

### **Bangor University**

DOCTOR OF PHILOSOPHY

Evaluation of PTCa/PEKK composite sensors for acoustic emission detection

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Award date: 2002

Awarding institution: Bangor University

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# **Evaluation of PTCa/PEKK composite sensors for**

# acoustic emission detection

# Thesis submitted for the degree of Doctor of Philosophy

I'W DDEFNYDDIO YN Y LLY October 2002 UNIG TO BE CONSULTED IN THE **Pablo Marin-Franch** 

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### Acknowledgments

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I would like to dedicate this thesis to the late Dr Dilip Das-Gupta for his encouragement, supervision and always wise advise, which made this thesis possible. His passion for science will always inspire me.

I would like to thank my supervisors Professor Martin Taylor, Professor John Lewis for their guidance and needed support in the late stages of the project. My gratitude to Dr Dave Tunnicliffe from BAE systems for his supervision and financial support.

I would like also to thank my colleagues Dr Walter Sakamoto, Dr Tony Martin and Oscar Fernandez for their always useful discussions and help and specially for their infinite patience. Also thanks to the Erasmus students of the group who always brought new ideas and challenging questions to the project: Jose Antonio, Luis, Barbara, Filipe, Paolo, Diego and Marco.

My gratitude to the technical staff in the department, specially Gwyn, Don, Albert, Ivor, Ian, John and Miles, who have provided excellent technical and practical assistance during the time of this project. Thanks are also due to the administration staff who could manage to understand my 'funny' accent, in particular Lynne, Yvonne, Wendy and Julie.

Thanks to my mates in the department, Toto (and family), Colin, Chris, Peter, German, Brynmor, Paul, Nacho... Thanks for the good atmosphere of this "small united nations" department and also thanks for the good, although some of them vague, pub chatting memories.

I would like to express my gratitude to my family, Rosa, Gregorio, Rosilla, Toni, Ivan, Eva and Monica for their love and support. I thank specially Ana for always encouraging me and for coping with my ups and downs during the 3 years of the PhD.

### Summary

This thesis reports for the first time the fabrication and characterisation of novel electroactive ceramic/polymer composite films of calcium modified lead titanate (PTCa) and poly (ether ketone ketone).

Composite sensors with different concentrations of ceramic were fabricated using a hot pressing technique. The PTCa ceramic was treated using titanate coupling agent in order to improve sample quality. Dielectric measurements have been performed to study sample characteristics. Piezoelectric and pyroelectric properties of the composites have been measured and the mixed connectivity cube model used to determine the relative amounts of 0-3 and 1-3 connectivity. The advantages and limitations of the model have been discussed. Additionally, some mechanical properties of the composites have been assessed to study their potential ability to detect acoustic emission (AE) in carbon fibre reinforced composites (CFRC).

The composite sensors were placed on and inserted into different panels in order to compare their ability to detect AE in both surface mounted and embedded modes. The composite sensors have been shown to have less sensitivity than the low profile lead zirconium titanate (PZT) ceramic and the porous polypropylene (PP) polymer sensors, but they were found to have more suitable mechanical and thermal properties than the ceramic and polymer respectively for embeddeding in CFRC panels. PTCa/PEKK 60/40% sensors embedded in a CFRC panel have been shown to be capable of detecting the two components of the plate waves, namely, extensional and flexural mode. In addition, it has been shown that the surface mounted PTCa/PEKK composites with 60% volume of ceramic loading can locate simulated AE with high accuracy using triangulation techniques. Finally, it has been shown that the sensors can detect real AE from fibre delamination in a CFRC beam.

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# Chapter 1: Introduction

### **1.1 Introduction**

It has been estimated that 50% of maintenance costs could be reduced with on-line monitoring of aerospace structures since unnecessary inspections would be eliminated. Thus, the development of Health and Usage Monitoring Systems (HUMS) is an active area of research in aerospace structure applications. There are several methods for monitoring damage in such structures, Acoustic Emission (AE) being one of them. An AE source generated by the release of energy as a result of a failure mechanism produces dynamic stress waves that propagate through the structure.

There is a variety of AE sensors which convert the mechanical signal to an electrical signal, including, ferroelectric ceramics, piezoelectric polymers, piezo-composites, optical fibre cavity sensors and micro-electro-magnetic-systems (MEMS) based sensors. Additionally, there are other piezoelectric transducers, such as corona-poled porous polymer foams which could be also be used for AE sensing applications.

### 1.2 Aim of the project

The aim of the present project was to fabricate composite piezoelectric sensors, with appropriated electroactive and mechanical properties, which could be embedded in carbon reinforced fibre composites (CRFC) in order to monitor the health of aerospace structures by means of AE detection. Prior to embedding in CRFC the sensor properties were studied in order to ensure that the composites meet the requirements for optimum detection. Subsequently, the sensors were embedded in CRFC panels and simulated AE tests were carried out.

### 1.3 Choice of Sensor

For many years ferroelectric ceramics have been conventionally used for piezoelectric applications. Low profile ferroelectric ceramic sensors, such lead zirconate titanate (PZT), due to their size, can be embedded in composite structures. However, these materials possess a high stiffness which makes them fragile. To overcome this problem, flexible piezoelectric polymers such as, poly(vinylidene fluoride) (PVDF), have been considered as an alternative. The problem with PVDF and other electroactive polymers is that they cannot be embedded in CFRC structures due to their low melting point. Furthermore, electroactive porous polymer foams can be considered as a potential candidate for AE sensor, but their piezoelectric response can be affected or even eliminated when embedded under pressure. Other sensors such as optical fibre cavity sensors and micro-electro-magnetic-systems (MEMS) based sensors do not appear to have the bandwidth to compete with broadband piezoelectric sensors. Thin film piezolike composites, calcium modified lead titanate/poly(ether ketone ketone) (PTCa/PEKK), possess good mechanical properties compared with those of the ceramic alone and can be embedded in CFRC due to the high melting point of the PEKK polymer, although their electroactive properties are less attractive than that of the ceramic.

Composite materials are fabricated where there is a need to combine properties that cannot be achieved with a single phase material. The design of a composite material will vary, depending on its applications, which may range from agricultural to medical or aerospace. When used for monitoring the integrity of a structure, a piezoelectric transducer must combine high piezoelectric coefficients with the appropriate mechanical properties to provide good sensitivity and good acoustic impedance matching with the structure. Usually, this combination of properties is difficult to obtain in a single phase material and conflicting requirements must be optimised by combining two or more materials.

Due to their ease of fabrication, 0-3 connectivity composites, where the ceramic grains are randomly embedded in the polymer matrix without self-connection in any direction, are not expensive to manufacture. Different types of 0-3 electroactive ceramic/polymer

composite have been developed throughout the years. During the lasts few decades, studies of the electroactive properties of several different composites, such as, PZT/epoxy (Pauer 1973, Furukawa et al 1976), lead titanate (PT)/epoxy and PTCa/epoxy (Banno and Saito 1983), PZT/PVDF (Yamada et al 1982), PTCa/poly(vinylidene fluoride/trifluoroethylene) (P(VDF-TrFE)) (Dias and Das-Gupta 1994) and PTCa/epoxy (Wenger and Das-Gupta 1999) have been made. These studies will be summarised in chapter 2. It has been established also that composites with high ceramic loading and/or with ceramic grain size comparable to that of the sample thickness, possess a certain degree of both 0-3 and 1-3 connectivity and are termed mixed-connectivity composites. These are also discussed in chapter 2.

In the present study a composite consisting of PTCa in the thermoplastic polymer PEKK was employed. The ferroelectric ceramic PTCa is obtained from ceramic lead titanate (PbTiO<sub>3</sub>) by doping the Pb<sup>2+</sup> sites with Ca<sup>2+</sup>. The doping of lead titanate (PT) with calcium increases the electromechanical anisotropy. The electromechanical anisotropy of PTCa ceramic leads to a high value of the  $d_h=d_{33}+2d_{31}$  coefficient. This doping process lowers the Curie temperature of the ceramic (Yamashita et al 1981), which makes PTCa a material easier to pole at a reduced temperature (suitable for polymers) than PT or lead zirconate titanate (PZT). In addition to improved mechanical properties, PTCa has a lower permittivity than PZT resulting in high values of the piezoelectric g coefficients, which leads to a high piezoelectric figure of merit.

The PEKK polymer has excellent chemical resistance and high temperature stability. Having a melting point of 305<sup>o</sup>C, PEKK is a good candidate for fabrication of high temperature ceramic/polymer composite sensors. The flexibility of PEKK, will make the PTCa/PEKK composite a much flexible material than the PTCa ceramic. PEKK has a low permittivity (3.6) which will result in a low permittivity composite and hence in high piezoelectric and pyroelectric figures of merit.

Prior to embedding the composites in CRFC it was necessary to investigate the sensor properties in order to establish that the composites meet the requirements for optimum detection of AE. For that purpose, dielectric, pyroelectric, piezoelectric and ferroelectric measurements were performed on them.

Dielectric spectroscopy can provide information about space charge present in the composites, which can be due to charges trapped in the ceramic/polymer interfaces, ions or moisture. From these features the quality of the sensor can be assessed. Measurements of the piezoelectric coefficients,  $d_{33}$  and  $d_{31}$ , and the electromechanical coupling coefficient,  $k_t$ , can reveal how good the composite sensor will be for ultrasonic applications. Hysteresis measurements will provide information about the ferroelectric properties of the composite. In addition, pyroelectric measurements were carried out in order to complete the characterisation of the electroactive properties of the sensor and reveal any potential pyroelectric applications. Finally, the elastic compliance of the composites was calculated from  $\epsilon$ ,  $k_t$  and  $d_{33}$ .

### **1.4 Detection of Acoustic Emission**

Simulated AE tests have been carried out in different CFRC panels to evaluate the ability of the piezoelectric composites to detect and locate mechanical waves in such structures in both surface mounted and embedded modes. These tests indicate how well the sensor will detect mechanical failure, such as fibre breakage, delaminations fibre-matrix debonding and matrix cracking in the CRFC structure. For that purpose, standard ball bearing drop and pencil lead break tests have been performed. Finally, real AE has been induced and the response of the sensor studied by means of a double cantilever beam experiment.

### **1.5 Thesis Outline**

In chapter one the thesis aims are presented together with a thesis outline. In chapter two, the relevant background concepts relating to electroactivity are given, additionally, the materials used are described. Furthermore, the basic concepts of composites are reviewed. Finally, acoustic emission as a non-destructive technique is introduced. Chapter three includes theoretical models used to describe the composite properties and the lossy resonator. Chapter four study the propagation of plate waves.

The fabrication and polarisation of composite samples is reported in chapter five. In chapter six, the characterisation of dielectric and the electroactive properties of composites is studied. Chapter seven discusses the application of the mixed connectivity model to the different composite properties. Chapter eight deals with the evaluation of the acoustic emission sensors in the surface mounted and embedded mode, their response to simulated and real AE is also discussed. Chapter nine summarises the general conclusions of the thesis and suggests future work.

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# Chapter 2: Literature Review

### **2.1 Introduction**

In this chapter, the basic concepts of dielectric spectroscopy and electroactivity (pyro-, piezo- and ferroelectricity) will be introduced. The materials used during this work, i.e., calcium modified lead titanate (PTCa) and poly(ether ketone ketone) (PEKK) will be introduced. Additionally, the necessity for the fabrication of diphasic ceramic/polymer composites will be discussed as well as a description of their basic properties will be included. Finally, the use of piezoelectric composites for acoustic emission (AE) detection as a non-destructive technique (NDT) will be described.

### 2.2 Dielectrics in electric fields

Dielectric materials can be divided into two main groups, 'polar' and 'non-polar'. In nonpolar materials the centre of charges of the positive and negative charges in each molecule is the same in the absence of an external electric field, i.e. there is a symmetrical distribution of the charge.

If a non-polar material is placed in an external electric field the positive and negative charges of the molecules of the dielectric experience a displacement in the external field direction, moving away from each other, resulting in a polarisation of the molecules of the material.

In polar dielectrics the molecules possess a dipole moment even in the absence of an external electric field. This is due to the charge distribution in the molecules not being

symmetrical. In the absence of an external field, the average dipole moment is zero due to the random orientation of the molecules.

When a low static electric field, E is applied to a dielectric material the induced polarisation in the material, P is proportional to the field and the relationship is given by,

$$\mathbf{P} = (\varepsilon - \varepsilon_0)\mathbf{E} \tag{2.1}$$

where P and E, which are vectors, are in the same direction,  $\varepsilon$  is the permittivity of the material and  $\varepsilon_0$  is the permittivity of free space. The contributions to the polarisation, P and therefore to the permittivity,  $\varepsilon$ , in a dielectric material arise from electrons in the atomic structure, ionic species, permanent dipoles and interfacial or space charge.

The permittivity,  $\varepsilon$  has a frequency dependence which can be represented by a complex quantity as follows,

$$\varepsilon = \varepsilon' + i\varepsilon'' = \varepsilon'(1 + i\tan\delta_e) \tag{2.2}$$

where  $tan \delta_e$  is the dielectric loss. It is possible to express  $\varepsilon'$  in terms of  $\varepsilon''$  and vice versa using Hilbert transforms (Jonscher 1983), i.e.

$$\varepsilon'(f) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\varepsilon''(x)}{(x-f)} dx + \varepsilon_{\infty}$$
(2.3)

$$\varepsilon''(f) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\varepsilon'(x)}{(x-f)} dx \quad .$$
(2.4)

These are the so-called Kramers-Kronig relations, where P is the Cauchy principal value of the integral, f the frequency and x is a variable. Because the real part of the permittivity,  $\varepsilon'$ , cannot be experimentally measured at low frequencies, the imaginary part of the permittivity,  $\varepsilon''$ , is experimentally obtained, fitted using a relaxation law and  $\varepsilon'$  calculated from equation (2.3).

When the dielectric material is placed in an alternating electric field, the polarisation will tend to follow the field variations. If the frequency is high enough some type of dipoles will not be able to follow the field changes and their contributions to the permittivity reduces. This effect is known as dielectric relaxation. Debye proposed a permittivity response function,  $\varepsilon(f)$ , (Debye 1929) given by,

$$\varepsilon(f) \propto \frac{1}{1 + if / f_p}$$
(2.5)

where  $f_p$  is the frequency at which the maximum dielectric loss occurs. But since the recognition that the behaviour predicted by the Debye model, which does not consider interactions between the dipoles, was derived for gases and liquids but not for solids, various alternative forms for the permittivity-frequency response have been proposed. Thus, the Cole-Cole function (Cole et al 1941) has the form,

$$\varepsilon(f) \propto \frac{1}{1 + (if/f_p)^{1-\alpha}}$$
(2.6)

where  $\alpha$  is a fitting parameter in the range (0,1). This function gives a broader but symmetrical loss peak than the Debye function. The Fuoss-Kirwood function (Fuoss et al 1941) is given by,

$$\varepsilon(f) \propto \frac{2(f/f_p)\gamma}{1+(if/f_p)^{2\gamma}}$$
(2.7)

where  $\gamma$  is a fitting parameter. The Davidson-Cole function (Davidson et al 1951) has the form,

$$\varepsilon(f) \propto \frac{1}{\left(1 + if / f_{p}\right)^{\beta}}$$
(2.8)

where  $0 < \beta < 1$ . From this function an asymmetrical loss peak is obtained. The William-Watts function (Williams et al 1970) is given by,

$$\varepsilon(f) \propto \sum_{S-1}^{\infty} \frac{\Gamma(\Delta S)}{(S-1)!} \left[ \frac{(e^{(-i\Delta\pi/2)})^S}{f^{\Delta} f_p^{-\Delta}} \right]^S$$
(2.9)

where  $\Gamma$  is the Lambda function and  $\Delta$  is a fitting parameter. A generalisation of the previous functions is the two parameter Havriliak-Negami function (Havriliak et al 1966) which has the form,

$$\varepsilon(\mathbf{f}) \propto \frac{1}{\left[1 + (\mathbf{i}\mathbf{f}/\mathbf{f}_{p})^{1-\alpha}\right]^{\beta}}$$
(2.10)

where  $\alpha$  and  $\beta$  are fitting parameters which have no physical significance. Even though all these empirical functions are suitable for fitting to experimental data, the best results are achieved with the two parameter Havriliak-Negamy function. However, none of these mathematical models offer any physical interpretation in terms of material properties (Jonscher 1983).

Several theories have been proposed to explain the dielectric behaviour, the theory of Dissado and Hill being the most complete. Dissado and Hill (1983, 1984) developed a quantum mechanical theory to address the cases that the Debye theory does not solve. The main difference between these two theories is that the Debye theory considers superposition of independent dipoles, while the Dissado-Hill theory considers many-body interactions in condensed matter (Dissado et al 1984). The Dissado-Hill theory explains both the dipolar relaxation and the quasi DC processes.

In the Dissado-Hill theory for dipolar relaxations, the dipoles are seen as connected with other dipoles through the structure. Dissado considers condensed matter as being composed of clusters, with each cluster a spatially limited region with a partially regular structural order of individual units. Two kinds of interactions are observed, intra-cluster motions and inter-cluster exchanges, and each of these processes will give their own characteristic contribution to the permittivity function. In the intra-cluster motions, the relaxation of a dipole will produce a 'chain' response in its neighbour dipoles and the reaction of the neighbour dipoles will, in turn, affect the first dipole. The overall effect will be seen as a single cluster dipole moment relaxation. The inter-cluster exchange is due to dipoles near the edge of the cluster interconnecting to a neighbouring cluster. This process is seen as 'noise' on the macroscopic relaxation. The total dynamic permittivity function is given by,

$$\varepsilon(\mathbf{f}) \propto \left(1 + i\frac{\mathbf{f}}{\mathbf{f}_{p}}\right)^{1-n'} \cdot {}_{2}F_{1}\left(1 - n', 1 - m'; 2 - n'; \frac{\mathbf{f}_{p}}{\mathbf{f}_{p} + i\mathbf{f}}\right)$$
 (2.11)

where  $f_p$  is the frequency of maximum  $\varepsilon''$ , n' and m' are in the range of 0<n', m'<1 and  ${}_2F_1$  is the Gaussian hypergeometric function.

The Dissado and Hill theory also described the quasi-DC (QDC) relaxation or Low Frequency Dispersion (LFD), which is observed in carrier dominated systems and is characterised by the absence of peaks. In this case, Dissado and Hill (1984) consider two types of mechanisms, a short time and high frequency behaviour occurring above a characteristic frequency,  $f_c$ , (intra-cluster motions) and a long time and low frequency scale behaviour occurring below  $f_c$  (inter-cluster exchange). Intra-cluster motions are due to charge hopping between sites within the cluster reducing the overall cluster polarisation and inter-cluster exchange is due to exchange of charges between the clusters. For QDC processes, the permittivity function is given by,

$$\varepsilon(f) \propto \left(\frac{f_{c}}{f_{c} + if}\right)^{1-n''} \cdot {}_{2}F_{1}\left(1 - n'', 1 + p; 2 - n''; \frac{f_{c}}{f_{c} + if}\right)$$
(2.12)

where n" and p are in the range of 0 < n", p<1. The Jonscher 'universal' law, both for dipole relaxation and for QDC processes, is obtained from the asymptotic limits of the Dissado-Hill theory.

According to Jonscher (1983), the behavior of the dipolar dielectric system follows a 'universal' law, given by,

$$\varepsilon''(f) \propto \frac{1}{(f/f_p)^{-m'} + (f/f_p)^{1-n'}}$$
 (2.13)

Where n' and m' are related to the entropy of the system. n' is related with the structural ordering in an average cluster whereas m' gives the degree of ordering within the cluster array. The expression obtained for QDC processes obeys a power law,

$$\varepsilon''(f) \propto f^{-n''} \tag{2.14}$$

where n" is again related to the entropy of the system.

### 2.3 Electroactive properties of materials

The electroactive properties of a material, i.e. pyroelectricity, piezoelectricity and ferroelectricity, depend on the symmetry of the crystal structure. Although there is an exception, corona poled porous polymer foams are piezoelectric but do not possess a crystalline structure. Crystals can be classified in 7 crystal systems according to their symmetry. These are triclinic, monoclinic, orthorhombic, rhombohedral, tetragonal, hexagonal and cubic, where the cubic structure is the most symmetric and the triclinic group the least. These systems can be divided into 32 point groups depending on their symmetry with respect to a point. The materials which display electroactive properties are those that present asymmetry.

From the 32 crystal groups, 11 have a centre of symmetry and therefore are non-polar. From the 21 remaining, 20 are piezoelectric. One point group, which has no symmetry centre, has other symmetry elements which can combine to produce the same effect. Only 10 of these piezoelectric materials have a unique polar axis and therefore have spontaneous polarisation and are also pyroelectric. Within this group, the materials that have the ability to switch the polarisation from one state to another are known as ferroelectric.

