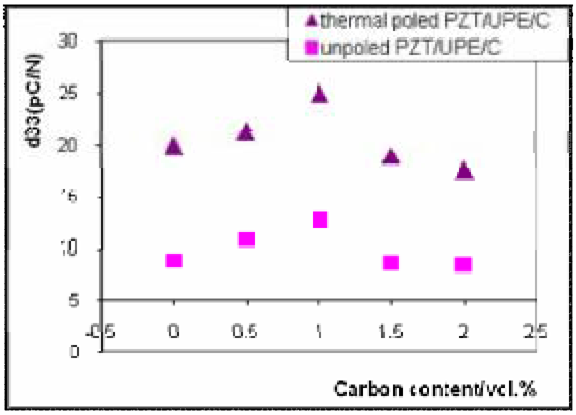

***Fig.(1) : Charge piezoelectric constant as a function of Carbon contents.***

It may be observed that the highest value of $d_{33}$ Coefficient was observed with PZT/UPE/C sample of 49/50/1 vol. % composition. Adding 1.0 vol. % of carbon the $d_{33}$ piezo-coefficient increases in comparison with the composite without the semiconductor phase. The piezoelectric activity displayed by this composite is due the ceramic phase. Although the space charges are there when an electric field of 6.5 kV is applied, they just help to stabilize the polarization and have no contribution to the piezoelectric coefficient unlike in porous and polar polymers.

***Table (1)***
***Composites composition volume percent of semiconductor.***

| ***Sam-ple*** | ***PZT (vol.%)*** | ***UPS (vol.%)*** | ***C (vol.%)*** |
|---|---|---|---|
| 1 | 50 | 50 | 0.0 |
| 2 | 49.5 | 50 | 0.5 |
| 3 | 49 | 50 | 1 |
| 4 | 48.5 | 50 | 1.5 |
| 5 | 48 | 50 | 2 |

The UPE 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, creatinga continuous electric flux path, thus making the poling process more efficient. Above 1.0 vol. % of carbon content the piezo- activity is reduced as shown in Fig.(1), possibly because the electrical conductivity of the composite has increased so much[8,9].

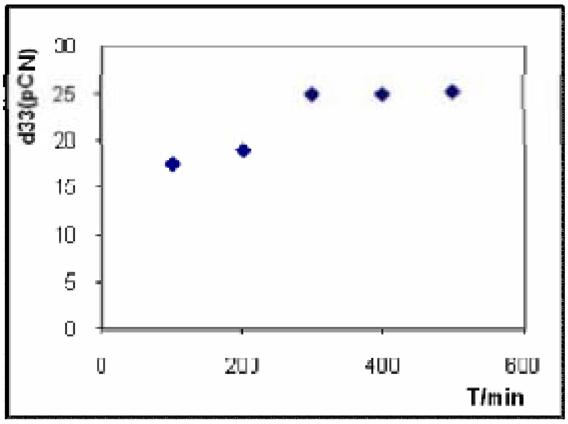

*Fig.(2) : Variation of piezoelectric oefficient with the poling time for PZT/UPE/C composite with 49/50/1 vol.%.*

Fig.(2) shows the piezoelectric constants of PZT/UPE/C (49/50/1) as a function of poling time .It appears that a very short poling time of 7h was enough to polarize this composite while without carbon the composite require almost 24 h to be poled. 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 [10] the field acting on the ceramic (PZT) is controlled by the ratio of the electrical conductivity of the polymer to that of the ceramic ($\sigma_p/\sigma_c$).

Fig.(3, 4) shows the behavior of the permittivity and dielectric loss respectively of PZT/UPE/C composite with 49/50/1- vol. % for poling temperature of 100 °C.

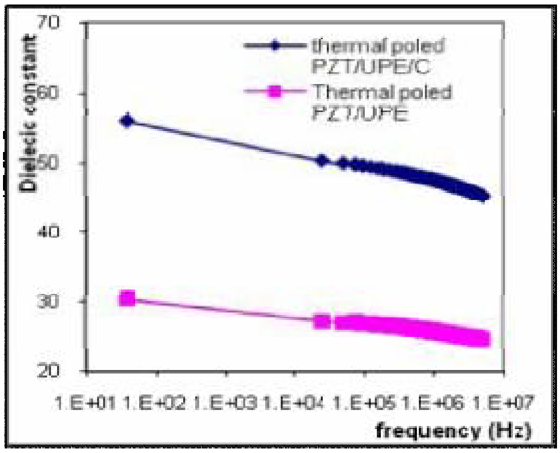

*Fig.(3) : Frequency dependence of dielectric constant for 49/50/1 film composite.*