### 2.3.1 Piezoelectricity

Piezoelectricity is an effect that can be observed in certain single dielectric crystals and in certain multicrystalline ceramics. It takes place when a mechanical compression or tension produces a voltage across the material. The application of mechanical stress to piezoelectric crystals polarises them and the resultant polarisation is proportional to the stress (direct effect). The inverse effect, namely the mechanical response to electrical stress, is manifested in all piezoelectric crystals. The piezoelectric properties can be described by the following equations (Smits 1976),

$$\begin{pmatrix} S \\ D \end{pmatrix} = \begin{pmatrix} s^{E} & d' \\ d & \varepsilon^{T} \end{pmatrix} \begin{pmatrix} T \\ E \end{pmatrix}$$
(2.15)

$$\begin{pmatrix} T \\ D \end{pmatrix} = \begin{pmatrix} c^{E} & -e' \\ e & \epsilon^{s} \end{pmatrix} \begin{pmatrix} S \\ E \end{pmatrix}$$
 (2.16)

$$\begin{pmatrix} T \\ E \end{pmatrix} = \begin{pmatrix} c^{D} & -h' \\ -h & \beta^{s} \end{pmatrix} \begin{pmatrix} S \\ D \end{pmatrix}$$
 (2.17)

$$\begin{pmatrix} \mathbf{S} \\ \mathbf{E} \end{pmatrix} = \begin{pmatrix} \mathbf{s}^{\mathrm{D}} & \mathbf{g}' \\ -\mathbf{g} & \boldsymbol{\beta}^{\mathrm{T}} \end{pmatrix} \begin{pmatrix} \mathbf{T} \\ \mathbf{D} \end{pmatrix}$$
(2.18)

where S is the strain, D the dielectric displacement, T the stress, E the electric field, s is the elastic compliance, c is the elastic stiffness constant,  $\varepsilon$  the dielectric permittivity, d, e, h and g are the piezoelectric coefficient tensors and  $\beta$  is defined as the inverse of the permittivity matrix. Note that all the variables are tensors and that the suffix ' denotes a transposed tensor. The superscripts denote variables which are held constant. The piezoelectric coefficients appearing in equations (2.15) to (2.18) can be now defined as;

$$\mathbf{d}_{ij} = \left[\frac{\partial \mathbf{D}_{i}}{\partial \mathbf{T}_{j}}\right]_{\mathrm{E}} = \left[\frac{\partial \mathbf{S}_{j}}{\partial \mathbf{E}_{i}}\right]_{\mathrm{T}}$$
(2.19)

$$g_{ij} = -\left[\frac{\partial E_i}{\partial T_j}\right]_{D} = \left[\frac{\partial S_j}{\partial D_i}\right]_{T}$$
(2.20)

$$\mathbf{e}_{ij} = \left[\frac{\partial \mathbf{D}_i}{\partial \mathbf{S}_j}\right]_{\mathbf{E}} = -\left[\frac{\partial \mathbf{T}_j}{\partial \mathbf{E}_i}\right]_{\mathbf{S}}$$
(2.21)

$$\mathbf{h}_{ij} = -\left[\frac{\partial \mathbf{E}_i}{\partial \mathbf{S}_j}\right]_{\mathbf{D}} = -\left[\frac{\partial \mathbf{T}_j}{\partial \mathbf{D}_i}\right]_{\mathbf{S}}$$
(2.22)

The subscripts i and j indicate the direction of the response and the applied stimulus respectively. Note that the first equalities in equations (2.19) and (2.20) are due to the direct piezoelectric effect whereas the second equalities are from the inverse effect. From equations (2.21) and (2.22) it can be shown that the coefficients are related, namely,

$$\frac{d_{ij}}{g_{ii}} = \varepsilon^{T}_{ii}$$
(2.23)

$$\frac{\mathbf{e}_{ij}}{\mathbf{h}_{ij}} = \varepsilon^{s}{}_{ii} \tag{2.24}$$

$$\frac{\mathbf{e}_{ij}}{\mathbf{d}_{ij}} = \mathbf{c}^{\mathrm{E}}_{ii} \tag{2.25}$$

$$\frac{\mathbf{h}_{ij}}{\mathbf{g}_{ij}} = \mathbf{c}^{D}_{ii} \tag{2.26}$$

The  $d_{ij}$  and  $g_{ij}$  are piezoelectric strain coefficients, which provide a measure of the response of a piezoelectric sensor in the receiver mode, whereas  $e_{ij}$  and  $h_{ij}$  are piezoelectric stress coefficients, which are related to the output of a piezoelectric actuator in the transmitting mode. From equations (2.23) to (2.26), it can be observed that for full characterisation of a piezoelectric material only  $\varepsilon^{T}$ ,  $c^{E}$  and d need to be measured since all the other coefficients can be derived.

Like the permittivity,  $\varepsilon$ , c and d have a frequency dependence which can be represented by complex quantities as follows

$$c = c' + ic'' = c'(1 + i \tan \delta_m)$$
 (2.27)

$$d = d' + id''$$
 (2.28)

where  $tan\delta_m$  is the mechanical loss. Note that the frequency dependence of d is very small in ceramic and ceramic/polymer composite materials and will be considered negligible in the following. The mechanical loss,  $tan\delta_m$ , is the inverse of the mechanical quality factor,  $Q_m$ , of the piezoelectric material. Since a high value of  $Q_m$  results in a low acoustic energy absorption in the material, a small value of  $Q_m$  is desirable for a sensor of acoustic emission.

The hydrostatic  $d_h$  coefficient is another important piezoelectric coefficient, which arises in hydrostatic applications, and is given, in a perovskite ceramic (Smits 1976), by

$$d_{h} = 2d_{31} + d_{33} . (2.29)$$

The effective electromechanical coupling coefficient k is defined in order to measure the ability of piezoelectric materials to convert mechanical energy input into electrical energy output or vice versa. It is given by,

$$k^{2} = \frac{\text{mechanical energy converted to electrical energy}}{\text{input of mechanical energy}}$$

$$= \frac{\text{electrical energy converted to mechanical energy}}{\text{input of electrical energy}}$$
(2.30)

The effective electromechanical coupling coefficient, k, is a  $3\times3$  matrix and depends on the direction of the stress and the electric field. The thickness electromechanical coefficient, k<sub>t</sub> is an important feature in poled thin films and can be expressed as a function of the piezoelectric strain coefficients g, the permittivity  $\varepsilon$  and the elastic stiffness using the expression (Moulson 1990),

$$\mathbf{k}_{t} = (\mathbf{\epsilon}_{33}^{\mathrm{S}} \mathbf{c}_{33}^{\mathrm{D}})^{1/2} \mathbf{g}_{33} .$$
 (2.31)

A useful piezoelectric figure of merit (FOM<sub>h</sub>) is given by (Dias et al 1994),

$$FOM_{h} = d_{h}g_{h}$$
(2.32)

which describes the effectiveness of the piezoelectric sensor, where  $g_h=g_{33}+2g_{31}$  is defined in a similar manner to the hydrostatic piezoelectric coefficient,  $d_h$ .

### 2.3.2 Pyroelectricity

Certain piezoelectric crystals, when heated or cooled, develop electric charges of opposite sign at their ends; this effect is known as pyroelectricity. A crystal is pyroelectric if it possesses a net dipole moment per unit cell, which means that the centre of charges of the positive charge is displaced from that of the negative charge. This can be proved to imply a lower symmetry for the crystal point group than for a piezoelectric material.

The pyroelectric coefficient at constant strain, p, is defined as the rate of change of the remanent polarisation, P, with temperature when the material is heated (or cooled) at constant rate. The clamped state (i.e. S=0) pyroelectric coefficient is defined as (Moulson et al 1990)

$$p^{S} = \left(\frac{dP}{d\theta}\right)_{E,S}$$
(2.33)

where  $\theta$  is the temperature. However, the clamped state is not of much use since for practical applications as pyroelectric sensors, the sample is in a stress-free condition, i.e. T=0. In this case an additional contribution, due to the piezoelectric effect needs to be included in the definition of pyroelectric coefficient (Kepler et al 1978, Furukawa 1989), i.e.,

$$p = p^{S} + \alpha d / s^{E}$$
(2.34)

where  $\alpha$  is the linear expansion coefficient. A third contribution to the pyroelectric current can be included in the right hand side of equation (2.34). This contribution takes place when there is a gradient of temperature in the pyroelectric transducer (Colling 1980, Lang et al 1986).

It can be shown that, due to their tetragonal symmetry, ferroelectric ceramics have only one non-zero component in their pyroelectric coefficient tensor (Furukawa 1989), namely,

$$\mathbf{p} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \mathbf{p}_{33} \end{pmatrix}$$
(2.35)

The symbol p will be employed instead of p<sub>33</sub> in the following.

A suggested figure of merit (FOM<sub>p</sub>) for pyroelectric materials is (Dias et al 1994)

$$FOM_{p} = \frac{p}{\varepsilon}$$
(2.36)

which reflects the voltage responsivity of a pyroelectric material.

### 2.3.3 Ferroelectricity

Only dielectric materials with a particular atomic structure are ferroelectric. A material is defined as ferroelectric if it has, in the absence of an electric field, two crystal orientations, which can be shifted from one to another by an electric field (Lines et al 1977). In such materials, the relationship between the induced polarisation in the crystal and the applied electric field is non-linear and follows an hysteresis loop as in figure 2.1. The main characteristic of ferroelectric materials is that when the electric field is removed there will be a remanent polarisation,  $P_r$ , and a coercive electric field,  $E_c$  needs

to be applied in order to obtain a zero value of induced polarisation. The spontaneous polarisation,  $P_s$  is the extrapolation of the saturation polarisation to zero electric field.



Figure 2.1: Hysteresis loop of a ferroelectric material.

The hysteresis loop can be explained by the presence of domains in the ferroelectric. A domain is a microstructural region in which the polarisation is saturated in a particular direction. In a non-polarised ferroelectric, the polarisation of individual domains is orientated in such a way that the net polarisation of the crystal is zero. When an external field is applied, the domains whose components of polarisation are in the direction of the field enlarge at the expense of less favourably orientated domains. At high fields, the material may form a single domain. Any further increase in polarisation with increasing field will then arise from normal polarisation mechanisms, so that the polarisation-field relation is linear. If the field is removed, a part of the oriented domain polarisation ( $P_s$ ), since there will be a tendency for some domains to resume their original orientation. The coercive field of a multi-domain polycrystalline ferroelectric will be higher than that of a

single crystal due to defects and internal strains within the crystallites impeding the poling process.

A feature of many ferroelectric materials is that near their Curie temperature,  $\theta_c$ , above which spontaneous polarisation falls to zero, the dielectric permittivity,  $\varepsilon$ , exhibits a strong temperature dependence. The permittivity reaches a peak at  $\theta_c$  following the Curie-Weiss law

$$\varepsilon = \frac{C}{\theta - \theta_{c}}$$
(2.37)

where  $\theta$  is the temperature, C is the Curie constant. The disappearance of spontaneous polarisation above  $\theta_c$  is due to a phase transition occurring in the ferroelectric material. This transition from the ferroelectric to the paraelectric state is accompanied by a change in lattice structure, normally to one of higher symmetry. In the paraelectric state, due to the absence of spontaneous polarisation, the hysteresis loop disappears, showing the normal linear relationship between polarisation and field



*Figure 2.2*: Dependence of saturation polarisation of different dielectric materials on temperature (Braithwaite et al 1990).

The spontaneous polarisation returns as the dielectric material cools and reaches a saturation value at lower temperatures. Figure 2.2 shows the temperature dependence of

the saturation polarisation exhibited by various ferroelectric materials together with their respective Curie temperatures, where the spontaneous polarisation vanishes.

### 2.4 Single Phase Materials and Electroactive Composites

### 2.4.1 Ferroelectric ceramics

Ferroelectric ceramics are composed of polycrystalline grains separated by grain boundaries. Each grain has one or several polarization domains. In theory, the multidomain state can be transformed into a single domain by applying an external electric field. In ceramics, however, the random orientation of grains and the 'frictions' associated with grain boundaries will reduce the maximum polarisation that can be achieved. Therefore the spontaneous polarization of ceramics will be lower than that of a single crystal. In the absence of an electrical field, the ferroelectric properties of ceramics change with time when subjected to mechanical stresses or temperature changes.

### 2.4.1.1 Barium titanate

One of the most important ferroelectric ceramics is barium titanate (BaTiO<sub>3</sub>) which belongs to a family of crystals possessing the 'perovskite' structure. The structure is based on the general formula ABO<sub>3</sub>, where A is a mono or divalent metal and B is a tetra- or pentavalent metal. Above its Curie temperature, BaTiO<sub>3</sub> has a cubic unit cell composed of octahedral O<sup>2-</sup> centred around Ti<sup>4+</sup> ions placed in each corner of the cubic cell and with the large Ba<sup>2+</sup> ion placed in the middle of the cube as shown in figure 2.3. When the ceramic is cooled below its Curie temperature the crystal structure undergoes a phase transition to a structure possessing a lower degree of symmetry. This is due to the distortion of the unit cell from the symmetrical cubic structure by a displacement of the Ti<sup>4+</sup> cation to off-centre positions. This displacement also produces a distortion in the octahedral cage. Thus the unit cell becomes tetragonal in shape having a dipole moment along the c axis, see figure 2.4. This transition occurs at  $125C^{\circ}$ . Two more transitions to lower symmetry structures occur at 0 C<sup>o</sup> (tetragonal-orthorhombic) and -80  $C^{\circ}$  (orthorhombic-rhombohedral) respectively. The displacement of a Ti<sup>4+</sup> ion produces a chain effect on the others ions in the crystal, making them all displace in the same direction and resulting in a net overall polarisation within the crystal.



*Figure 2.3:* Barium titanate crystal showing the perovskite structure with corner sharing octahedral cages containing the  $Ti^{4+}$  ion and the central  $Ba^{2+}$  ion.







Cubic  $\rightarrow$  Tetragonal (125 °C)

Tetragonal  $\rightarrow$  Orthorhombic (0 °C)

```
Orthorhombic→Rhombohedral (-80 °C)
```



*Figure 2.4*: Phase transition of  $BaTiO_3$  showing the displacement directions of the  $Ti^{4+}$  ions.

In the ferroelectric state, the energy of the Ti<sup>4+</sup> ion as a function of its displacement along the c axis is as shown in figure 2.5 where the origin corresponds to the no distortion situation. It forms a potential well centred on the non-displacement position and it has two equal local minima, one at each side of the origin. The ion will tend to be at a lower energy configuration but the application of an electrical field along the c axis may provide enough energy for the cation to overcome the energy barrier and 'jump' to the other local minimum. This will reverse the direction of the polarisation of the unit cell producing, by reducing the energy barrier of the neighbouring ions, a chain effect which switches the total polarisation of the crystal.



Displacement of Ti4+ from central position

*Figure 2.5*: Energy as a function of  $Ti^{4+}$  ion displacement along the c-axis.

Near to their transition temperatures  $BaTiO_3$  and many other ferroelectric ceramics are very susceptible to the applied field, giving rise to high values of their permittivities. The greater temperature dependence is observed close to the para-ferroelectric phase transition, figure 2.6.



Figure 2.6: Temperature dependence of the relative permittivity of  $BaTiO_3$  measured in the a and c directions (Moulson et al 1990).

### 2.4.1.2 Calcium modified lead titanate (PTCa)

Calcium modified lead titanate (PTCa) is obtained from the ferroelectric ceramic lead titanate (PT) by doping the  $Pb^{2+}$  sites with  $Ca^{2+}$ . PT is a perovskite ceramic similar to BaTiO<sub>3</sub>. Due to its high tetragonal distortion, resulting in a spontaneous polarisation of 0.81 Cm<sup>-2</sup> (Jaffe et al 1971), PbTiO<sub>3</sub> should be a good ferroelectric material. However, it is a ceramic difficult to maintain in sintered form as it cools down below its Curie temperature. In order to overcome such problem, the doping of pure lead titanate with lanthanide and alkaline earth elements has been studied during the 1980's (Gallego-Juarez 1989, Wersing et al 1989). This process improved both the mechanical and electroactive properties of the ceramic. The most interesting of the dopants was found to be Ca<sup>2+</sup> (Yamashita et al 1981).

The doping of PT with calcium by substituting 24% of the lead atoms with  $Ca^{2+}$  atoms on the A sites, increases the electromechanical anisotropy thus decoupling the d<sub>31</sub> and d<sub>33</sub> coefficients. The electromechanical anisotropy of PTCa ceramic leads to a high value of the d<sub>h</sub> coefficient. This doping process lowers the Curie temperature of the ceramic to 260 °C (Yamashita et al 1981), which makes PTCa an easier material to pole at a reduced temperature than pure PT or lead zirconate titanate (PZT). Thus PTCa is suitable for forming ferroelectric ceramic/polymer composites. In addition to improved mechanical stability on cooling through its Curie temperature, PTCa has a lower permittivity than PZT resulting in high values of the piezoelectric g coefficients, which leads to a high piezoelectric figure of merit (FOM<sub>p</sub>).

### 2.4.2 Non-electromechanically active Polymers

Many polymers, although not electromechanically active, possess the mechanical properties which make them suitable to host the ceramic for electroactive ceramic/polymer composites.

### 2.4.2.1 Poly(ether ketone ketone) Polymer

Poly(ether ketone ketone) (PEKK), due to its excellent chemical resistance, low moisture absorption, low flammability, high temperature stability and good processability, has been used in recent years for multiple aerospace applications. Having a melting point of 305<sup>0</sup>C, PEKK is a good candidate for fabrication of high temperature ceramic/polymer composite sensors that potentially can be embedded in carbon fibre reinforced composites.

The synthesis of PEKK follows a Friedel-Crafts polycondensation of diphenyl ether (DPE) and terephthanoyl chloride (T) to form the T isomer,



Additionally, PEKK can follow a polycondensation of DPE and isophthaloyl (I) to give the I isomer,



PEKK has a Young's modulus of 4.5 GPa which is about two orders of magnitude smaller than that of the PTCa ceramic (183 GPa). This will make a PTCa/PEKK composite a much more flexible material than the ceramic alone. PEKK has a permittivity of 3.3 which suggests that the polymer is slightly polar although it does not show electroactive properties after being poled. The low permittivity of PEKK will result in a low permittivity of the composite and hence in high piezoelectric and pyroelectric figures of merit (see equations 2.32 and 2.36). Additionally, PEKK has a dielectric loss at room temperature of 0.004 at 1 kHz. This polymer also possesses a high electrical resistivity in the range of  $10^{14} \Omega m$ , therefore PTCa/PEKK composites will require a high poling field in order to polarise the ceramic. 24 MV/m will be the limiting poling field since this is the value of the dielectric strength of the polymer.

Sample preparation conditions, especially the manner of cooling from the melt, will influence the crystallisation rate of the polymer. Differential Scanning Calorimetry (DSC) shows (figure 2.7) that the majority of the polymer is in the crystalline phase rather than the amorphous form since the peak observed at the glass transition temperature ( $T_g$ =154 °C) is relatively small.



*Figure 2.7:* DSC of PEKK showing the glass transition occurring at  $T_g = 154$  °C and melting at  $T_m = 304$  °C.

### 2.4.3 Ferroelectric composite materials

Composite materials are fabricated where there is a need to combine properties that cannot be achieved with a single phase material. The design of a composite material will vary depending on its applications, which may range from agricultural to medical or aerospace. When used for monitoring the integrity of a structure a piezoelectric transducer must combine high piezoelectric coefficients with the appropriate mechanical properties to provide good acoustic impedance matching with the structure. Usually, this combination of properties is difficult to obtain in a single phase material, therefore conflicting requirements must be optimised by combining two or more materials. Piezoelectric ceramics possess, in general, high electromechanical coupling coefficients  $(k_t)$  and piezoelectric charge coefficients  $(d_{33} \text{ and } d_h)$  and low dielectric losses  $(\tan \delta_e)$ . These properties make piezoelectric ceramics attractive as transducer materials. On the other hand, ceramics are brittle, non-flexible and non-formable. They have high densities, which give large acoustic impedances, and also have large permittivities, which reduce their piezoelectric figure of merit (FOM). Moreover, ceramics have a high mechanical quality factor  $(Q_m)$  which leads to a 'ringing' effect that lowers the absorption of acoustic energy.

Although, non-polar polymers are not electromechanically active, they have low density, are highly flexible and have low dielectric permittivities. Hence, by mixing the required amount of ceramic filler with the polymer matrix the resulting properties of the composite material may be properly adjusted. A trade-off will exist between the mechanical properties, such as, density, flexibility, mechanical factor and their dielectric and piezoelectric properties, i.e., electromechanical coupling coefficients ( $k_t$ ) and piezoelectric charge coefficients ( $d_{33}$  and  $d_h$ ). Flexible composite materials with a higher piezoelectric figure of merit ( $d_hg_h$ ) than the ceramic can be fabricated although their electromechanical coupling coefficients will be lower.

The phases in composite materials may be spatially self-connected in one or more dimensions. The degree and type of connectivity controls the mechanical, electrical and thermal fluxes between the phases. In a two-phase or diphasic system there are ten different ways or connectivity patterns of self-connection of the constituent phases (Newnham et al 1978). This can be expressed with two digits, denoting the connectivity of the filler and the connectivity of the matrix respectively.

The ten cases represented in figure 2.8 are: 0-0, 0-1, 0-2, 0-3, 1-1, 1-2, 1-3, 2-2, 2-3, and 3-3, where a cube represents the composite block. The first digit refers to the connectivity of the filler and the second to that of the host material. A composite made of particles of ceramic powder embedded in a polymer matrix will be indicated as a 0-3 composite, whereas a composite consisting of fibres implanted in a matrix will be

denoted as a 1-3 composite. Note that this classification does not specify the connectivity directions.

In the case of n constituent phases in the composite the number of connectivity phases is given by

$$\frac{(n+3)!}{3!n!} . (2.38)$$

Hence 20 patterns will be obtained for the three phase composite, 35 for four phases, 56 for five components etc.



Figure 2.8: Ten different connectivity patterns of diphasic materials (Newnham et al 1978).

The physical properties of the composite will depend on the individual properties of the phases. These can be classified as sum, combined and product properties. A sum property is a property which derives from an equation which, following the mixing rules (Newnham et al 1978), includes an averaging of the analogous properties of the constituent phases, so that the composite property value is bounded by the corresponding property values of the constituent phases. An example of this property is the density. A combination property requires the averaging of more than one property of the constituent phases. An example of this is given by a figure of merit, which involves more than one material property. The pyroelectric figure of merit  $p/\varepsilon$  depends both on the pyroelectric coefficient and on the permittivity and due to their different rules of mixing, the pyroelectric FOM<sub>p</sub> can be greater or smaller than any of its constituent phases. The more complex ones are the product properties. Product properties originate from a coupling between two properties which do not match in the constituent phases and hence produce an entirely different property in the final composite. For example, the coupling of the piezoelectric effect in the ceramic with the linear expansion of the composite produces an additional contribution to the pyroelectric effect.

The physical properties and the quality of the ferroelectric ceramic/polymer composites depend on the size of the composite ceramic grain, the uniformity and thickness of the composite material, the interfacial effects and the porosity of the composite.

### 2.4.3.1 0-3 electroactive composites

Due to their ease of fabrication, 0-3 composites are not expensive to manufacture. These composites can have up to 70% of ceramic by volume fraction (Banno et al 1983). On the other hand, 1-3 composites, have better electroactive properties, in some cases greater than the ceramic alone. However, they are more expensive to produce than 0-3 composites.

Different types of 0-3 electroactive ceramic/polymer composites have been developed throughout the years. Studies of piezo- and dielectric properties of PZT/epoxy with 25% of ceramic loading have been carried out by different researchers (Pauer 1973, Furukawa et al 1976). However the composites showed low electroactive properties in

comparison with those of the ceramic. Other ceramic fillers such as, PT and PTCa, were used by Banno and Saito (1983) and composites with ceramic loading as high as 70% were manufactured. It was found that PT with quenched ceramic grains, had the best properties for hydrophone applications.

Yamada et al (1982) developed composites incorporating a high percentage of PZT (67%) in the electroactive polymer poly(vinylidene fluoride) (PVDF) and high piezoelectric coefficients were obtained. Furthermore, Abdullah and Das-Gupta (1990) found that PZT/PVDF composites had a pyroelectric figure of merit higher than that of the PZT ceramic. A similar result was achieved by Dias and Das-Gupta (1994) using PTCa ceramic and poly(vinylidene fluoride/trifluoroethylene) (PVDF-TrFE). In addition, high piezoelectric coefficients were also found. Wenger et al (1999) fabricated composites of PTCa/(PVDF-TrFE) and PTCa/epoxy and showed the ability of these sensors to detect AE waves.

0-3 ceramic/polymer composites are difficult to polarise because of the high resistivity of the polymers compared with the electroactive ceramic, which results in a low local field seen by the ceramic (Sa-Gong et al 1983). This phenomenon occurs because the majority of the electric field applied during poling is dropped across the polymer matrix. To increase the local field the applied field can be increased but the electrical strength of the ceramic and the sample quality will limit the maximum field that can be applied. To ease the poling process, a conductive third phase can be used. This will create a continuous electric flux path between the ceramic grains (Sa-Gong et al 1983).

Dias and Das-Gupta (1994) found that quenched ceramic grains gave better electroactive properties than milled ceramic grains, this is due to the mechanical damage caused to the ceramic grains during the milling process. Another important factor in composite fabrication is the grain size.

It has been reported that an increase in the ceramic grain size results in an increase in the dielectric permittivity and the piezoelectric coefficients (Pardo et al 1988). On the other hand, the bigger the ceramic grain, the harder it is to pole the sample due to a lowering
of the breakdown strength with increase in the grain size (Reed et al 1990). It was also found that the hydrostatic figure of merit was independent of the grain size.

It has been noticed also that, in composites with bigger ceramic grains, the particles are more likely to be in contact with each other while in composites with smaller grains, the particles are more likely to be surrounded by polymer. Research has been carried out in order to assess the dependency of the piezoelectric and dielectric properties on the ratio between the composite thickness, t and the average particles size, <G> (Pardo 1988). It was found that composites with high <G>/t ratio tended to behave as 1-3 connected composites and demonstrated good electroactive properties. When t/<G> had a low value, the electroactive properties decreased dramatically, from which it was concluded that the composites possessed a certain degree of heterogeneity, possessing a distribution of 0-3 and 1-3 connectivity and so were termed mixed-connectivity composites. Further discussion of the way in which the connectivity determines the dielectric and electroactive parameters of composites is given in chapter 3.

### 2.5 Applications: Measurement of Acoustic emission

There is a wide range of applications for piezo- and pyroelectric transducers although this thesis has concentrated on acoustic emission (AE) applications.

AE is one of the key non-destructive inspection techniques with the potential to both detect and locate damage sites continuously in structures in a non-destructive manner. An AE transducer senses the dynamic stress waves propagating through a structure, which have been generated by the release of energy as a result of a failure mechanism.

Piezoelectric ceramics have already been used as low profile sensors for detecting AE. Owing to their small size, low profile sensors can be either surface mounted flush with the structure or even embedded within it. Potentially, this can improve their response and resistance to environmental effects. However, the potential applications of piezoelectric ceramics as embedded sensors for structural damage detection are restricted due to their relatively high stiffness and fragility. In order to overcome this problem use has been made in recent years of ceramic/polymer thin film composite sensors, which combine the high piezoelectric properties of ferroelectric ceramics and the viscoelastic properties of polymers.

#### 2.5.1 AE as a non-destructive testing method

Acoustic emission is defined as "the class of phenomena where transient elastic waves are generated by the rapid release of energy from sources located within the material, or the transient elastic waves so generated" (ASTM 1982).

AE in structures can be generated from many different mechanisms, which include, damage inducing impacts, initiation and growth of damage, movement, fretting, etc. Additionally, background effects can arise from non-damage impacts, component rubbing, structural vibrations and electromagnetic noise. In fibre reinforced composites typical damage mechanisms include, intra-laminar and longitudinal matrix cracking, delaminations and fibre-matrix debonding, fibre fracture and interface de-bonding within adhesive/co-cured layers. In metallic structures, fatigue cracks and corrosion are the main contribution to structural degradation.

AE tests can provide information about the AE source by simply measuring waveform parameters of the stress wave generated, such as amplitude and frequency. Alternatively, information can also be obtained from other characteristics of the wave, such as, AEevent counting and rate statistics, such as rate of signal arrival or energy at the sensor. Figure 2.9 shows the basic characteristics of a AE stress wave.

The AE technique differs from other non-destructive techniques (NDT) in two significant ways. First, the energy that is detected is released from within the test object rather than provided by the test method. Secondly, the AE method is capable of detecting the dynamic process associated with the degradation of structural integrity. AE is not directional and the majority of AE sources appear as point sources radiating spherical elastic wave. Therefore the sensor needs only to be located in the vicinity of the AE source. Additionally, tests can be undertaken while the structure is in operation



allowing continuous monitoring and giving warning so catastrophic failure of the system can be prevented.

Figure 2.9: Illustration of an Acoustic Emission wave pattern.

However, one of the main problems in AE detection in fibre reinforced composites is the attenuation of the wave resulting in a reduced sensitivity at increasing distances. In order to overcome this difficulty, closer sensor spacing is required. Another disadvantage of AE monitoring compared with other NDT is the irreversible nature of some processes, for example, the Kaiser effect (1950), meaning that each AE event would occur only once. Therefore the inspection must have a 'now-or-never' quality.

The acoustic wave form will be dependent on the source type, the propagation path and the sensor characteristics. The characterisation of the source is difficult due to the complexity of the waveforms. Since AE detection always involves the presence of a surface, a practical representation of a real structure is that of an infinite plate, a solid bounded by two parallel planes. An acoustic wave propagating in the plate from the surface will have two components, dilatational (longitudinal if curvature is neglected) and distortional or equivoluminal (transverse) (Auld 1973). In addition, surface waves or Rayleigh waves may be generated. The wave components will be reflected in both surfaces creating multiple components echoing back and forth between the two surfaces. Therefore, the signal waveform received some distance from the source will change significantly from the original.

In addition, the detected AE signal will depend on the characteristics of the sensor, such as acoustic impedance, frequency response bandwidth, piezoelectric coefficient, electromechanical coupling coefficient (Martin et al 1999, Wenger et al 1999, Dias et al 1996), which will distort further the detected wave. To minimise this interference, the right choice of measuring sensor must be made. The main considerations in the choice of the AE sensor are the frequency response, the sensitivity and the environmental and physical characteristics. AE sources emit over a wide frequency band, typically in the range from the audio to 50 MHz. A common frequency range for AE testing is around 300 kHz, so a good sensor response in that range is desirable.

There is a variety of AE sensors, these include, ferroelectric ceramics, piezoelectric polymers and piezo-composites, which convert the mechanical signal to an electrical signal. Available commercial sensors are generally packaged in robust electrically shielded cases. These sensors can be designed to either amplify particular frequencies (narrow band or resonant sensors) or to produce a broadband response. The downside of these sensors is that they can only be used in the surface mounted mode.

Low profile ferroelectric ceramics, such as PZT, having a wide frequency bandwidth, can be embedded and therefore environmental effects and mechanical degradation of the sensors can be minimized. However, these materials possess a high stiffness which makes them easy to break. Piezoelectric polymers such as, poly(vinylidene fluoride) (PVDF), cannot be embedded in structures such as carbon fibre reinforced composite (CFRC), due to its low melting point. Thin film piezo-composites, like PTCa/PEKK, possess good mechanical properties compared with those of the ceramic and can be embedded due to the high melting point of the PEKK polymer. Composite sensors also possess a wide frequency bandwidth (Dias at al 1994, Wenger et al 1999). The downside is that the peak-to-peak response is much lower than that of the ceramic.

In recent years, other types of AE sensors have been developed, such as, optical fibre cavity sensors and micro-electro-magnetic-systems (MEMS) based sensors although they do not appear to have the bandwidth to compete with piezoelectric sensors (Martin et al 2001).

#### 2.5.2 Plate waves

Many structures constructed from composite materials are plate-like, i.e., the length and width of the plate are much larger than its thickness. The approach to AE investigation in these types of structures has been to analyse the AE signals in terms of their plate-wave mode characteristics. Waves propagate in this type of structure in modes whose propagation characteristics are dependent on the plate thickness, flexibility, density and boundary conditions. Lamb's homogeneous equations govern the propagation in these materials, and their solution are the so-called Lamb or Rayleigh-Lamb waves (Lamb 1917; Rayleigh 1945).

Lamb waves can be divided into three types. The first causes normal deformation and is symmetric with the central plane of the plate, the so-called symmetric mode. The second has normal deformations which are anti-symmetric about the mid-plane of the plate and are termed anti-symmetric modes. The third mode has transverse deformations which are parallel with the plane of the plate and are termed shear horizontal (SH) modes. All three types of waves possess, theoretically, infinite dispersive modes. (A wave is said to be dispersive when its velocity depends on the frequency (Meeker et al 1964, Graff 1975)).

Although Lamb's homogeneous equations (Lamb 1917) describing the propagation of elastic waves in thin plates provide exact solutions, with boundary conditions to satisfy a plate of infinite lateral dimensions, these are problematic to derive. This is because the cost of applying exact theory is to escalate the complexity of the governing equations and boundary conditions. Approximations can be made for deriving the equations of motion which describe the propagation of the lowest order of each wave type at low frequencies. This approximate theory is known as classical plate theory (CPT), which will be described in chapter 4. These waves are known as plate waves, with the

symmetric plate wave termed the extensional wave (figure 2.10), the anti-symmetric wave called the flexural wave (figure 2.11) and the horizontal shear wave called the SH plate wave.

The extensional plate wave velocities are non-dispersive (independent of frequency) whereas the flexural plate wave velocities are dispersive in nature with a square root dependence on the frequency of the wave. In addition, the extensional plate wave propagates faster and with higher frequency than the slower and lower frequency flexural plate wave.



Figure 2.10: Illustration of the extensional wave mode.



Figure 2.11: Illustration of the flexural wave mode.

Mindlin (1951) developed the most popular approach to an approximate theory of isotropic plate waves. He formulated a two-dimensional theory of flexural motions of isotropic elastic plates deduced from the three-dimensional equations of elasticity. The theory included the effects of rotational inertia and shear. Mindlin's approximate theory

for flexural waves in a plate showed good agreement with the exact solutions, even for short wavelengths.

If the effects of rotational inertia and shear are neglected the theory reduces to the CPT which is only valid for waves with wavelength approximately 16 times bigger than the plate thickness (Medick 1961).

A theory neglecting the rotational inertia and shear effects was developed by Graff (1975) outlining a normal-mode approach for solving the classical flexural equation of motion for the case of infinite, thin isotropic and orthotropic plates. Prosser (1991) applied this normal-mode expansion approach to AE source plate waves in thin aluminium and composite plates. For wavelengths greater than 16 times the plate thickness good agreement was found (Gorman and Prosser 1996). But best agreement was found between the theory and the experimental results for the isotropic aluminium plate than the composite plate (Prosser 1991). Prosser and Gorman (1990) also showed the absence of the in-plane shear mode within the frequency range of the measurements and that the extensional and flexural modes dominated the AE signal.

In laminate composite materials the effects of rotational inertia and shear appear significantly and cannot be neglected (Tang et al 1987; Prosser 1991). Chow (1971) proposed a higher-order plate theory, taking into account the effects of rotational inertia and shear, in order to improve the agreement with the experimental results for these materials. However, a normal-mode expansion approach to the solutions of the equation of motion for this method has not yet been formulated, due to complexities arising within the calculations.

#### 2.5.3 Continuous structural monitoring of composite structures

In order to have an optimum continuous monitoring of structures, the significant levels of damage must not be missed (False negatives) and non-significant levels of damage must not be reported (False positives). Additionally, the damaged region must be correctly identified. In order to diagnose damage the following levels of information are required: Damage detection, damage location, damage classification and damage sizing.

The first stage of monitoring damage is being able to detect its presence. Composites exhibit complex damage mechanisms, primarily due to the different properties between the reinforced fibres and the matrix. From these damage mechanisms (enumerated in section 2.5.1) the concern is primarily focused on delaminations and debonding as these are both difficult to inspect and can significantly reduce the 'health' of the structure. Although fibre fracture is a significant damage mechanism it is often visible and would normally require the structure to be repaired regardless of the extent of the damage. It should also be pointed out that delamination usually precedes fibre fracture.

The location of an AE source is normally calculated with reasonable accuracy by comparing the arrival times of stress waves at an array of sensors. This method is known as triangulation. The arrival time is either based upon time stamping where the signal exceeds a threshold or by comparing the arrival times of the extensional and flexural mode (modal analysis) (Watson et al 2001). The latter method reduces problems associated with time stamping provided the sensors can detect both modes.

Each AE source has a particular set of characteristics. Damage characterisation can be used to monitor a particular damage mechanism in a structure by filtering out all other sources of AE. In composites, the detection of delaminations and fibre fracture is possible since the other characteristics of the stress wave can be filtered by different methods, such as filters, guard sensors, etc. This technique must rely on a statistical build up of AE events and not on detecting a few events. Both damaged and undamaged structures emit AE events but whilst the latter may emit a few events per second, damaged structures emit thousands.

Damage sizing from AE relies on the assumption that the AE events are generated at the crack tip in fatigue cracks and from the edges of delamination as they grow. With fatigue cracks this assumption has been demonstrated (Martin et al 2001). For delaminations it is less clear because, in general, delaminations in composites do not grow until relatively high strain levels have been reached. Instead it is more likely to

detect AE produced by rubbing between the delaminated surfaces as the structure is loaded. In this case the assumption must be that AE events are generated over the whole area of the delamination and not just the edges. One potential method is to produce a contour map of high energy events indicating the regions of highest concentration.

### 2.6 Conclusion

The basic concepts of dielectric materials, with special attention to electroactive materials, have been introduced. Pyro-, piezo- and ferroelectric properties have been outlined. The materials used during this work have been described and these properties discussed.

The need to use composite materials to overcome the problems arising from the use of single phase materials has also been discussed. The basic concepts of composite ferroelectric ceramic/polymer material and the concept of phase connectivity have been introduced.

AE detection as a non-destructive method as been described as an application of piezoelectric composites. The conventional approach to AE analysis of signals is seen to be limited and other approaches, such as waveform analysis, have gained considerable interest. Plate wave analysis has received much attention and some background to this field has been provided.

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# Chapter 3: Transducer Models

# 3.1 Introduction

As mentioned in chapter 2, the electromechanical and therefore transducer properties of a diphasic composite such as PTCa/PEKK are governed by the properties of the constituent phases and the manner of their connection. Connectivity will now be discussed in more detail and the various electromechanical parameters of the composite derived. From these it is then possible to determine the practical piezoelectric properties of the composite film transducer. In addition, the expression of the impedance of the transducer acting as a free resonator is derived.

# 3.2 Connectivity and electromechanical parameters

Binary composite systems have been studied by a number of workers (Pauer 1973, Furukawa et al 1976, Newnham et al 1978, Yamada et al 1982, Banno 1985, Dias and Das-Gupta 1996) and several models have been employed to describe the electroactive properties.

#### 3.2.1 Models for 0-3 Composites

The simplest models are 0-3 composite models and two may be singled out. Yamada et al (1982) proposed a model for a binary system composed of ellipsoidal ceramic particles randomly dispersed in a continuous polymer matrix (Figure 3.1) from which expressions for the dielectric permittivity, piezo- and pyroelectric coefficients of the composite can be obtained. The permittivity,  $\varepsilon$  of the composite is given by,

$$\varepsilon = \varepsilon^{p} \left[ 1 + \frac{\eta' \phi^{c} \left( \varepsilon^{c} - \varepsilon^{p} \right)}{\eta' \varepsilon^{p} + \left( \varepsilon^{c} - \varepsilon^{p} \right) \left( 1 - \phi^{c} \right)} \right]$$
(3.1)

where  $\varepsilon^{c}$  and  $\varepsilon^{p}$  are the dielectric constants of the ceramic and the polymer respectively,  $\phi^{c}$  is the volume fraction of the ceramic in the composite and  $\eta'$ . is a parameter dependent on the shape of the ellipsoidal particles and their orientation in relation to the composite film.



Figure 3.1: Binary system proposed by Yamada (Yamada et al. 1982).

Assuming that the polymer matrix is not electroactive, expressions for the piezoelectric and pyroelectric coefficients d and p are as follows,

$$d = \alpha \phi^{c} G d^{c} \tag{3.2}$$

$$\mathbf{p} = \alpha \phi^{c} \mathbf{G} \mathbf{p}^{c} \tag{3.3}$$

where G, the local field is given by

$$G = \frac{\eta' \varepsilon}{\eta' \varepsilon + (\varepsilon^{\circ} - \varepsilon)}$$
(3.4)

and  $\alpha$  is the ceramic poling ratio (unity for full polarisation and zero for total absence of polarisation in the ceramic), p<sup>c</sup> and d<sup>c</sup> are the pyroelectric and the piezoelectric constants respectively of the ceramic.

Yamada et al (1982) reported that a shape factor,  $\eta'$  of 8.5 was the optimum value to fit the experimental values with the theoretical model for composites of PZT/PVDF with different ceramic volume fractions. This value for the shape factor,  $\eta'$ , implied that the ratio of the ellipsoidal axes was 2.8, with the long axis perpendicular to the composite surface. This was not reasonable considering that in the fabrication process, pressure was applied in the thickness direction of the films which would tend to align the long axis parallel to the surface.

Banno (1983) suggested that the ceramic particles could be considered spheroidal in shape with dimensions compared with those of the composite material appearing bigger in the thickness direction than in the other two perpendicular directions of the film. Hence, the shape factor,  $\eta'$ , would appear to have been stretched in the thickness direction. This means that  $\eta'$  is not an absolute measure of the shape of the ceramic grains but takes into consideration the dimensions of the film into which they are embedded. Figure 3.2 shows the experimental values of the permittivity of PTCa/PEKK composites with different ceramic loadings which have been fitted to Yamada's model using different shape factors. It is shown that in this case a shape factor of  $\eta' = 8.5$  is the best fit.



*Figure 3.2:* Theoretical plot of the permittivity for three values of the Yamada shape factor in a *PTCa/PEKK* composite together with the experimental data for this composite.