The dielectric constant increased markedly with the 1%vol. of C after polarization. However, for the poled PZT/UPE composited the UPE might have formed an in sulating layer over the grains of PZT [11]. The high permittivity data were obtained by equations [12, 13]:

$$\in' = \frac{tC}{\in^0 A} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$\in'' = \frac{t}{\omega \in^o RA} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

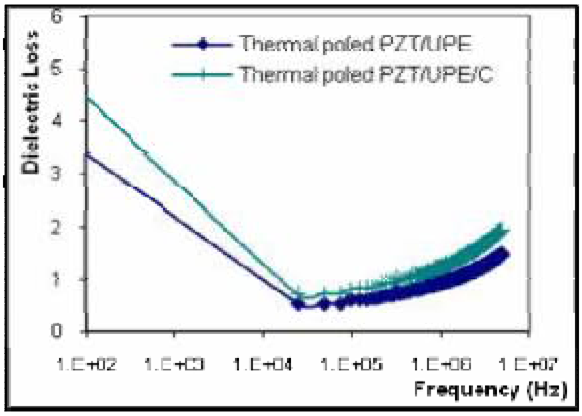

*Fig.(4): Variation of dielectric loss of frequency of PZT/UPE/C with 49/50/1 vol.%.*

Fig.(4) shows the behavior of dielectric loss of PZT/UPE/C composite with 49/50/1 vol.% composition high dielectric loss is observed at low (1kHz) and high (beyond 1MHz) frequencies. High loss at low frequency results from the interfacial polarization which increases with the alignment of crystalline regions with direction of poling field. Also be observed that the loss factor increases with the increasing of semiconductor phase in the composite, for poling temperature of 100 °C. It is suggested that the enhancement of tan δ may arise from an increasing interfacial polarisation. Higher values of dielectric loss create difficulty to apply voltage required for poling and the piezoelectric activity decreases as shown in Fig.(1).

Optical micrographs of poled PZT/UPE/C composites of 49/50/1 vol.% shown in Fig.(5) and (6) respectively. The micro structure in Fig.(5) show the ceramic particles are randomly distributed over the continuous polymer matrix. The presence of PZT may change the morphology of UPE and the polar phase increases. This structure is masked by the PZT content.

***Fig. (5) :Optical micrograph of PZT/UPE composite Showing voids bounded by PZT particles.***

The morphology of surface in Fig.(6) shows rough surface where granulation of PZT and carbon powder become apparent for 1%higher volume fraction of carbon. Also reveal a number of voids that are surrounded by ceramic particles. These voids are likely to be introduced during manufacturing which can cause failure in the composite film under testing. Thus, optical microscopic examination is useful to evaluate the soundness of composite films.

These alternate microstructures should show different mechanical and dielectric properties.

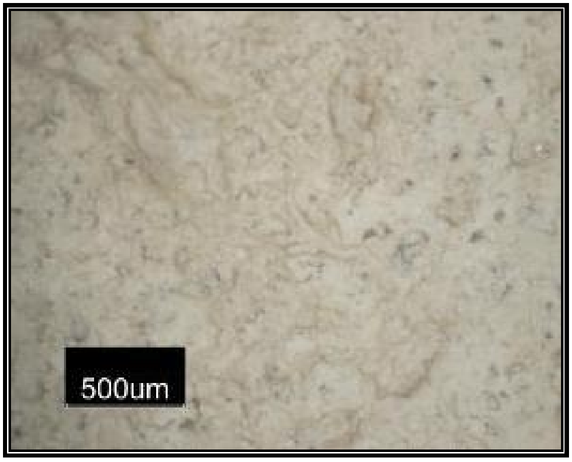

***Fig. (6) : Optical micrograph of PZT/UPE/C composite with 0.1%C volume fraction showing voids bounded by PZT and C particles.***

## 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 d33 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. 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/UPE). The dielectric constant of the composite seems to be influenced by the C powder rather than PZT/UPE. composites show decline in dielectric constant at high frequency.

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## الخلاصة

تم في هذا البحث دراسة الاجهادية الكهربائية (البيزوكهربائية) والعازلية لمتراكب سيراميك –بوليمر المحضر من سيراميك الـــ "PZT" وراتنج بوليمر البولي استر غير المشبع(UPE) غير المطعم، والمطعم بمسحوق شبه الموصل (كاربون) بكسر حجمي 1%. لقد بينت النتائج ان القيم العزلية الكهربائية للمتراكب المطعم بالكاربون اعلى من تلك لمتراكب سيراميك بوليمر غير المطعم. كما بينت النتائج العملية لمعاملات الاجهادية الكهربائية لـــ"PZT/UPE/C" للنسب 49/50/1 ان اضافة طور شبه الموصل للمتراكب خلق مسار فيض كهربائي مستمر بين حبيبات الـــ"PZT"، وقد امكن استقطاب هذا المتراكب بفولتية واطئة ووقت اقل بالمقارنة مع المتراكب غير المطعم