Furukawa et al (1976, 1979) proposed a model for binary systems in which spherical ceramic grains were embedded in the polymer matrix which was in turn, surrounded by a homogeneous medium whose properties approximate the average composite properties (figure 3.3).



Figure 3.3: Furukawa model for 0-3 composites (Furukawa et al 1976)

Expressions for permittivity,  $\varepsilon$ , elastic stiffness, c and piezoelectric coefficients, d, e, g and h, were obtained and compared with experimental results. The expressions, using the values of the permittivity, elastic constant and the piezoelectric coefficients of the constituent phases are given by,

$$\varepsilon = \frac{2\varepsilon^{p} + \varepsilon^{c} - 2\phi^{c}(\varepsilon^{p} - \varepsilon^{c})}{2\varepsilon^{p} + \varepsilon^{c} + \phi^{c}(\varepsilon^{p} - \varepsilon^{c})}\varepsilon^{p}$$
(3.5)

$$c = \frac{3c^{p} + 2c^{c} - 3\phi^{c}(c^{p} - c^{c})}{3c^{p} + 2c^{c} + 2\phi^{c}(c^{p} - c^{c})}c^{p}$$
(3.6)

$$d = \phi^{c} L_{T} L_{E} d^{c}$$
(3.7)

 $e = \phi^{c} L_{s} L_{E} e^{c}$ (3.8)

$g = \phi^{c} L_{T} L_{D} g^{c}$	(3.9)
$\mathbf{h} = \phi^{c} \mathbf{L}_{S} \mathbf{L}_{D} \mathbf{h}^{c}$	(3.10)

where  $L_T$ ,  $L_S$ ,  $L_D$  and  $L_E$  are the local field coefficients with respect to T, S, D and E respectively. In general the local field coefficients are defined as,

$$\mathbf{x}^{c} = \mathbf{L}_{\mathbf{x}} \mathbf{x} \tag{3.11}$$

where x can be T, S, D or E. For example, in the case of the electric field E, the local electric field coefficient,  $L_E$ , is the ratio of the applied field in the composite as a whole to the local electric field produced in the ceramic phase.

The local coefficients can be derived in terms of the properties of the constituent phases of the binary system (Furukawa et al 1979) and are given by the following equations,

$$L_{T} = \frac{5c^{\circ}}{3(1-\phi^{\circ})c^{p} + (2+3\phi^{\circ})c^{\circ}}$$
(3.12)

$$L_{s} = \frac{5c^{p}}{(3+2\phi^{c})c^{p}+2(1-\phi^{c})c^{c}}$$
(3.13)

$$L_{E} = \frac{3\varepsilon^{p}}{(2+\phi^{c})\varepsilon^{p} + (1-\phi^{c})\varepsilon^{c}}$$
(3.14)

$$L_{\rm D} = \frac{3\epsilon^{\rm c}}{2(1-\phi^{\rm c})\epsilon^{\rm p} + (1+2\phi^{\rm c})\epsilon^{\rm c}} .$$
 (3.15)

This model is valid for ceramic/polymer composites with very low ceramic concentration. Above concentrations of 10-20% the experimental values of d and  $\varepsilon$  were found to be significantly higher than the predicted ones. In order to reduce the discrepancy the composite was considered to have a mixed connectivity pattern (Pardo et al 1988). Hence the total volume fraction of the ceramic,  $\phi^{c}$  will have a contribution,  $\phi^{c}_{0-3}$  of ceramic with 0-3 connectivity and the rest,  $\phi^{c}_{1-3}$  will have 1-3 connectivity. Using the ratio of the ceramic grain size,  $g_{s}$ , and the composite thickness, t, Monte Carlo

simulations were carried out to calculate  $\phi^c_{0-3}$  and  $\phi^c_{1-3}$ , and an expression for the piezoelectric constant,  $d_{33}$  was obtained in the form

$$d_{33} = (\phi_{1-3} + \phi_{0-3}\alpha L_E)L_T d^c$$
(3.16)

where all the parameters have already been described. Good agreement was found between equation 3.16 and the experimental data in the region of transition between 0-3 and 1-3 connectivity, when the grain size was of the same order as the sample thickness.

#### 3.2.2 The general connectivity approach

In the previous models the ceramic grains were assumed to be small enough to consider a quasi-homogeneous medium around them. However, this assumption is not correct if the ceramic grain size is comparable to the sample thickness and/or the ceramic loading of the composite is high. Since the majority of the useful ferroelectric composites fall in one of the latter cases a new model should be considered that takes into account these facts. For this purpose the concept of connectivity is employed.

In the case of a diphasic composite the two simplest cases are the parallel connectivity and the series connectivity of two-dimensional structures (figure 3.4). These structures have a 2-2 connectivity and will form the building blocks of the 0-3 composite (Newnham 1978).



Figure 3.4: Parallel and series connectivities with their respective orientation of the polarisation vector.

The calculated properties, for the case of parallel connectivity, of the elastic compliance,  $s_{ij}$ , the piezoelectric coefficient,  $d_{ij}$ , the permittivity,  $\varepsilon$ , the pyroelectric coefficient, p, and the linear expansion coefficient,  $\alpha$  are listed below (Newnham 1978, Smith et al 1991, Smith 1993). Note that the superscripts c, p refer to ceramic and polymer phases respectively while the absence of superscripts denotes composite properties.

$$\frac{1}{s_{33}} = \frac{\phi^{c}}{s_{33}^{c}} + \frac{\phi^{p}}{s_{33}^{p}}$$
(3.17)

$$\frac{\mathbf{s}_{13}}{\mathbf{s}_{33}} = \frac{\phi^{c} \mathbf{s}_{13}^{C}}{\mathbf{s}_{33}^{c}} + \frac{\phi^{P} \mathbf{s}_{13}^{P}}{\mathbf{s}_{33}^{P}}$$
(3.18)

$$s_{11} = \phi^{c} s_{11}^{c} + \phi^{p} s_{11}^{p} - \frac{(s_{13}^{c} - s_{13}^{p})^{2} s_{33} \phi^{c} \phi^{p}}{s_{33}^{c} s_{33}^{p}}$$
(3.19)

$$s_{12} = \phi^{c} s_{21}^{c} + \phi^{p} s_{12}^{p} - \frac{(s_{13}^{c} - s_{13}^{p})^{2} s_{33} \phi^{c} \phi^{p}}{s_{33}^{c} s_{33}^{p}}$$
(3.20)

$$\frac{d_{33}}{s_{33}} = \frac{\phi^c d_{33}^c}{s_{33}^c} + \frac{\phi^p d_{33}^p}{s_{33}^p}$$
(3.21)

$$d_{31} = \phi^{c} d_{31}^{c} + \phi^{p} d_{31}^{p} + \frac{\left(d_{33}^{c} - d_{33}^{p}\right)\left(s_{13}^{c} - s_{13}^{p}\right)s_{33}\phi^{c}\phi^{p}}{s_{33}^{c}s_{33}^{p}}$$
(3.22)

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$$\varepsilon = \phi^{c} \varepsilon^{c} + \phi^{p} \varepsilon^{p} - \frac{\left(d_{33}^{c} - d_{33}^{p}\right)^{2} s_{33} \phi^{c} \phi^{p}}{s_{33}^{c} s_{33}^{p}}$$
(3.23)

$$p = \phi^{c} p^{c} + \phi^{p} p^{p} - \frac{\left(d_{33}^{c} - d_{33}^{p}\right)\left(\alpha^{c} - \alpha^{p}\right)s_{33}\phi^{c}\phi^{p}}{s_{33}^{c}s_{33}^{p}}$$
(3.24)

$$\frac{\alpha}{s_{33}} = \frac{\phi^{c} \alpha^{c}}{s_{33}^{c}} + \frac{\phi^{d} \alpha^{p}}{s_{33}^{p}} .$$
(3.25)

The properties of the series connectivity diphasic composite are also obtained as a function of both the properties of the constituent phases and their respective volume fractions,

$$s_{33} = \phi^c s_{33}^c + \phi^p s_{33}^p - \frac{(d_{33}^c - d_{33}^p)^2 \phi^c \phi^p}{a_1} - \frac{2[(d_{33}^c - d_{33}^p)a_3 - (s_{13}^c - s_{13}^p)a_1]^2 \phi^c \phi^p}{(a_2 a_1 - 2a_3^2)a_1} (3.26)$$

$$\frac{\mathbf{s}_{13}}{\mathbf{s}_{11} + \mathbf{s}_{12}} = \frac{\phi^{c} \mathbf{s}_{13}^{C}}{\mathbf{s}_{11}^{c} + \mathbf{s}_{12}^{c}} + \frac{\phi^{P} \mathbf{s}_{13}^{P}}{\mathbf{s}_{11}^{P} + \mathbf{s}_{12}^{P}}$$
(3.27)

$$\frac{1}{\mathbf{s}_{13} + \mathbf{s}_{12}} = \frac{\phi^{c}}{\mathbf{s}_{11}^{c} + \mathbf{s}_{12}^{c}} + \frac{\phi^{P}}{\mathbf{s}_{11}^{P} + \mathbf{s}_{12}^{P}}$$
(3.28)

$$\frac{\mathrm{d}_{33}}{\varepsilon} = \frac{\phi^{\mathrm{c}}\mathrm{d}_{33}^{\mathrm{c}}}{\varepsilon^{\mathrm{c}}} + \frac{\phi^{\mathrm{p}}\mathrm{d}_{33}^{\mathrm{p}}}{\varepsilon^{\mathrm{p}}}$$
(3.29)

$$d_{31} = \frac{d_{31}^{p} (s_{11}^{c} + s_{12}^{c}) \varepsilon^{c} \phi^{p} + d_{31}^{c} (s_{11}^{p} + s_{12}^{p}) \varepsilon^{p} \phi^{c}}{a_{2} a_{1} - 2a_{3}^{2}}$$
(3.30)

$$\frac{1}{\varepsilon} = \frac{\phi^{c}}{\varepsilon^{c}} + \frac{\phi^{p}}{\varepsilon^{p}}$$
(3.31)

$$\frac{p}{\varepsilon} = \frac{p^{c}\phi^{c}}{\varepsilon^{c}} + \frac{p^{p}\phi^{p}}{\varepsilon^{p}}$$
(3.32)

$$\alpha = \phi^{c} \alpha^{c} + \phi^{p} \alpha^{p} \tag{3.33}$$

$$a_1 = \varepsilon_0 (\phi^c \varepsilon^c + \phi^p \varepsilon^p)$$
(3.34)

$$a_{2} = \phi^{p}(s_{11}^{c} + s_{12}^{c}) + \phi^{c}(s_{11}^{p} + s_{12}^{p})$$
(3.35)

$$a_{3} = \phi^{c} d_{31}^{p} + \phi^{p} d_{31}^{c} . \qquad (3.36)$$

Figures 3.5 and 3.6 show the pyroelectric and piezoelectric coefficients of PTCa/PEKK composites calculated using the series and parallel connectivities respectively. It can be observed that the parallel connectivity structure gives higher values than the series connectivity structure. It is been shown that this occurs also with other ceramic/polymer composites (Dias et al 1996). The experimental data will fall in the region between the pure series and pure parallel connectivity branch.

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Figure 3.5: Pyroelectric coefficient for parallel and series connectivity composites



Figure 3.6: Piezoelectric coefficient for parallel and series connectivity composites

In order to simulate 0-3 composites, the so called cubes model was proposed by Pauer in 1973. This model consists of a cube with unit dimensions made of the host polymer matrix in which another smaller cube made of the ceramic is embedded (Figure 3.7 (a)). The aim is to find out the dimensions, m, of the smaller cube that matches the properties of the composite. This model was later modified by Banno (1985). In the 'modified cubes' model the ceramic block has an additional degree of freedom in that its height, n is independent of its length and width which remained equal to m, see figure 3.7 (b).



Figure 3.7: Cube models for 0-3 connected composites. (a) Simple cube, (b) Banno's modified cube and (c) mixed connectivity cubes

Therefore, upon varying both n and m, pure series (0-3) or parallel (1-3) connectivity can be obtained. In this model a difficulty arises when n has values close to 1. In this case, the electromechanical properties change rapidly making it difficult to identify the dimensions of the ceramic parallelepiped as can be seen in figure 3.8. Additionally, it should be noticed that both connectivities can never coexist in the 'modified cubes' model.

To overcome the limitations arising from Banno's model a mixed connectivity model was proposed by Dias and Das-Gupta (1996). The mixed connectivity model considers that both parallel and series connectivity exist in the composite. For this purpose the ceramic is represented as a cube of dimensions m in which a fraction of cross-section nm×nm extends between the electrodes across the full height of the unit cube shown in figure 3.7 (c). The composite is now viewed as a triphasic system with mixed 0-3, 1-3 connectivity.



*Figure 3.8*: Permittivity contour plots for composites of PTCa/PEKK in the n-m plane of the Banno cube model. The dotted line represents constant ceramic volume fraction, the continuous line represents constant permittivity.

Now the ceramic volume fractions are given by:

$$\phi^{c} = m^{3} + (nm)^{2} (1-m)$$
(3.37)

$$\phi^{c}_{ser} = m \tag{3.38}$$

$$\phi^{\rm ser} = m^2 (1 - n^2) \tag{3.39}$$

$$\phi_{\text{par}}^{c} = (\text{nm})^2 \tag{3.40}$$

where  $\phi^{c}_{par}$  is the fraction of the ceramic with parallel connectivity. The properties of the cube, and therefore the composite, are given by considering the series branch in parallel

with the ceramic phase and with the polymer phase. Thus the expressions for the elastic compliance,  $s_{ij}$ , the piezoelectric coefficient,  $d_{ij}$ , the permittivity,  $\varepsilon$  the pyroelectric coefficient, p, and the linear expansion coefficient,  $\alpha$  are now given by, (the subscripts 'ser' and 'par' denote series and parallel connected phases respectively)

$$\frac{1}{s_{33}} = \frac{\phi_{par}^{c}}{s_{33}^{c}} + \frac{\phi_{par}^{p}}{s_{33}^{p}} + \frac{\phi_{ser}^{ser}}{s_{33}^{ser}}$$
(3.41)

$$\frac{\mathbf{s}_{13}}{\mathbf{s}_{33}} = \frac{\phi_{par}^{c} \mathbf{s}_{13}^{c}}{\mathbf{s}_{33}^{c}} + \frac{\phi_{par}^{p} \mathbf{s}_{13}^{p}}{\mathbf{s}_{33}^{p}} + \frac{\phi_{ser}^{ser} \mathbf{s}_{13}^{ser}}{\mathbf{s}_{33}^{ser}}$$
(3.42)

$$s_{11} = \phi_{par}^{c} s_{11}^{c} + \phi_{par}^{p} s_{11}^{p} + \phi^{ser} s_{11}^{ser} - \frac{\left(s_{13}^{c} - s_{13}^{p}\right)^{2} s_{33} \phi_{par}^{c} \phi_{par}^{p}}{s_{33}^{c} s_{33}^{p}} - \frac{\left(s_{13}^{c} - s_{13}^{p}\right)^{2} s_{33} \phi_{par}^{c} \phi^{ser}}{s_{33}^{c} s_{33}^{s}} - \frac{\left(s_{13}^{ser} - s_{13}^{p}\right)^{2} s_{33} \phi_{par}^{p} \phi^{ser}}{s_{33}^{p} s_{33}^{ser}}$$
(3.43)

$$s_{12} = \phi_{par}^{c} s_{12}^{c} + \phi_{par}^{p} s_{12}^{p} + \phi_{ser}^{ser} s_{12}^{ser} - \frac{\left(s_{13}^{c} - s_{13}^{p}\right)^{2} s_{33} \phi_{par}^{c} \phi_{par}^{p}}{s_{33}^{c} s_{33}^{p}} - \frac{\left(s_{13}^{c} - s_{13}^{p}\right)^{2} s_{33} \phi_{par}^{c} \phi_{par}^{s}}{s_{33}^{c} s_{33}^{s}} - \frac{\left(s_{13}^{ser} - s_{13}^{p}\right)^{2} s_{33} \phi_{par}^{p} \phi_{ser}^{ser}}{s_{33}^{p} s_{33}^{s}}$$
(3.44)

$$\frac{d_{33}}{s_{33}} = \frac{\phi_{par}^{c} d_{33}^{c}}{s_{33}^{c}} + \frac{\phi_{par}^{p} d_{33}^{p}}{s_{33}^{p}} + \frac{\phi_{ser}^{ser} d_{33}^{ser}}{s_{33}^{ser}}$$
(3.45)

1

$$d_{31} = \phi_{par}^{c} d_{31}^{c} + \phi_{par}^{p} d_{31}^{p} + \phi_{ser}^{ser} d_{31}^{ser} + \frac{\left(d_{33}^{c} - d_{33}^{p}\right)\left(s_{13}^{p} - s_{13}^{c}\right)s_{33}\phi_{par}^{c}\phi_{par}^{p}}{s_{33}^{c}s_{33}^{p}} + \frac{\left(d_{33}^{c} - d_{33}^{p}\right)\left(s_{13}^{p} - s_{13}^{c}\right)s_{33}\phi_{par}^{c}\phi_{par}^{p}}{s_{33}^{c}s_{33}^{p}} + \frac{\left(d_{33}^{c} - d_{33}^{p}\right)\left(s_{13}^{p} - s_{13}^{ser}\right)s_{33}\phi_{ser}^{ser}\phi_{par}^{p}}{s_{33}^{ser}s_{33}^{p}} + \frac{\left(d_{33}^{e} - d_{33}^{p}\right)\left(s_{13}^{p} - s_{13}^{ser}\right)s_{33}\phi_{ser}^{ser}\phi_{par}^{p}}{s_{33}^{ser}\phi_{par}^{ser}} + \frac{\left(d_{33}^{e} - d_{33}^{p}\right)\left(s_{13}^{p} - s_{13}^{ser}\right)s_{33}\phi_{ser}^{ser}\phi_{par}^{p}}{s_{33}^{ser}\phi_{par}^{p}} + \frac{\left(d_{33}^{e} - d_{33}^{p}\right)\left(s_{13}^{p} - s_{13}^{ser}\right)s_{33}\phi_{ser}^{ser}\phi_{par}^{p}}{s_{33}^{ser}\phi_{par}^{p}}} + \frac{\left(d_{33}^{e} - d_{33}^{p}\right)\left(s_{13}^{p} - s_{13}^{ser}\right)s_{33}\phi_{ser}^{p}\phi_{par}^{p}}{s_{33}^{ser}\phi_{par}^{p}}} + \frac{\left(d_{33}^{e} - d_{33}^{p}\right)\left(s_{13}^{e} - s_{13}^{ser}\right)s_{33}\phi_{ser}^{p}\phi_{par}^{p}\phi_{par}^{p}}{s_{33}^{ser}\phi_{par}^{p}}} + \frac{\left(d_{33}^{e} - d_{33}^{e}\right)\left(s_{13}^{e} - s_{13}^{ser}\phi_{par}^{p}\phi_{par}^{p}\phi_{par}^$$

$$\varepsilon = \phi_{par}^{c} \varepsilon^{c} + \phi_{par}^{p} \varepsilon^{p} + \phi^{ser} \varepsilon^{ser} - \frac{\left(d_{33}^{c} - d_{33}^{p}\right)^{2} s_{33} \phi_{par}^{c} \phi_{par}^{p}}{s_{33}^{c} s_{33}^{p}} \qquad (3.47)$$

$$- \frac{\left(d_{33}^{c} - d_{33}^{ser}\right)^{2} s_{33} \phi_{par}^{c} \phi^{ser}}{s_{33}^{c} s_{33}^{ser}} - \frac{\left(d_{33}^{ser} - d_{33}^{p}\right)^{2} s_{33} \phi^{ser} \phi_{par}^{p}}{s_{33}^{ser} s_{33}^{p}} \qquad (3.47)$$

$$p = \phi_{par}^{c} p^{c} + \phi_{par}^{p} p^{p} + \phi^{ser} p^{ser} + \frac{(d_{33}^{c} - d_{33}^{p})(\alpha^{p} - \alpha^{c})s_{33}\phi_{par}^{c}\phi_{par}^{p}}{s_{33}^{c}s_{33}^{c}s_{33}^{c}} + \frac{(d_{33}^{e} - d_{33}^{e})(\alpha^{p} - \alpha^{ser})s_{33}\phi_{par}^{e}\phi_{par}^{p}}{s_{33}^{c}s_{33}^{e}s_{33}^{e}} + \frac{(d_{33}^{ser} - d_{33}^{e})(\alpha^{p} - \alpha^{ser})s_{33}\phi_{par}^{ser}\phi_{par}^{p}}{s_{33}^{ser}s_{33}^{e}s_{33}^{e}}$$
(3.48)

$$\frac{\alpha}{s_{33}} = \frac{\phi_{par}^{c}\alpha^{c}}{s_{33}^{c}} + \frac{\phi_{par}^{d}\alpha^{p}}{s_{33}^{p}} + \frac{\phi_{ser}^{ser}\alpha^{ser}}{s_{33}^{ser}} .$$
(3.49)

Again, the composite properties can be represented in contour charts as a function of the connectivity parameters n and m. These connectivity parameters provide the percentage of 1-3 connectivity in the composites. In figure 3.9 is shown a n-m plane representing the permittivity of PTCa/PEKK composites using the mixed connectivity cube model. Here n=1 represents a pure 1-3 connectivity composite and n=0 the Pauer cube model. It can be observed that no rapid change of the property occurs when n approaches unity.



**Figure 3.9**: Permittivity contour plots for composites of PTCa/PEKK in the n-m plane for the mixed connectivity cube model. The dotted line represents constant ceramic volume fraction; the continuous line represents constant permittivity

# 3.3 The Piezoelectric transducer

In section 3.2, it has been possible to derive the various mechanical and electrical coefficients of the composite film. Excitation by a sinusoidally oscillating electrical

field will generate a mechanical response in the film of stress and displacement waves which will be determined by these coefficients. This is now considered.

For the analysis of the impedance spectra of lossy materials, assumptions are made that the lateral dimensions of the piezoelectric resonator are large compared to its thickness so as to enable a one-dimensional analysis to be made, the so-called thickness mode (Bui et al. 1977). Figure 3.10 shows the one-dimensional resonator and the associated electrical and acoustical variables upon which the derivation of the analysis is based.



*Figure 3.10:* Piezoelectric film acting as a free resonator in air showing the electrical and acoustic terminal variables. F is the force, v the velocity, I current, V voltage and I thickness.

The piezoelectric equations relating the stress, T, the strain, S, the electric displacement, D, and electric field, E, which govern the behaviour of the resonator vibrating in the thickness mode, are given by (Ohigashi 1976)

$$T = c^{*D} S - hD \tag{3.50}$$

$$E = 1/\varepsilon^{*S} D - hS$$
(3.51)

Here h is the piezoelectric coefficient,  $c^{*D}$  is the elastic stiffness constant at constant electric displacement and  $\epsilon^{*S}$  is the dielectric permittivity at constant strain. The elastic stiffness constant at constant electric displacement,  $c^{*D}$ , and the dielectric permittivity at constant strain,  $\epsilon^{*S}$ , are complex quantities since the materials we are interested in possess mechanical and electrical losses

$$c^{*D} = c^{D} (1 + i\omega\eta/c^{D})$$
 (3.52)

$$\varepsilon^{*S} = \varepsilon^{S} (1 - i \tan \delta_{e})$$
(3.53)

where  $\omega$  is the angular frequency,  $\eta$  is the acoustical damping factor and  $\omega \eta/c^D$  and  $\tan \delta_e$  are the mechanical and dielectric loss factors respectively. Now by considering the acoustic equations (Bui et al. 1977) given by,

$$\frac{\mathrm{dT}}{\mathrm{dz}} = \mathrm{i}\omega\rho\mathrm{v} \tag{3.54}$$

$$\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}\mathbf{z}} = \mathrm{i}\omega\mathbf{S} \tag{3.55}$$

where  $\rho$  is the density and v is the particle velocity in the *z*-direction, the wave equation for a lossy material can be obtained by substituting equation (3.52) and (3.55) into equation (3.50) and then differentiating with respect to z to obtain,

$$\frac{\partial T}{\partial z} = \left(\frac{c^{D} + i\omega\eta}{i\omega}\right) \frac{\partial^{2} v}{\partial z^{2}} - h \frac{\partial D}{\partial z} . \qquad (3.56)$$

Since the current is conserved, the dielectric displacement must be uniform in the z-direction, i.e.

$$\frac{\partial \mathbf{D}}{\partial z} = 0 \tag{3.57}$$

and thus substituting equations (3.54) and (3.57) into equation (3.56) the wave equation for the lossy material is obtained,

$$\frac{\partial^2 \mathbf{v}}{\partial z^2} + \left(\frac{\omega^2 \rho}{\mathbf{c}^D + \mathrm{i}\omega\eta}\right) \mathbf{v} = 0.$$
(3.58)

The general solution to equation (3.58) has the form,

$$v = C_1 \cos(\gamma' z) + C_2 \sin(\gamma' z)$$
(3.59)

where  $C_1$  and  $C_2$  are constants which can be found from the boundary conditions imposed at the faces of the piezoelectric material (Bui et al. 1977),  $\gamma'$  is the transmission constant. The wave propagation constant,  $\gamma=i\gamma'$ , is a complex quantity of the form  $\gamma=\alpha+i\beta$ , where  $\alpha$  is the attenuation or absorption coefficient and  $\beta$  is the wave number.

Substituting equation (3.59) into equation (3.58) leads to the relationship

$$\gamma'^{2} = \frac{\omega^{2} \rho}{c^{D} + i\omega\eta}$$
(3.60)

which can be expressed as

$$\gamma' = \frac{\omega}{v_s} (1 + i\omega\eta/c^D)^{-1/2}$$
(3.61)

where

$$\mathbf{v}_{s} = \left(\frac{\mathbf{c}^{\mathrm{D}}}{\rho}\right)^{1/2} \tag{3.62}$$

is the velocity of sound in the material.

If we assume small acoustic losses such that

$$\psi = \frac{\omega \eta}{c^{D}} << 1 \tag{3.63}$$

then

$$\gamma' \approx \frac{\omega}{v_s} \left( 1 - i \frac{\psi}{2} \right)$$
(3.64)

whence

$$\alpha = \beta \frac{\Psi}{2} = \beta \frac{\omega \eta}{2c^{D}}$$
(3.65)

$$\beta = \frac{\omega}{v_s} = \omega \sqrt{\frac{\rho}{c^{D}}} \quad . \tag{3.66}$$

The acoustic quality factor,  $Q_m$ , can be expressed in terms of the wave attenuation coefficient  $\alpha$  and wave number  $\beta$  as

$$Q_{m} = \frac{\beta}{2\alpha} = \frac{c^{D}}{\omega \eta} .$$
(3.67)

The boundary conditions, see figure 3.10, are,

$$v_{1} = v(0) v_{2} = -v(1) F_{1} = -AT_{1}(0) F_{2} = -AT_{2}(1)$$
(3.68)

Substituting the first two boundary conditions into equation (3.59) gives,

$$\mathbf{C}_1 = \mathbf{v}_1 \tag{3.69}$$

$$C_2 = -\left(\frac{v_2 + v_1 \cos(\gamma' 1)}{\sin(\gamma' 1)}\right). \tag{3.70}$$

Thus equation (3.59) becomes

$$\mathbf{v} = \frac{\mathbf{v}_1 \sin(\gamma' [1-z]) - \mathbf{v}_2 \sin(\gamma' z)}{\sin(\gamma' 1)}$$
(3.71)

By considering the final two boundary equations along with equations (3.50), (3.55) and (3.71) it is possible to express the two acoustic variables  $F_1$  and  $F_2$  and the electrical voltage V in terms of  $v_1$ ,  $v_2$  and I, thus, characterising the acoustic resonator as a three-port network. The derivative of equation (3.71), with respect to z, is substituted into equation (3.55) to give

$$S = \frac{-\gamma' v_1 \cos(\gamma' [1-z]) - \gamma' v_2 \cos(\gamma' z)}{i\omega \sin(\gamma' 1)}$$
(3.72)

and substituting this expression for S in equation (3.50) gives

$$T = \left(c^{D} + i\omega\eta\right)\left(\frac{-\gamma' v_1 \cos(\gamma' [1-z]) - \gamma' v_2 \cos(\gamma' z)}{i\omega \sin(\gamma' 1)}\right) - hD \quad (3.73)$$

The third boundary condition,  $F_1 = -AT(0)$ , where A is the electrode area, gives  $F_1$  in terms of  $v_1$  and  $v_2$  as,

$$F_1 = \frac{B\cos(\gamma' l)}{i\sin(\gamma' l)} v_1 + \frac{B}{i\sin(\gamma' l)} v_2 + hAD$$
(3.74)

where

$$\mathbf{B} = \left(\mathbf{c}^{\mathrm{D}} + i\omega\eta \left(\frac{\gamma'}{\omega}\right)\mathbf{A} = \left(\mathbf{c}^{\mathrm{D}} + i\omega\eta\right)^{1/2}\rho^{1/2}\mathbf{A} = z_0 \left(1 + i\frac{\omega\eta}{c^{\mathrm{D}}}\right)^{1/2}\mathbf{A}$$
(3.75)

where  $z_0 = \rho v_s$  is the specific acoustic impedance of the material.  $F_2$  can be obtained in terms of  $v_1$  and  $v_2$  in a similar manner to  $F_1$ , giving

$$F_2 = \frac{B}{i\sin(\gamma'1)}v_1 + \frac{B\cos(\gamma'1)}{i\sin(\gamma'1)}v_2 + hAD . \qquad (3.76)$$

The voltage across the transducer is given by

$$V = \int_{0}^{1} E dz$$
 (3.77)

and can be represented in terms of  $v_1$  and  $v_2$  by considering equations (3.77), (3.51) and (3.72) yielding

$$V = \int_{0}^{1} E dz = \frac{h}{i\omega} v_1 + \frac{h}{i\omega} v_2 + \frac{Dl}{\epsilon^{*S}} .$$
(3.78)

Since I the total current through the transducer will be given by,

$$I = i\omega AD \tag{3.79}$$

equations (3.74), (3.76) and (3.78) can be expressed in terms of I as,

$$F_{1} = -iB\cot(\gamma' 1)v_{1} - iB\csc(\gamma' 1)v_{2} + \frac{h}{i\omega}I$$
(3.80)

$$F_{2} = -iB\csc(\gamma' l)v_{1} - iB\cot(\gamma' l)v_{2} + \frac{h}{i\omega}I$$
(3.81)

$$V = \frac{h}{i\omega} v_1 + \frac{h}{i\omega} v_2 + \frac{1}{i\omega C^s} I$$
(3.82)

where

$$C^{s} = \varepsilon^{s} (1 - i \tan \delta_{e}) A / l$$
(3.83)

is the clamped (constant strain) capacitance of the sample transducer. Equations (3.80) to (3.82) can be represented in terms of a 3x3 matrix as,

$$\begin{bmatrix} F_{1} \\ F_{2} \\ V \end{bmatrix} = -i \begin{bmatrix} B \cot(\gamma' 1) & B \csc(\gamma' 1) & h \\ B \csc(\gamma' 1) & B \cot(\gamma' 1) & h \\ h \\ \omega & h \\ \omega & \omega & \omega \\ \end{bmatrix} \begin{bmatrix} v_{1} \\ v_{2} \\ I \end{bmatrix}.$$
(3.84)

The matrix enables the determination of the electrical impedance of a lossy resonator transducer by solving for V/I with the appropriate acoustic terminations  $F_1$  and  $F_2$ .

For a piezoelectric material resonating freely in air, forces acting at its faces can be assumed to be zero, i.e.  $F_1=F_2=0$ . Applying this condition to equation (3.84) it is seen that the electrical impedance  $Z(\omega)$  is given by,

$$Z(\omega) = \frac{1}{i\omega C^{s}} - \frac{2}{iB} \left(\frac{h}{\omega}\right)^{2} \tan\left(\frac{\gamma' l}{2}\right)$$
(3.85)

where the first term represents the impedance associated with the capacitance,  $Z_e$ , of the sample and the second term represents the acoustic impedance,  $Z_{ac}$ . From the real and

imaginary part of the electrical impedance, an expression for the electromechanical coupling coefficient, k<sub>t</sub>, can be obtained.

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# Chapter 4:

# Acoustic wave propagation in plate-like structures

# 4.1 Introduction

In general, film transducers will be close-coupled to plate-like structures and will be required to detect acoustic waves propagating in them. In this chapter the general characteristics of acoustic waves in orthotropic plates will be discussed. (isotropic plates are a particular case).

# 4.2 Classical plate theory of extensional waves

The equations of motion governing the propagation of an elastic wave in a solid structure are (using Einstein summation),

$$\frac{\partial T_{ij}}{\partial x_{j}} + \rho f_{i} = \rho \frac{\partial^{2} u_{i}}{\partial t^{2}}$$
(4.1)

where  $T_{ij}$  is the stress,  $\rho$  is the density,  $f_i$  is the body force per unit mass of material and  $u_i$  are the displacements, (u, v, w), along the  $x_i$  axes, (x, y, z). If the material is assumed very thin and under the condition of plane stress, i.e.,  $T_{xz} = T_{zx} = T_{yz} = T_{zy} = T_{zz} = 0$ , then the two equations of motion are given by,

$$\frac{\partial T_{xx}}{\partial x} + \frac{\partial T_{xy}}{\partial y} + \rho f_x = \rho \frac{\partial^2 u}{\partial t^2}$$
(4.2)

and

$$\frac{\partial T_{xy}}{\partial x} + \frac{\partial T_{yy}}{\partial y} + \rho f_y = \rho \frac{\partial^2 v}{\partial t^2} . \qquad (4.3)$$
The generalised Hooke's law for the case of a thin plate and planar stress is represented by the following equations,

$$T_{xx} = \frac{Y_{xx}}{(1 - \mu_{xy}\mu_{yx})} S_{xx} + \frac{\mu_{xy}Y_{xx}}{(1 - \mu_{xy}\mu_{yx})} S_{yy}$$
(4.4)

$$T_{yy} = \frac{\mu_{yx} Y_{yy}}{(1 - \mu_{xy} \mu_{yx})} S_{xx} + \frac{Y_{yy}}{(1 - \mu_{xy} \mu_{yx})} S_{yy}$$
(4.5)

$$T_{xy} = G_s \gamma_{xy} \tag{4.6}$$

where  $S_{ij}$  are the components of the strain tensor, Y is Young's modulus,  $\mu$  Poisson's ratio,  $G_s$  the shear modulus and  $\gamma_{xy} = \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}$ . The strain tensor,  $S_{ij}$ , is defined as,

$$\mathbf{S}_{ij} = \frac{1}{2} \left( \frac{\partial \mathbf{u}_i}{\partial \mathbf{x}_j} + \frac{\partial \mathbf{u}_j}{\partial \mathbf{x}_i} \right). \tag{4.7}$$

Substitution of the stress definitions given by the generalised Hooke's law, equations (4.4) to (4.6), together with the definition of small-strain, equation (4.7), into the equation of motion (equations (4.2) and (4.3)), results in,

$$\frac{Y_{xx}}{(1-\mu_{xy}\mu_{yx})} \left( \frac{\partial^2 u}{\partial x^2} + \mu_{xy} \frac{\partial^2 v}{\partial x \partial y} \right) + G_s \left( \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 v}{\partial x \partial y} \right) + \rho f_x = \rho \frac{\partial^2 u}{\partial t^2}$$
(4.8)  
$$\frac{Y_{yy}}{(1-\mu_{xy}\mu_{yx})} \left( \mu_{xy} \frac{\partial^2 u}{\partial x \partial y} + \frac{\partial^2 v}{\partial y^2} \right) + G_s \left( \frac{\partial^2 u}{\partial x \partial y} + \frac{\partial^2 v}{\partial x^2} \right) + \rho f_y = \rho \frac{\partial^2 v}{\partial t^2} .$$
(4.9)

The new equations of motion (4.8) and (4.9) govern the propagation of the extensional plate waves in an orthotropic plate. SH plate waves have not been considered since they have not been observed during the present work on AE plate wave signals.

If the plate wave is represented by a sinusoidal plane wave, propagating along the x-axis with no displacement in the y-axis direction and the body force is assumed zero, then the particle displacement in the x-direction is given by (Prosser 1991),

$$\mathbf{u} = \mathbf{A}_0 \mathbf{e}^{\mathbf{i}(\omega t - \mathbf{k}\mathbf{x})} \tag{4.10}$$

where  $A_0$  is the amplitude,  $\omega$  is the angular frequency and k the wave number, which is related to the phase velocity of the extensional wave,  $c_e$ , by,

$$c_e = \frac{\omega}{k} . \tag{4.11}$$

By substituting equation (4.10) into equation (4.8), and using the definition of  $c_e$ , the phase velocity of the extensional wave in the x-direction can be shown to be,

$$c_{e} = \left(\frac{Y_{xx}}{\rho(1 - \mu_{xy}\mu_{yx})}\right)^{1/2} .$$
 (4.12)

Using similar assumptions the phase velocity for the extensional wave travelling along the y-axis is given by,

$$c_{e} = \left(\frac{Y_{yy}}{\rho(1 - \mu_{xy}\mu_{yx})}\right)^{1/2}.$$
 (4.13)

From these expressions it can be seen that the extensional plate wave velocity is independent of the frequency, i.e., it is a non-dispersive mode.

## 4.3 Classical plate theory of flexural waves

The normal mode-expansion method for the flexural mode vibration in a finite isotropic plate is described by Graff (1975). In this section, a deviation from this method is used to obtain the equations of motion for the case of an orthotropic plate. The effects of rotational inertia and shear will be neglected.

For the description of flexural waves, an element of an orthotropic plate with thickness h and lateral dimensions dx and dy is considered, see figure 4.1. The bending moments,  $M_{xx}$  and  $M_{yy}$ , per unit length arise from the distributions of normal stresses, while the twisting moments  $M_{xy}$  and  $M_{yx}$ , per unit length and the shearing forces  $Q_{xx}$  and  $Q_{yy}$ , per unit length arise from the shearing stresses. The external force per unit area is denoted by q.



*Figure 4.1*: Element of a thin orthotropic plate of dimensions dx, dy and h, showing shear forces  $Q_{ij}$ , bending and twisting moments,  $M_{ij}$  and external loads, q.

The three equations of motion are given by,

$$-Q_{xx} dy + \left(Q_{xx} + \frac{\partial Q_{xx}}{\partial x} dx\right) dy - Q_{yy} dx + \left(Q_{yy} + \frac{\partial Q_{yy}}{\partial y} dy\right) dx + q dy dx = \rho h dx dy \frac{\partial^2 w}{\partial t^2}$$

$$(4.14)$$

$$M_{yy} dx - \left(M_{yy} + \frac{\partial M_{yy}}{\partial y} dy\right) dx - M_{xy} dy + \left(M_{xy} + \frac{\partial M_{xy}}{\partial x} dx\right) dy + Q_{yy} dy dx = 0$$

$$(4.15)$$

$$M_{xx} dy - \left(M_{xx} + \frac{\partial M_{xx}}{\partial x} dx\right) dy + M_{yx} dx - \left(M_{yx} + \frac{\partial M_{yx}}{\partial y} dy\right) dx + Q_{xx} dy dx = 0.$$
(4.16)

w(x, y, z) is the displacement of the mid-point of the plate. Cancellation of terms in equations (4.14) to (4.16) result in,

$$\frac{\partial Q_{xx}}{\partial x} + \frac{\partial Q_{yy}}{\partial y} + q = \rho h \frac{\partial^2 w}{\partial t^2}$$
(4.17)

$$\frac{\partial M_{yy}}{\partial y} + \frac{\partial M_{xy}}{\partial x} - Q_{yy} = 0$$
(4.18)

$$\frac{\partial M_{xx}}{\partial x} + \frac{\partial M_{yx}}{\partial y} - Q_{xx} = 0 . \qquad (4.19)$$

Upon substituting equation (4.18) and (4.19) into equation (4.17) a single equation of motion is obtained in terms of the moments and the normal acceleration, viz.,

$$\frac{\partial^2 M_{xx}}{\partial x^2} + \frac{\partial^2 M_{yx}}{\partial x \partial y} + \frac{\partial^2 M_{yy}}{\partial y^2} + \frac{\partial^2 M_{xy}}{\partial y \partial x} = \rho h \frac{\partial^2 W}{\partial t^2} . \qquad (4.20)$$

Classical plate theory assumes that when an element of the plate undergoes pure bending the cross sections of the plate remain plane and perpendicular to the mid-plane of the plate. This assumption leads to the constraint that the deformations of the plate are small. Thus, the strains can be shown to be given by,

$$S_{xx} = -z \frac{\partial^2 w}{\partial x^2}$$
(4.21)

$$S_{yy} = -z \frac{\partial^2 w}{\partial y^2}$$
(4.22)

and the shear strain given by,

$$\gamma_{yx} = -z \frac{\partial^2 w}{\partial x \partial y} . \qquad (4.23)$$

The stresses can be obtained from Hooke's law (equations (4.4) to (4.6)),

$$T_{xx} = \frac{Y_{xx}Z}{\left(1 - \mu_{xy}\mu_{yx}\right)} \left(\frac{\partial^2 w}{\partial x^2} + \mu_{yx}\frac{\partial^2 w}{\partial y^2}\right)$$
(4.24)

$$T_{yy} = \frac{Y_{yy}Z}{\left(1 - \mu_{xy}\mu_{yx}\right)} \left(\frac{\partial^2 w}{\partial y^2} + \mu_{xy}\frac{\partial^2 w}{\partial x^2}\right)$$
(4.25)

$$T_{xy} = -2G_s z \frac{\partial^2 w}{\partial x \partial y} . \qquad (4.26)$$

The bending and twisting moments are found from integration over the thickness of the plate as,

$$M_{xx} = \int_{-h/2}^{h/2} T_{xx} z dz = -D_{xx} \left( \frac{\partial^2 w}{\partial x^2} + \mu_{yx} \frac{\partial^2 w}{\partial y^2} \right)$$
(4.27)

$$M_{yy} = \int_{-h/2}^{h/2} T_{yy} z dz = -D_{yy} \left( \frac{\partial^2 w}{\partial y^2} + \mu_{xy} \frac{\partial^2 w}{\partial x^2} \right)$$
(4.28)

$$M_{xy} = \int_{-h/2}^{h/2} T_{xy} z dz = -D_{xy} \frac{\partial^2 w}{\partial x \partial y} = -M_{yx}$$
(4.29)

where

$$D_{xx} = \frac{h^3}{12} \frac{Y_{xx}}{\left(1 - \mu_{xy} \mu_{yx}\right)}$$
(4.30)

$$D_{yy} = \frac{h^3}{12} \frac{Y_{yy}}{\left(1 - \mu_{xy} \mu_{yx}\right)}$$
(4.31)

$$D_{xy} = \frac{h^3}{6}G_s . (4.32)$$

Thus, substituting equations (4.27) to (4.29) into (4.20), the equation of motion becomes,

$$D_{xx} \frac{\partial^4 w}{\partial x^4} + (D_{xx}\mu_{yx} + 2D_{xy} + D_{yy}\mu_{xy})\frac{\partial^2 w}{\partial x^2 \partial y^2} + D_{yy}\frac{\partial^4 w}{\partial y^4} - q = -\rho h \frac{\partial^2 w}{\partial t^2} .$$
(4.33)

To examine the dispersion characteristics of the flexural mode of propagation assumptions are made that there are no body forces present and that an harmonic plane wave is propagating along the x-direction of the form,

$$w = A_0 e^{i(\omega t - kx)} . ag{4.34}$$

Substituting equation (4.34) into equation (4.33), the phase velocity,  $c_f$ , of a flexural wave propagating along the x-direction is obtained as,

$$c_{f} = \left(\frac{D_{xx}\omega^{2}}{\rho h}\right)^{1/4}.$$
4.35)

A similar assumption is made to obtain the phase velocity along the y-direction,

$$c_{f} = \left(\frac{D_{yy}\omega^{2}}{\rho h}\right)^{1/4}.$$
(4.36)

Equations (4.35) and (4.36) show the dispersive nature of the flexural mode, whose phase velocity has a square root dependency on the frequency of the wave. It is noted that the velocity increases with increasing frequency without limit. This is due to the assumptions made in the classical plate theory. However, for thin plates and low frequencies, where the assumptions are valid, the predicted flexural mode behaviour agrees with that of the exact theory.

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# Chapter 5: Preparation of PTCa/PEKK composites

## **5.1 Introduction**

The precise aim of this work was to obtain flexible, composite piezoelectric sensors that can be embedded in carbon reinforced fibre composites (CRFC) for on-line monitoring of the health of structures. Since the embedding process involves curing temperatures of 120-130 °C, the high melting point of poly(ether ketone ketone), 305 °C, makes PTCa/PEKK composites good candidates for successful embedding.

The electromechanical properties of the composites will depend on the properties and relative amounts of the constituent phases, the most important factor being the connectivity of the phases. This depends on the method of fabrication which has to be chosen carefully therefore.

In the following sections the description of the raw materials, i.e., PTCa ceramic powder and PEKK pellets, will be given as well as the chemical treatment of the PTCa grain with titanate coupling agent. Additionally, the mixing of the phases and the preparation of the composite films by means of a hot press will be described. Finally, the deposition of aluminium electrodes and the polarisation of the samples is explained.

# 5.2 Raw materials

There are several methods which can be used to produce the ceramic powder. These include the mixed oxide route, the co-precipitation of precursor powder from an aqueous solution and other wet chemical routes, such as the sol-gel method. The PTCa ceramic powder used in this project was provided by GEC-Marconi laboratories and was prepared via the mixed oxide route.

In the mixed oxide route, reported by Moulson et al (1990), the calcium-modified lead titanate is obtained by reacting the appropriate amounts of titanium dioxide, lead carbonate or lead oxide and calcium oxide along with any other dopants, such as, magnesium, cobalt or tungsten. Mixing is usually undertaken in a ball-mill, which has the effect of eliminating aggregates of the individual powders and tends to reduce the particle size. As the compound forms during calcination, it is necessary for the particle size to be small, thus encouraging the interdiffusion of neighbouring particles.

Calcination of the powder occurs at temperatures between 800 °C and 900 °C in air over several hours. The calcinated powder usually consists of coarse aggregates of particles which are further milled prior to sintering at temperatures between 1000 and 1200 °C. This results in a polycrystalline material consisting of grains coupled to each other via grain boundaries. The sintered material is then quenched to produce ceramic powder with an average size of 10  $\mu$ m. The chemical composition of the PTCa ceramic supplied by GEC-Marconi is,

The polymer component of the composite, poly(ether ketone ketone) (PEKK) was supplied by Du Pont Laboratories. The reaction of diphenyl ether (DPE) with different mixtures of terephthaloyl chloride (T) and isophthaloyl chloride (I) leads to the synthesis of PEKK polymers with different structures, morphology and properties. Based on a comparison of measured thermal properties, such as, glass transition temperature,  $T_g$  and melting point,  $T_m$  of fabricated PEKK films with results given in the literature (Sauer et al 1996) it is suggested that the PEKK polymer used during this project has a 60/40 ratio of T and I isomers, i.e., it is PEKK (60/40).

#### 5.3 Chemical treatment of the ceramic grain surface

Before mixing the ceramic with the polymer, the PTCa ceramic grains were chemically treated with a titanate coupling agent supplied by Kenrich Petrochemicals Inc. This chemical treatment improves the compatibility between the inorganic ceramic and the organic polymer (Cai et al 1997). The aim of this treatment was to modify the surface properties of the ceramic particles and hence to strengthen the connection of the ceramic to the polymer. Monoalkoxy and neoalkoxy type titanium-derived coupling agents react with substrate surface protons at the inorganic interface resulting in the formation of matrix compatible/reactive organic monomolecular layers on the organic surface according to the following alcoholysis mechanism (Monte 1985),

$$MOH + R'O - Ti(O - X - R - Y)_3 \longrightarrow MO - Ti(O - X - R - Y)_3 + R'OH$$

where M is the substrate, H the surface proton, R'O the monohydrolyzable group, Ti the tetravalent titanium, X the binder functional group, R the thermoplastic functional group and Y the thermoset functional group. Figure 5.1 shows the monomolecular titanate layer formed by the alcoholysis reaction mechanism of a monoalkoxy or neoalkoxy titanate coupling agent with the idealised proton-bearing surface of an inorganic particle.

However, most inorganics do not have the idealised surface pictured in figure 5.1, but are, in fact, irregular and agglomerated. Figure 5.2 is more realistic and illustrates on the left, an agglomerated inorganic particulate having moisture and air voids mixed into an organic vehicle without titanate present. On the right, is shown the particulate separation and elimination of air and water achieved using the titanate agent resulting in better mechanical properties, improved dispersion and better corrosion resistance (Monte 1985).



*Figure 5.1*: The reaction of a mono or neo-alkoxy tri organo functional titanate coupling agent with the proton-bearing surface of an inorganic ceramic particle. The result is the formation of an organic titanium monomolecular layer on the surface.



*Figure 5.2*: The dispersion effect of coupling agglomerated inorganic particles with a monoalkoxy or neoalkaxy titanate agent in an organic phase.

#### 5.4 Preparation of mixed connectivity PTCa/PEKK composites

Due to the simpler connectivity pattern, composites with 0-3 connectivity, figure 5.3, are cheaper and easier to fabricate than 1-3 composites. Larger thinner samples can be manufactured with less processing time than that required for 1-3 composites. On the other hand, 0-3 composites possess lower electroactive properties than 1-3 composites. For the 0-3 composites, the method of fabrication will be determined by the type of polymer used. With a thermoplastic polymer, like PEKK, the ceramic powder may be mixed with the polymer above its melting temperature and then cooled down to obtain the composite material. Alternatively, the polymer could be dissolved and then mixed with the ceramic. Upon evaporation of the solvent the composite sample is obtained.



**Figure 5.3**: Low ceramic volume fraction 0-3 connectivity composite where the ceramic grains are not connecting the sample faces and the polymer is connected to itself with 3 degrees of connectivity.

Mixed connectivity composites are essentially fabricated in the same way as 0-3 composites. If the volume fraction of the ceramic is increased in the 0-3 composite until some of the ceramic grains are in contact with each other and extend between the sample faces, the sample will possess some degree of 1-3 connectivity (see figure 5.4). Mixed connectivity can also occurs if the sample thickness is comparable to the ceramic grain size. The appearance of 1-3 connectivity in an 0-3 composite enhances the electroactive properties of the sensor.



Figure 5.4: High ceramic volume fraction composite showing 0-3 and 1-3 connectivity.

#### 5.4.1 Mixing and pressing

The required amounts of PTCa and PEKK in the composite for a desired ceramic volume fraction  $\phi^c$  are calculated from,

$$M_{c} = M_{p} \frac{\rho_{c}}{\rho_{p}} \left( \frac{\phi^{c}}{1 - \phi^{c}} \right)$$
(5.1)

where M is the mass,  $\rho$  is the density and the subscripts p and c denote the polymer and ceramic respectively. Once the mass of the polymer is known and knowing the densities of the constituent phases, the mass of the ceramic can be calculated from equation (5.1). The density of the composite is then given by

$$\rho = \phi^{c} \rho_{c} + (1 - \phi^{c}) \rho_{p}$$
(5.2)

After mixing the two phases the composite is placed in a hot press (figure 5.5). Thin films of 250  $\mu$ m are obtained after applying a pressure of 20 MPa for 3 hours at a temperature of 320-345 °C, which is above the polymer melting point (305 °C). The pressing temperature depended on the ceramic concentration in the composite, higher temperature was needed for high ceramic loading composites. Note that no vacuum was

used while pressing the sample due to experimental limitations. These operating parameters were found to be optimum in order to allow the ceramic to spread evenly within the polymer matrix.

The thickness of the film was reduced to approximately 180  $\mu$ m after re-pressing the samples with the same processing conditions. An average 5% of thickness variation was observed within each sample. Surface quality also improved when samples were re-pressed.

The resulting samples had an elastic compliance,  $s_{33}$  in the range  $100-350\times10^{-12}$  Pa<sup>-1</sup>, compared with  $10\times10^{-12}$  Pa<sup>-1</sup> for the PTCa ceramic. The composite samples were found to be more flexible than the ceramic sensors. Chapter 6 includes results of the composite compliance with different ceramic loadings.



Figure 5.5: Schematic of the pressing operation

#### 5.4.2 Electroding and poling

Circular aluminium electrodes were provided by evaporating aluminium wire from a tungsten filament, heated at  $1200^{\circ}$ C under a vacuum of  $10^{-5}$  torr, through a circular mask of 10mm diameter placed on the film surface. The process was repeated for the other side of the film. The vacuum was obtained using rotary and diffusion pump (figure 5.6).



Figure 5.6: Schematic of the aluminium evaporation process.

After depositing the electrodes, the samples were poled under a steady electric field,  $E_p$ . A step voltage was applied between the electrodes to induce a polarisation in the film direction. The consequent current had a steady resistive component  $I_R$  together with a polarisation component  $I_p(t)$  which gradually decreased to zero as polarisation proceeded.

The rate at which the polarisation P changes has been given by Landauer et al (1956) as

$$\frac{\mathrm{dP}}{\mathrm{dt}} = v \left( \mathbf{P}_{\mathrm{S}} - \mathbf{P} \right) \mathrm{e}^{-\alpha/\mathrm{E}_{\mathrm{p}}}$$
(5.3)

where v is a rate constant independent of the field and polarisation,  $P_s$  the saturation polarisation and  $\alpha$  is a constant. Solving equation (5.3) yields,

$$\mathbf{P} = \mathbf{P}_{\mathrm{S}} - \left(\mathbf{P}_{\mathrm{S}} - \mathbf{P}_{\mathrm{0}}\right) \mathbf{e}^{-\mathrm{tv}\mathbf{e}^{\alpha/\mathrm{E}_{\mathrm{P}}}}$$
(5.4)

where  $P_0$  is the initial polarisation. It is seen that the polarisation time reduces as  $E_p$  is increased and thus, for efficient poling,  $E_p$  should be as close to the breakdown field as possible.

Note that when poling mixed connectivity composites, part of the ceramic will have 1-3 connectivity. This is a parallel branch that will experience the total poling field and will be fully polarised. However, the ceramic having 0-3 connectivity is a series branch and will experience a field that is dependent on the electrical properties of the polymer and the ceramic. The series branch is essentially a two layer system with fractional thicknesses m and 1-m for the ceramic and polymer respectively, so that, the magnitude of the electric field experienced by the ceramic,  $E_{cer}$ , is (Dias et al 1996),

$$E_{cer} = \frac{E_p \rho_c}{\rho_c m + \rho_p (1 - m)}$$
(5.5)

where  $\rho_c$  and  $\rho_p$  are the resistivities of the ceramic and the polymer respectively. As a consequence, the polarising field may be less than  $E_p$ .

The PTCa/PEKK composites were poled by applying a field of 10 MV/m across the sample at a temperature of 150 °C for 30 minutes. This was found to be appropriate for obtaining a high piezoelectric strain coefficient,  $d_{33}$ , without inducing an electrical breakdown in the sample. The samples were heated in a glass beaker containing hot insulating silicone oil, a magnetic stirrer being used to circulate the hot oil to provide an even distribution of the temperature, see figure 5.7.

The poling voltage was provided by a TREK power supply. In order to avoid electrical breakdown, the voltage was increased slowly (5 minutes approximately) and the current monitored until the desired poling field was reached.



Figure 5.7: The poling apparatus.

The microscopic structure of the composite films was examined using a scanning electron microscope (SEM). The films were broken by snapping to reveal the cross-section and aluminium evaporated on the exposed surface. The films were then mounted vertically onto sample holders for the microscope. Figure 5.8 shows the SEM image of a PTCa/PEKK composite with 30% volume fraction of ceramic. It can be observed that the ceramic grains (dark grains) are surrounded by polymer matrix giving 0-3 connectivity.

Figure 5.9 shows the SEM picture of a PTCa/PEKK composite with 60% vol. fraction of ceramic. In this case, it can be observed that some ceramic grains are in contact with each other. These areas have higher ceramic connectivity. However, to have 1-3 connectivity in the composite, intercommunication of ceramic grains has to occur throughout the bulk to form a path from one film surface to the other. The SEM micrographs also show that for both composites the polymer efficiently wetted the surface of the ceramic grains, thus showing that there is good adhesion between the constituent phases.



Figure 5.8: SEM picture of PTCa/PEKK composite with 30/70 vol%.. The bar indicates 10µ m



Figure 5.9: SEM picture of PTCa/PEKK composite with 60/40 vol%. The bar indicates 10µm.

## **5.6** Conclusion

In this chapter the method used for fabricating the PTCa/PEKK composite films has been described, including surface ceramic chemical treatment, hot pressing, evaporation of electrodes and poling. Furthermore, SEM images were obtained in order to study the microstructure of the composites. The fabrication conditions primarily are determined by the electrical and thermal properties of the PEKK polymer matrix.

It was shown how flexible ceramic/polymer composites with a high values of elastic compliance,  $s_{33}$ , were obtained. In addition, these sensors are able to work at high temperatures since the melting temperature of the polymer is very high (T<sub>m</sub>=305 °C).

This suggests that PTCa/PEKK composites can be successfully embedded in carbon fibre reinforced composites for AE detection.

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# Chapter 6: Sensor characterisation

#### **6.1 Introduction**

This chapter reports the characterisation of the dielectric and electroactive properties of the PTCa/PEKK composite sensors. Dielectric spectroscopy in the frequency range of  $10^{-5}$  to  $10^{5}$  Hz was performed and the pyroelectric, p, piezoelectric d<sub>33</sub> and d<sub>31</sub> coefficients, the electromechanical coupling coefficient, k<sub>t</sub> and hysteresis loops were obtained. All the measurements were performed for PTCa/PEKK composites with 30, 40, 50 and 60% of ceramic by volume fraction. It is important to notice that due to the composite fabrication method, which will produce samples with slightly different ceramic loadings from that predetermined by equation 5.1 the experimental results may vary from one sample to another. This error will be discussed for each case. The error bar in the figures indicate the total range.

#### **6.2 Dielectric measurements**

Dielectric measurements were performed over the range  $10^{-5}$  to  $10^{5}$  Hz with the aim of determining sample quality, the main indicator of which was taken to be the existence of relaxation peaks at low frequency. These measurements also yielded values for the relative permittivity,  $\varepsilon'$ , to be used later when calculating the piezo- and pyroelectric figures of merit. Note that our composite system will be considered isotropic for its relative permittivity, i.e,  $\varepsilon_{33} = \varepsilon_{31} = \varepsilon'$ .

To cover this wide range of frequencies three methods were used namely, a standard ac bridge measurement using a General Radio Bridge (Model 1616), a lock-in technique using a DSP Lock-in Analyser (7265) and the observation of the discharge current using a Keithley programmable electrometer (model 617).

Well known relationships were used to extract values for the relative permittivity,  $\varepsilon'$ , and dielectric loss,  $\varepsilon''$ . Bridge measurements were quite reliable as consistent results were obtained for similar samples. However, the low frequency measurements presented some noise problems. Three frequency ranges may be distinguished, namely

# (a) $10 \text{ Hz} \le f \le 10^5 \text{ Hz}$

In this range the capacitance, C, and conductance, G, of the samples yield values for  $\varepsilon'$  and  $\varepsilon''$  using the following relations

$$\varepsilon' = \frac{Cd}{A\varepsilon_{\circ}} \tag{6.1}$$

$$\varepsilon'' = \frac{\mathrm{Gd}}{2\pi \mathrm{fA}\varepsilon_0} \tag{6.2}$$

where  $\varepsilon_0$  is the permittivity of free space, d and A the thickness and the electrode area of the sample and f the frequency at which the measurement is made.

# (b) $10^{-2} \text{Hz} \le f \le 10 \text{Hz}$

In this frequency range a signal voltage of amplitude  $V_{ac}$  is applied to the sample and the in-phase,  $I_y$ , and quadrature,  $I_x$ , components of the resultant current are measured using the lock-in amplifier. Values for  $\varepsilon'$  and  $\varepsilon''$  are readily obtained since (Limbong 2000)

$$\varepsilon' = \frac{I_{y}d}{2\pi f \varepsilon_{0} A V_{ac}}$$
(6.3)

and,

$$\varepsilon'' = \frac{I_x d}{2\pi f \varepsilon_0 A V_{ac}} . \tag{6.4}$$

## (c) $10^{-5}$ Hz $\le f \le 10^{-2}$ Hz

To assess sample properties in the low-frequency regime it is easier to undertake measurements in the time domain and use the Hamon approximation to transform the data to the frequency domain. Samples were subjected to a steady electric field of  $10^5$  V/m for 30 hours. The sample was then short-circuited and the discharge current, I(t), monitored for 3 hours.

The Hamon approximation (Hamon, 1952) may then be used to obtain ɛ", viz.

$$\varepsilon'' = \frac{I(t)d}{2\pi f_{\rm h} A \varepsilon_0 V} \tag{6.5}$$

where V is the voltage required to establish the initial electric field and  $f_h$  is the Hamon frequency given by  $f_h=0.1/t$ , where t is the elapsed time from short circuiting the sample.

The dielectric loss spectrum obtained using the above techniques may then be fitted to the universal 'law' proposed by Jonscher (Jonscher 1983), which has the form,

$$\varepsilon''(f) \propto \frac{1}{(f/f_p)^{-m'} + (f/f_p)^{1-n'}}$$
 (6.6)

where 0 < m' < 1 and 0 < n' < 1 are arbitrary fitting parameters and  $f_p$  is the peak frequency.

In carrier dominated systems, such as ceramic/polymer composites, an additional term is needed to take into account the low frequency dispersion (LFD). At low frequencies the response rises obeying a power law, which has the form,

$$\varepsilon''(f) \propto f^{n''-1}. \tag{6.7}$$

Using the Kramers-Kronig relations,  $\varepsilon'(f)$  can be obtained from  $\varepsilon''(f)$ 

$$\varepsilon'(f) = \varepsilon'_{\infty} + P \int_{-\infty}^{\infty} \frac{\varepsilon''(x)}{(x-f)} dx$$
(6.8)

where P is the Cauchy principal value and  $\varepsilon'_{\infty}$  is the value of  $\varepsilon'(f)$  at high frequencies. This provides the values of  $\varepsilon'(f)$  in the frequency range of  $10^{-5}$  Hz to  $10^{5}$  Hz.

Figure 6.1 shows the dielectric loss in the frequency range of  $10^{-4}$  to  $10^{-2}$  Hz for PTCa/PEKK 30/70% vol. composites. One of them was prepared with ceramic grains chemically treated with titanate coupling agent whereas for the other the ceramic grains were not treated at all. Both sets of experimental data were fitted using the Jonscher function.



**Figure 6.1**: Dielectric spectroscopy in the frequency range  $10^{-4}$  to  $10^{-2}$  Hz of the treated and non-treated PTCa/PEKK 30/70%vol.  $f_p = 5x10^{-4}$ Hz.

It can be observed that for the composite fabricated with non-treated ceramic there is a relaxation peak at 10<sup>-3</sup> Hz which is absent in the treated ceramic composite. A loss peak occurring at such low frequencies is generally attributed to space charge in the sample (Scarpa et al 1996) and probably arises from trapped charges in the ceramic/polymer interfaces. The disappearance of the peak in the composite when the ceramic has been

chemically treated is due to a reduction in the concentration of trapped space charge at the interfaces suggesting that better connection has been achieved between the phases.

Figure 6.2 shows the dielectric loss for the PEKK polymer and the chemically treated PTCa/PEKK composites with ceramic volume fractions 30, 40, 50 and 60%. The experimental data has been fitted with the Jonscher function giving good agreement. In all cases, including the pure polymer, a single peak is observed centred at around  $10^{-1}$  Hz. Also, at low frequencies, a steady increase of the loss is observed.



**Figure 6.2**: Dependence of loss on frequency in the range  $10^{-5}$  to  $10^{5}$  Hz for PEKK and the treated PTCa/PEKK composites with 30, 40, 50 and 60% ceramic volume fractions.  $f_p = 5x10^{-2}$ 

PTCa ceramic has a relaxation peak in the GHz range (Moulson 1990). The relaxation of clustered water has been shown to occur in the MHz region (Pethig 1992) while the relaxation peak due to trapped charges occurs around  $10^{-3}$  Hz. Therefore, the peak seen in figure 6.2 at ~0.1 Hz is likely to be due to impurities in the polymer phase. The increase of the dielectric loss at low frequencies is due to quasi-DC processes. The main

contribution to the quasi-DC process in the composites is due to the ceramic as can be observed from figure 6.2, where low frequency dielectric losses increase with the ceramic volume fraction.

Figure 6.3 shows the frequency dependence of the relative permittivity for the PEKK polymer and the chemically treated PTCa/PEKK composites with ceramic volume fractions 30, 40, 50 and 60%. It is seen that above ~1 Hz the relative permittivity,  $\varepsilon'$  is constant for all cases. Below ~1 Hz,  $\varepsilon'$  increases owing to the presence of the relaxation process with  $f_p \sim 5 \times 10^{-2}$  Hz (figure 6.2). As expected,  $\varepsilon'$  increases with increasing ceramic content (see table 6.1). For all the composites, the Jonscher 'universal law' fitted to the data in figure 6.2 was used to obtain the corresponding 'theoretical' curve for  $\varepsilon'$  using the Kramers-Kronig relation (equation 6.8). The resulting curves are shown as the continuous curves in figure 6.3. Except for the composite with the highest ceramic loading at low frequencies, the fit with data obtained directly from the bridge and lock-in is good.



**Figure 6.3**: Frequency dependence of the relative permittivity in the range  $10^{-2}$  to  $10^{5}$  Hz of the *PEKK and the treated PTCa/PEKK composites with 30, 40, 50 and 60% ceramic volume fraction.* 

Note that since the piezoelectric and pyroelectric figures of merit are proportional to the inverse of the permittivity (equations 2.32 and 2.36), an increase of the permittivity at low frequencies leads to a poor response of the composites in the receiver mode in that frequency range. Figure 6.4 shows the effect of ceramic loading on the conductivity of samples measured at 1 KHz and at room temperature. Sample conductivity increases super-linearly with increasing ceramic loading. This suggests that poling will be achieved more easily in the samples with high ceramic content.



Figure 6.4: Conductivity versus ceramic volume fraction. of PTCa/PEKK composites.

Table 6.1 summarises the results obtained for the relative permittivity, the dielectric loss and the conductivity for the different composites and single phases.

*Table 6.1*: Dielectric properties of PTCa/PEKK composites and their single phases, measured at 1 KHz at room temperature (All results are average values with a relative error of 5-10%).

Property	PEKK	PTCa/PEKK 30/70 vol%	PTCa/PEKK 40/60 vol%	PTCa/PEKK 50/50vol%	PTCa/PEKK 60/40vol%	PTCa (*)
Relative permittivity, $\epsilon'$	3.6	15	19	24.8	36.3	209-230
Dielectric loss, ε''	0.01	0.09	0.15	0.29	0.55	2.5
Conductivity (10 <sup>-10</sup> S)	5.5	19.6	32.7	63.3	120	500
(*) Wenger 1999b						

#### **6.3 Piezoelectric Measurements**

In this section, in order to characterise the piezoelectric properties of the composite sensors, both the piezoelectric  $d_{33}$  and  $d_{31}$  coefficients and the electromechanical coupling coefficient,  $k_t$ , were measured.

#### 6.3.1 Piezoelectric strain coefficients, d<sub>ij</sub> and g<sub>ij</sub>

The  $d_{33}$  coefficient was obtained using a Pennebaker Model 8000 Piezo  $d_{33}$  tester and AC voltmeter (figure 6.5). In this experiment, a known AC stress was applied in the direction of the thickness of the samples and the voltage produced across a series connected capacitor was measured. The measured voltage in mV represented directly the  $d_{33}$  value in pC/N. Prior calibration of the instrument was undertaken with a known ceramic. Results of  $d_{33}$  for the different composites are summarised in table 6.2. The obtained values of  $d_{33}$  were measured for at least 10 samples of each type and the relative error ranged from 5 to 10%.



Figure 6.5: Sketch of the d<sub>33</sub> experiment.

Figure 6.6 shows the super-linear increase of  $d_{33}$  with the ceramic loading. This positive deviation from linear dependence is probably due to an increase in 1-3 connectivity with an increase of ceramic loading. This results in a better poling efficiency and therefore in a higher piezoelectric  $d_{33}$  coefficient.



Figure 6.6: Plot of d33 against the ceramic volume fraction.

The values obtained are comparable to those reported by Wenger (1999) with PTCa/Epoxy composites. As expected, they are lower than for the ceramic alone ( $d_{33}$ =68 pC/N) because the polymer matrix is not electroactive. The values are also smaller than polypropylene (PP) foam ( $d_{33}$ =200 pC/N) but comparable with that for the electroactive polymer PVDF ( $d_{33}$ =-33 pC/N), but opposite in sign.

The  $g_{33}$  coefficients for different composites are obtained by substituting the measured values of  $d_{33}$  and  $\varepsilon_{33}$ , which is the relative permittivity,  $\varepsilon'$  in the thickness direction, into

equation 2.23. The results are given in table 6.2, and show that  $g_{33}$  decreases with increasing ceramic concentration in the composites.

The piezoelectric figure of merit,  $d_{33} \times g_{33}$  remains approximately constant for the different PTCa/PEKK composites but has a higher value than the piezoelectric figure of merit of the PTCa ceramic alone. The low relative permittivity of the PTCa/PEKK composites in comparison with that of the PTCa ceramic results in a higher  $g_{33}$  coefficient and therefore a higher  $d_{33} \times g_{33}$  product for the composites.

Property	E <sub>33</sub> (*)	$d_{33} (pCN^{-1})$	g <sub>33</sub> (VmN <sup>-1</sup> )	d <sub>33</sub> g <sub>33</sub> (TPa <sup>-1</sup> )
PTCa (**)	209-230	68	0.04	2.5
PEKK	3.6	0	0	0
PTCa/PEKK 30/70vol%	15	22	0.17	3.65
PTCa/PEKK 40/60vol%	19	25	0.15	3.7
PTCa/PEKK 50/50vol%	25	28	0.13	3.55
PTCa/PEKK 60/40vol%	36	34	0.11	3.65

 $(*) \varepsilon' = \varepsilon_{33}$ 

(\*\*) Wenger 1999b

The  $d_{31}$  coefficients for the composites were measured by suspending a weight from the lower end of a sample of dimensions 3.5 cm × 1 cm, which was rigidly clamped at its upper end, see figure 6.7. The weight was removed almost instantaneously by means of a solenoid lift and the charge developed across the sample electrodes was recorded on a storage oscilloscope. This process was repeated using different weights.



Figure 6.7: Sketch of the  $d_{31}$  experiment.

Figure 6.8 shows the voltage developed across the PTCa/PEKK 50/50% vol. sample for different applied weights. The slope of the linear plot in figure 6.8 yields the value of  $d_{31}$  coefficient, which is given by (Brockley 1979)

$$d_{31} = \frac{CVd}{lmg}$$
(6.9)

where C is a standard capacitance (the value of C used in this experiment was 10 nF which is much bigger than the capacitance of the sample), V is the developed voltage, d is the sample thickness, l is the length of the electrode and mg the force applied by the

weight. The standard capacitor C is used to measure the charge developed on the electrodes of the sample when force is applied. Note that long samples are desirable since more charge will be developed and a higher V will be developed across C.



**Figure 6.8:** Voltage developed across the PTCa/PEKK 50/50% vol sample for different applied weights.

The results of the  $d_{31}$  measured for the different composites are summarised in table 6.3. From the data it will be noticed that the value for  $d_{31}$  of the 60/40%vol. composite is higher than the value for the ceramic alone. This is due to the fact that  $d_{31}$  is a combination property depending on  $d_{31}$  and  $s_{33}$  of the constituent phases. The  $g_{31}$ coefficient and  $d_{31} \times g_{31}$  product of the different composites is calculated in the same manner as before and are also given in table 6.3.

Table 6.3: Piezoelect	ric $d_{31}$ , $g_{31}$ and $d_{31}x_{0}$	g <sub>31</sub> properties of PTCa	/PEKK composites and t	heir single phases.
Property	8 <sub>33</sub>	d <sub>31</sub> (pCN <sup>-1</sup> )	g <sub>31</sub> (x10 <sup>3</sup> VmN <sup>-1</sup> )	$d_{31} \times g_{31} (x10^{-15} \text{ Pa}^{-1})$
PTCa (*)	209-230	-3.1	-1.7	5.2
PEKK	3.6	0	0	0
PTCa/PEKK 30/70vol%	15	-	-	-
PTCa/PEKK 40/60vol%	19	-0.1	-0.6	0.06
PTCa/PEKK 50/50vol%	25	-0.4	-1.8	0.72
PTCa/PEKK 60/40vol%	36	-3.4	-10	34

(\*) Reference: Wenger 1999b

Note that the low  $d_{31}$  values obtained for the composites with 30, 40 and 50 % of ceramic volume fraction are due to the limitations both in sample quality and experimental set up. Firstly, the samples were thick and stretching them sufficiently in order to obtain a reasonable output voltage was found to be impossible with the existing experimental set up. Secondly, the weight was not instantaneously removed so that the voltage developed was lower than the expected value. Further discussion is given in chapter 7.

Using the measured coefficients, the piezoelectric hydrostatic coefficients, i.e.  $d_h$  and  $g_h$ , can now be calculated from the expressions

$$d_{h} = 2d_{31} + d_{33} \tag{6.10}$$

and

$$g_{h} = 2g_{31} + g_{33} . (6.11)$$

The values of  $d_h$  and  $g_h$  for the composites and the ceramic, together with the  $d_h \times g_h$  product are given in table 6.4, from which it is seen that the values of the  $d_h \times g_h$  product for the composites are slightly higher than that of the ceramic. Therefore, the piezoelectric composites are better sensors in the hydrostatic mode. This is due to (a) the anisotropy in the piezoelectric composites and (b) their low permittivity.

<b>Table 6.4</b> : Piezoelectric $d_{h}$ , $g_{h}$ and $d_{h}xg_{h}$ properties of PTCa/PEKK composites and their single phases.				
Property	E <sub>33</sub>	$d_h (pCN^{-1})$	$g_h (VmN^{-1})$	$d_h \times g_h (TPa^{-1})$
PTCa (*)	209-230	62	0.03	2
PEKK	3.6	0	0	0
PTCa/PEKK 30/70vol%	15	22	0.17	3.7
PTCa/PEKK 40/60vol%	19	25	0.15	3.65
PTCa/PEKK 50/50vol%	25	27	0.12	3.3
PTCa/PEKK 60/40vol%	33	27	0.1	2.7

(\*) Wenger 1999b

# 6.3.2 Measurement of the electromechanical coupling coefficient $k_{tb}$ the mechanical quality factor $Q_{m}$ , the acoustic impedanze, $z_0$ and the stress coefficients, $h_{33}$ and $e_{33}$ .

The thickness electromechanical coupling coefficient,  $k_t$ , the mechanical quality factor  $Q_m$ , and the acoustic impedance,  $Z_a$  can be obtained from the measurement of the complex impedance  $Z(\omega)$ , of the transducer vibrating as a free resonator in air at frequencies around its fundamental resonance peak.

As described in chapter 3, for a piezoelectric material resonating freely in air the electrical impedance  $Z(\omega)$  is given by,

$$Z(\omega) = \frac{1}{i\omega C^{s}} - \frac{2}{iB} \left(\frac{h_{33}}{\omega}\right)^{2} \tan\left(\frac{\gamma' l}{2}\right)$$
(6.12)

where the first term represents the impedance associated with the capacitance,  $Z_e$ , of the sample and the second term represents the complex acoustic impedance,  $Z_{ac}$ . The other parameters have already been defined. Assuming small mechanical losses, the complex acoustic impedance,  $Z_{ac}$  expanded about its fundamental resonance frequency becomes

$$Z_{ac}(\omega_0) = \frac{2}{z_0 A} \left(\frac{h_{33}}{\omega_0}\right)^2 \operatorname{coth}\left(\frac{\pi \psi}{4}\right) - \frac{i\psi}{z_0 A} \left(\frac{h_{33}}{\omega_0}\right)^2 \operatorname{coth}\left(\frac{\pi \psi}{4}\right)$$
(6.13)

where the fundamental harmonic mode has been considered ( $\lambda$ =21). From equation (6.13) an expression for the h<sub>33</sub> coefficient can be found which is related to the resonance parameters. This has the form

$$h_{33}^{2} = 2\pi^{2} R_{max} z_{0} A f_{0}^{2} \tanh\left(\frac{\pi\psi}{4}\right)$$
(6.14)

where

$$\mathbf{R}_{\max} = \operatorname{Re}(\mathbf{Z}_{\mathrm{ac}}(\boldsymbol{\omega}_0)) \ . \tag{6.15}$$

Using the complex capacitance of the sample,

$$C^{s} = C(1 - i \tan \delta_{e})$$
(6.16)

the electrical impedance,  $Z_e$  can be expanded into its real and imaginary parts. If small dielectric losses are assumed,  $Z_e$  becomes

$$Z_{e}(\omega) = -\frac{i}{\omega C} + \frac{\tan \delta_{e}}{\omega C}.$$
(6.17)

Considering now the possibility of an small additional frequency independent conduction through the sample and also the possibility of dielectric dispersion over the frequency range of measurements,  $Z_e$  can be rewritten as (Dias 1994)

$$Z_{e}(\omega) = R + \frac{A}{f^{\alpha}} - i\frac{B}{f^{\beta}}$$
(6.18)

where A, B  $\alpha$ ,  $\beta$  and R are adjustable parameters. Substitution of equations (6.18) and (6.14) into equation (6.13) gives the electrical impedance at the fundamental frequency of the sample acting as a free resonator as

$$Z_{e}(\omega) = R + \frac{A}{f^{\alpha}} - i\frac{B}{f^{\beta}} + i\frac{R_{max}}{\sqrt{1 + \psi\frac{f}{f_{0}}}} \left(\frac{f_{0}}{f}\right)^{2} \tanh\left(\frac{\pi\psi}{4}\right) \tan\left(\frac{\gamma' l}{2}\right). \quad (6.19)$$

By fitting the real and imaginary part of equation (6.19) to the experimental data, parameters at resonance can be calculated, such as, the mechanical quality factor  $Q_m=1/\psi$ , the velocity of sound  $v_s=2f_0l$ , the specific acoustic impedance  $z_0=\rho v_s$  and the stiffness constant  $c_{33}^{D}=z_0v_s$ . Additionally, the permittivity can be obtained from equation (6.17) using the following expression,

$$\varepsilon_{33}^{\rm S} = \frac{1}{2\pi f_0 A \varepsilon_0} \left( \frac{\mathrm{Im}(Z_e)}{\mathrm{Re}(Z_e)^2 + \mathrm{Im}(Z_e)^2} \right).$$
(6.20)

The expression for the electromechanical coupling coefficient,  $k_t$  given in chapter 2 can be rewritten as,

$$\mathbf{k}_{t} = (\varepsilon_{33}^{S})^{1/2} (\mathbf{c}_{33}^{D})^{-1/2} \mathbf{h}_{33} .$$
 (6.21)

Hence using equation (6.20), equation (6.1) and the expression for  $c_{33}^{D}$  (see above),  $k_t$  is obtained as a function of the resonance parameters,
$$k_t^2 = \frac{1}{2} \pi^2 R_{\max} f_0 C_0 \left( \psi^2 + 4 \right)^{1/2} \tanh(\pi \psi / 4)$$
 (6.22)

where  $f_0$  is the resonance frequency,  $C_0$  is the sample capacitance at  $f_0$ ,  $\psi$  is the width of the peak at middle height divided by the resonance frequency.  $R_{max}$  is the amplitude of the resonance peak of the real part of the impedance measured from the base line, where the base line is given by the first and second terms on the right side of equation (6.19).

A network analyser, Model HP8702A, was used to measure the real and imaginary part of the complex impedance around the resonance peak of the PTCa/PEKK composites. The sample was contained within a screened metal box. Calibration of the experiments were conducted prior to measurement to eliminate impedance contributions from the cables and the sample holder. A computer controlled the network analyser via a GPIP interface (figure 6.9).



Figure 6.9: Experimental set up for measuring the complex impedance of samples close to resonance.

Figure 6.10 shows the experimental and fitted real and imaginary parts of the impedance of PTCa/PEKK 60/40 %vol. in the neighbourhood of the fundamental resonance frequency. The values of  $k_t$  together with other properties for the different composites are summarised in table 6.5. Only the calculation of the 60/40 composite was repeated with a similar sample, due to the complexity of the calculation, and the relative error was ~5%. As expected, the values of  $k_t$ ,  $h_{33}$  and  $e_{33}$  coefficients in the composites are smaller than the corresponding values for the ceramic but do increase with the ceramic concentration.



**Figure 6.10:** *Experimental and theoretical plots of the real and imaginary impedance of PTCa/PEKK* 60/40% composite around the resonant peak.

Table 6.5: $k_t$ ancomposites and the	d other pr	operties ga phases act	tined from electing as free reso	trical impedan mators.	ice measuremer	nts on films of	PTCa/PEKK
Property	k,	Qn	z <sub>o</sub> (MRayls)	v <sub>s</sub> (ms <sup>-1</sup> )	с <sup>D</sup> <sub>33</sub> (GPa)	h <sub>33</sub> (GV/m <sup>2</sup> )	e <sub>33</sub> (C/m <sup>2</sup> )
PTCa (*)	0.47	1200	30	4350	183	6.6	12
PEKK			-	-	-	-	
PTCa/PEKK 30/70vol%	-	-	-	-	.=	1 <b>2</b>	
PTCa/PEKK 40/60vol%	0.1	9	6.8	1930	13	0.9	0.16
PTCa/PEKK 50/50vol%	0.17	7	8.2	2020	16.6	1.4	0.31
PTCa/PEKK 60/40vol%	0.2	8.4	9.4	2040	19	1.6	0.51

(\*) Reference: Wenger 1999b

It also can be observed that the PTCa/PEKK composites are much more flexible than the PTCa ceramic since their stiffness constant  $c_{33}^{D}$  is approximately an order of magnitude smaller. This leads to a low acoustic impedance  $z_0$  which will be closer to that of carbon reinforced fibre composites (CRFC) enabling good acoustic match with such materials.

The mechanical quality factor  $Q_m$  is related to the frequency response. A low value of  $Q_m$  leads to a wide bandwidth response. Thus, the low values of  $Q_m$  of the PTCa/PEKK composites make transducers from these materials suitable for AE detection since AE waves have different propagation modes and a range of associated frequencies from the KHz to the MHz range.

#### **6.4 Pyroelectric Measurements**

The pyroelectric coefficient p has been measured using the direct method, i.e. measuring the change in the dielectric displacement D resulting from a change in temperature,  $\theta$ .

The relationship between dielectric displacement, D and the polarisation P, is given by (Moulson 1990),

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \tag{6.23}$$

where E is the electric field and P is polarisation. For a poled sample with shorted electrodes so that the externally applied field is zero i.e. E=0,

$$\left(\frac{\partial D}{\partial \theta}\right)_{E=0,T} = \left(\frac{\partial P}{\partial \theta}\right)_{E=0,T} = \left(\frac{\partial (Q/A)}{\partial \theta}\right)_{E=0,T} \approx \frac{1}{A} \left(\frac{\partial Q}{\partial \theta}\right)_{E=0,T} \quad (6.24)$$

where Q is the liberated charge and T the stress. It is assumed that the electrode area A remains constant for the changes in temperature involved in the experiment. The pyroelectric coefficient p, can be expressed as,

$$p = \frac{1}{A} \left( \frac{\partial Q}{\partial \theta} \right)_{E=0,T} = \frac{1}{A} \frac{\partial Q}{\partial t} \frac{\partial t}{\partial \theta} = \frac{I}{A \partial \theta / \partial t}$$
(6.25)

where t is time, I is the current through the sample when the electrodes are short circuited and  $\partial \theta / \partial t$  is the rate of rise of sample temperature.

In the direct method, the sample is placed in a vacuum chamber provided with a temperature controller (Eurotherm 818). The sample electrodes are short-circuited through a programmable electrometer (Keithley 617) (figure 6.11).

The temperature was increased at a constant rate,  $\partial \theta / \partial t$ , of one degree per minute and the corresponding pyroelectric current measured. The value of the pyroelectric current was determined after three thermal excursions. In each one, the sample was heated up from 20°C to 90°C and then cooled down again to 20 °C. This was done in order to remove the effects of space charge so as to obtain a reversible pyroelectric current.



Figure 6.11: *Experimental set up for the pyroelectric measurements.* 

Figure 6.12 shows the results obtained during three successive thermal ramps applied to the PTCa/PEKK 50/50% vol. composite. During the first thermal ramp, the current rose monotonically to high values. On the second and third runs the currents were much smaller and were only weakly dependent on temperature. The decrease in current that occurred between the first and subsequent runs is indicative of space-charge, injected during poling at 150 °C, being removed from the sample.

The dependence of the pyroelectric coefficient on the temperature was obtained from the reversible pyroelectric current using equation (6.25). Table 6.6 shows the pyroelectric coefficient and the pyroelectric figure of merit obtained at room temperature for the different PTCa/PEKK composites and their single phases. The values of p were found to be strongly dependent on the sample thickness.



Figure 6.12: Thermally stimulated currents in PTCa/PEKK 50/50 %vol. composite ( $E_p=10MV/m$ ,  $T_p=150^{0}C$ ).

Table 6.6: Relative permittiv           measured at RT of PTCa/PEK	vity ε, pyroelectric Κ composites and t	coefficient p and pyroele heir single phases.	ctric figure of merit FOM <sub>p</sub>
Property	ε΄	p (μCm <sup>-2</sup> K <sup>-1</sup> )	p/ε' (μCm <sup>-2</sup> K <sup>-1</sup> )
PEKK	3.6	0	0
PTCa/PEKK 30/70vol%	15	4	0.3
PTCa/PEKK 40/60vol%	19	8.5	0.5
PTCa/PEKK 50/50vol%	25	17	0.7
PTCa/PEKK 60/40vol%	33	31	0.9
PTCa (*)	209-230	350	1.7

(\*) Dias 1994

The pyroelectric coefficient, p, for the best composite, i.e., PTCa/PEKK 60/40 vol%, is an order of magnitude smaller than that for the PTCa ceramic. This is due to the dielectric mismatch between the two constituent phases, which leads to poor poling of the ceramic in the composite. Another factor that can lead to low p values is the sample thickness. The samples obtained during this process had an approximate thickness of 200  $\mu$ m. A reduction in thickness down to 50  $\mu$ m would improve significantly the sensor performance (Dias 1994b).

Figure 6.13 shows the dependence of the p coefficient with the ceramic volume fraction. The pyroelectric coefficient increased super-linearly with the PTCa loading contrary to the expected linear dependence. However, the increase in 1-3 connectivity and therefore the parallel connected ceramic has to be considered. This will lead to a better poling and higher pyroelectric coefficient. Similar explanation can be applied to the FOM<sub>p</sub> dependence on the ceramic volume fraction observed in figure 6.14.



Figure 6.13: The pyroelectric coefficient at RT of PTCa/PEKK with different ceramic loadings.

Figure 6.15 shows the temperature dependence of the pyroelectric coefficient obtained for composites with different ceramic loading. All of the sensors have better performance at higher temperatures. This increase is more significant for the composite with 60 %vol. of ceramic. However, it has to be pointed out that a weak dependence on temperature is desirable in order have a stable sensor performance.



Figure 6.14: The pyroelectric figure of merit at RT of PTCa/PEKK with different ceramic loadings.



**Figure 6.15:** *Temperature dependence of the pyroelectric coefficient for PTCa/PEKK with different ceramic loading.* 

#### **6.5 Hysteresis measurements**

Hysteresis loops were performed for PTCa/PEKK composites with 30, 40, 50 and 60% ceramic volume fractions using different electric fields and frequencies. The Sawyer-Tower method was used for that purpose. In this method, a capacitance ( $C_0$ ) with a value much higher than the sample capacitance ( $C_s$ ) is placed in series with the composite transducer (figure 6.16). In ferroelectric materials there are three contributions to the hysteresis loops (equation 6.26) but only one of them is due to switching of permanent dipoles in the material. In order to obtain the polarisation due to the permanent dipoles, the positive ( $I_+$ ) and negative ( $I_-$ ) unipolar currents which arise only from the resistive (R) and capacitive (C) components of the dielectric are subtracted from the bipolar current,

$$I_{t} = A \frac{dP}{dt} + \frac{V}{R} + C \frac{dV}{dt}$$
(6.26)

where  $I_t$  is the total current through the sample, A the sample area, P the polarisation due to permanent dipoles, t is time and V the applied voltage. Therefore,

$$I_{pol} = I_{t} - (I_{+} + I_{-})$$
(6.27)

where  $I_{pol}$  is the current due to permanent dipoles. Therefore,

$$V_{pol} = V_t - (V_+ + V_-)$$
(6.28)

where the subscripts have the same meaning as before but V is now the voltage appearing across  $C_0$  (see circuit in figure 6.16). To perform the experiment, a switch with three branches, was connected between the sinusoidal function generator (Thurlby-Thandar TG230) and the high voltage amplifier (Trek 610C). The first branch introduced a short circuit, the second branch had a diode to produce a positive unipolar cycle and the third branch had a diode in the opposite direction to produce a negative unipolar cycle. The voltage applied and the voltage dropped across  $C_0$  were monitored using a digital storage oscilloscope (DSO) (Gould 4050). A PC was used to download

the experimental data (figure 6.17). The full , positive and negative half-wave fields were applied to the sample in turns and  $V_T$ ,  $V_+$  and  $V_-$  were measured across  $C_0$  respectively. Equation 6.28 was then used to calculate the real polarisation voltage,  $V_{pol}$ .



Figure 6.16: Circuit diagram for the Sawyer-Tower method.



Figure 6.17 : Diagram of the experimental set-up for the hysteresis measurement.

From the measured  $V_{\mbox{\scriptsize pol}}$  the polarisation can be calculated from the following expression,

$$P = C_0 \frac{V_{pol}}{A}$$
(6.29)

where all parameters have been defined already.

Figure 6.18 shows the hysteresis loop of the PTCa/PEKK 50/50% volume fraction composite. The sample was poled at room temperature with a poling field of 10MV/m and the frequency of the cycle was 1 Hz.



*Figure 6.18:* Hysteresis loops of the PTCa/PEKK 50/50 vol% composite at room temperature. Poling field 10MV/m and frequency 1Hz.

The roundness of the hysteresis loops indicate conduction through the sample, which can be due to interface-charges accumulated in the polymer/ceramic interfaces. This suggests that the composite has a high percentage of 0-3 connectivity. The high coercive fields of the loops indicate that the local field in the ceramic is low. This is a consequence of the mismatch between the permittivities of the constituent phases and the polymer shielding of the ceramic (Dias 1994b).

Figure 6.19 and 6.20 shows the remanent polarisation and coercive field of the PTCa/PEKK composite sensor with 60 % volume fraction of ceramic loading using different poling fields. The poling frequency was 1 Hz and the experiment was performed at room temperature. It can be observed from the figures that both the remanent polarisation and coercive field increase linearly with the applied field due to the better poling. Note that the highest value is obtained for a poling field of 10MV/m which is just below the breakdown field of the composite.



Figure 6.19: Remanent polarisation of the PTCa/PEKK 60/40 vol% composite for different poling fields at room temperature. Poling frequency 1Hz.



*Figure 6.20:* Coercive field of the PTCa/PEKK 60/40 vol% composite for different poling fields at room temperature. Poling frequency 1Hz.

Figures 6.21 and 6.22 show the remanent polarisation and the coercive field as a function of frequency respectively. From figure 6.21 it can be seen that the remanent polarisation decreases as the frequency increases. At high frequencies, the alignment of the domains is reduced because the dipole relaxation time is too long resulting in a lower remanent polarisation. Figure 6.22 shows the decrease of the coercive field with increasing frequency due to inefficient poling at high frequencies.



*Figure 6.21: Remanent polarisation of the PTCa/PEKK 60/40 vol% composite for different poling frequencies at room temperature. Poling field 10MV/m.* 



*Figure 6.22:* Coercive field of the PTCa/PEKK 60/40 vol% composite for different poling frequencies at room temperature. Poling field 10MV/m.

Figures 6.23 and 6.24 show the remanent polarisation and the coercive field as a function of ceramic volume fraction respectively. From figure 6.23 it can be seen that the remanent polarisation increases super-linearly with the ceramic loading. This positive deviation from the linear dependence can be due to the increase of 1-3 connectivity which allows more efficient poling of the ceramic phase. This suggests that composites with slightly higher ceramic volume fraction will be significantly better poled. A similar mechanism can be used to explain the super-linear increase of coercive field with ceramic loading observed in figure 6.24.



*Figure 6.23: Remanent polarisation of the PTCa/PEKK composites with different ceramic volume fractions at room temperature. Poling field 10MV/m and poling frequency 1Hz.* 



*Figure 6.24:* Coercive field of the PTCa/PEKK composites with different ceramic volume fractions at room temperature. Poling field 10MV/m and poling frequency 1Hz.

#### 6.6 Elastic compliance coefficient, s<sub>33</sub>

Finally, the elastic compliance coefficient,  $s_{33}$  of the composites was calculated. Equation (2.31) can be rewritten as,

$$s_{33} = d_{33}^2 / (\epsilon_0 \epsilon' k_t^2)$$
 (6.30)

where all the parameters have already been defined. Thus, using the obtained values of relative permittivity,  $\varepsilon'$  and piezoelectric coefficient, d<sub>33</sub> (table 6.2) and the electromechanical coupling coefficient, k<sub>t</sub>, (table 6.5), the values of the elastic compliance coefficient, s<sub>33</sub> can be calculated for the composites with 40, 50 and 60% ceramic loading. Table (6.7) shows the s<sub>33</sub> values for the different composites which are

considerably larger than for the PTCa ceramic. For the case of PTCa/PEKK 60/40% volume fraction composite, the compliance value is still 4 times bigger than the ceramic. Therefore, the composite sensors are much less brittle than the ceramic and there will be less chance of sensor damage when embedding the sensor in carbon fibre reinforced composites.

Property	ε'=ε <sub>33</sub>	d <sub>33</sub> (pCN <sup>-1</sup> )	k,	s <sub>33</sub> (TPa <sup>-1</sup> )
PTCa	209	62	0.47	11
PTCa/PEKK 40/60vol%	19	25	0.1	372
PTCa/PEKK 50/50vol%	25	28	0.17	123
PTCa/PEKK 60/40vol%	33	34	0.2	91

## **6.7Conclusions**

The characterisation of the PTCa/PEKK composite sensors has been carried out by means of dielectric spectroscopy, the measurement of the piezo- and pyroelectric coefficients and hysteresis loop measurements.

The dielectric spectroscopy has shown how the chemical treatment of the ceramic grains improve the composite quality. Additionally the measurements yielded the frequency response of the permittivity and hence the frequency dependence of the piezoelectric and pyroelectric figures of merit.

The piezoelectric measurements showed that the composites, especially the one with 60 % ceramic volume fraction, have a good combination of electroactivity and flexibility in comparison with the ceramic.

From the pyroelectric measurements it was found that although the p coefficient was comparable to other similar composites, it was very low in comparison with the ceramic p coefficient. This is due to the dielectric mismatch of the permittivities of the constituent phases and because relative thick samples were used. The hysteresis measurements showed how the ferroelectric properties of the composites changed for the different poling parameters at room temperature. Finally, the elastic compliance parameter,  $s_{33}$ , has been calculated using the relative permittivity,  $\varepsilon'$ , the piezoelectric coefficient,  $d_{33}$ , and the electromechanical coupling coefficient,  $k_t$ , showing that the composite sensors are much more flexible than the PTCa ceramic.

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# Chapter 7: Application of the mixed connectivity model

# 7.1 Introduction

The aim of this chapter is to use the experimental data reported in chapter 6 together with the mixed connectivity model (Chapter 3) in order to calculate the 1-3 connectivity of each PTCa/PEKK composite. Whether the experimental data and/or the model is reliable in each case in then discussed. In cases where the experimental data is not reliable the mixed connectivity model will be used to predict the expected values. The limitations of the mixed connectivity model are discussed where appropriate.

# 7.2 Application of the Mixed Connectivity Model

Table 7.1 summarises the measured dielectric and electroactive properties of the different PTCa/PEKK composites measured at room temperature. These values will be used to calculate the amount of 1-3 connectivity present in each composite and to discuss the differences between them.

Table 7.1: Piezo and diele	ctric properties	of PTCa/PEKK a	composites and the s	single phases.
Property	PTCa/PEKK 30/70 vol%	PTCa/PEKK 40/60 vol%	PTCa/PEKK 50/50vol%	PTCa/PEKK 60/40vol%
Dielectric constant, ε' (at 1 kHz)	15	19	24.8	36.3
Piezoelectric $d_{33}$ coefficient(×10 <sup>-12</sup> C/N)	22	25	28	34
Piezoelectric $d_{31}$ coefficient(×10 <sup>-12</sup> C/N)	Not observed	-0.1	-0.4	-3.4
Electromechanical coupling factor, k <sub>t</sub>	No peak observed	0.1	0.17	0.20
Pyroelectric coefficient(x10 <sup>-6</sup> C/m <sup>2</sup> K)	3.6	4.5	14.5	29.5

Figure 7.1 shows a m-n contour chart for the permittivity,  $\varepsilon'$  of PTCa/PEKK composites using the model. The continuous line represent constant values of permittivity obtained using the 1-3 cube mixed connectivity model (equation 3.47), and the dotted lines represent the constant volume fraction curves (equation 3.37). Each experimental value of permittivity (table 7.1) is located at the intersection of the known value of volume fraction of the composite and the corresponding value of the permittivity. Then the n and m values can be found and the percentage of 1-3 connectivity can be calculated using equation 3.40, which gives the percentage of ceramic in the parallel branch,  $\phi_{par}^{c}$ .



Figure 7.1: Permittivity contour chart for the PTCa/PEKK composites using the mixed connectivity model.

The values for n and m derived from the relative permittivity of each composite are summarised in table 7.2 together with the calculated parallel ceramic volume fraction (equation 3.40). Both n and m increase with increasing ceramic concentration resulting in a higher percentage of 1-3 connectivity. In the case of 30% ceramic loading composite, with  $\phi^{c}_{par}=0.036$  the percentage of ceramic bridging the electrodes is approximately 11.8%. For the composite with 60% ceramic loading and  $\phi_{par}^{c}=0.096$ , the percentage of ceramic with 1-3 connectivity is 16%. (Note that a  $\phi^{c}_{par}$  value of 6% in a composite with 50% of ceramic content means that 12% of the ceramic has 1-3 connectivity).

Table 7.2: n and m parameters for the mixed connectivity cube model for PTCa/PEKK					
derived from the permittivity.					
PTCa volume fraction (%)	n	m	φ <sub>par</sub> <sup>c</sup>		
30	0.29	0.65	0.036		
40	0.3	0.73	0.048		
50	0.31	0.79	0.06		
60	0.37	0.84	0.096		

Figure 7.2 shows the m-n contour chart for the  $d_{33}$  coefficient of PTCa/PEKK composites. Now the continuous lines represent constant values of the  $d_{33}$  coefficient obtained using equation 3.45. The dotted lines represent the constant volume fraction. The experimental  $d_{33}$  values listed in table 7.1 are located at the intersection of the corresponding ceramic percentage and the  $d_{33}$  value. The m and n values obtained from this contour chart (table 7.3) are very close to those obtained from the permittivity (table 7.2).

In this case, the percentage of 1-3 connectivity of the ceramic in the composite increases from 9% in the 30% ceramic volume fraction case to 16.7% in the 60% volume fraction case. These values are very close to the values obtained from permittivity measurements showing that the model gives reliable results (Dias et al 1994, Wenger et al 1999b).



Figure 7.2: d<sub>33</sub> contour chart for the PTCa/PEKK composites using the mixed connectivity model.

<b>Table 7.3:</b> n and m parameters of the mixed connectivity cube model for PTCa/PEKKderived from the $d_{33}$ coefficient.					
PTCa volume fraction %	n	m	φ <sub>par</sub> <sup>c</sup>		
30	0.25	0.66	0.027		
40	0.28	0.73	0.04		
50	0.31	0.79	0.06		
60	0.38	0.84	0.10		

Figure 7.3 shows the values of the average calculated  $\phi^{c}_{par}$ , using results from table 7.2 and 7.3, versus the ceramic volume fraction, from which it is seen that the 1-3 connectivity grows super-linearly with the ceramic loading. Such behaviour is consistent with the super-linear dependence of the experimental  $\epsilon$ ' and d<sub>33</sub> parameters observed in chapter 6.

However, these values have to be considered as 'apparent  $\phi^{c}_{par}$  values' for given poling conditions,  $E_{p}$ ,  $t_{p}$  and  $T_{p}$ , since different poling conditions will lead to different  $\epsilon'$  and  $d_{33}$  values, and thus to different n, m and  $\phi^{c}_{par}$  values.



*Figure 7.3*: Dependence of  $\phi_{par}^{c}$  on the ceramic volume fraction for the PTCa/PEKK composites.

Figure 7.4 shows the m-n contour chart for the  $d_{31}$  coefficient of PTCa/PEKK composites. The continuous line represent constant values of the  $d_{31}$  coefficient (equation 3.46). In this case only the experimental  $d_{31}$  value for the PTCa/PEKK 60/40% volume fraction is plotted since the  $d_{31}$  coefficients for the other composite

compositions are too low to appear in the graph (table 7.1). The m and n values obtained from the  $d_{31}$  of the 60% ceramic loading composite are 0.84 and 0.32 respectively, which are reasonably close to the values obtained from  $\varepsilon'$  and  $d_{33}$  measurements although slightly lower. The low values of  $d_{31}$  obtained for the other composites are thought to be due to the limitations in the experimental set up for these type of samples, as discussed in chapter 6.



Figure 7.4: d<sub>31</sub> contour chart for the PTCa/PEKK composites using the mixed connectivity model.

If we use the n and m values obtained previously, table 7.2 and 7.3, in the  $d_{31}$  chart, an estimate can be made of the expected value of  $d_{31}$  for the PTCa/PEKK composites

(figure 7.5). These calculated values, summarised in table 7.4, are comparable to the values obtained by other workers (Banno and Ogura 1992).

Table 7.4: d <sub>31</sub> coeffic	ient for the PTC	a/PEKK composites es	timated using the n	nixed connectivity
model.				
PTCa volume %	n	m	$\phi_{par}^{c}$	d <sub>31</sub> (pC/N)
30	0.25	0.66	0.03	-1.8
40	0.28	0.73	0.4	-2.2
50	0.31	0.79	0.6	-3
60	0.38	0.84	0.10	-4



*Figure 7.5*: Determined  $d_{31}$  values using the contour mixed connectivity chart for the PTCa/PEKK composites.

Figure 7.6 shows the m-n contour chart for the electromechanical coupling coefficient,  $k_t$  of PTCa/PEKK composites along with the experimental values given in table 7.1. The continuous lines represent constant values of  $k_t$ , obtained using equation 2.31. The values of n and m obtained are slightly lower than the values obtained from the permittivity and  $d_{33}$  coefficient leading to a lower  $\phi_{par}^{c}$  (table 7.5). This discrepancy in the  $k_t$  measurements is due to the fact that the electroactive ceramic powder embedded in the polymer possesses a distribution of grain sizes. This can lead to different resonance frequencies for the different grains and results in a broader and lower take this factor into account since the cube building blocks are all considered to have the same size which is equivalent to having ceramic grains of the same size distributed uniformly in the composite.



Figure 7.6: k<sub>t</sub> contour chart for the PTCa/PEKK composites using the mixed connectivity model.

Table 7.5: $n$ and $m$ parametercomposites derived from $k_t$ coef	rs of the mixed co ficient.	onnectivity cube mode	l for PTCa/PEKK
PTCa volume fraction (%)	n	m	φ <sub>par</sub> <sup>c</sup>
30		( <u>1777</u> )	
40	0.15	0.73	0.01
50	0.23	0.79	0.03
60	0.27	0.84	0.05

Figure 7.7 shows the m-n contour chart for the pyroelectric coefficient, p of PTCa/PEKK composites along with the experimental values given in table 7.1. The continuous line represent constant values of p, obtained from equation 3.48. Again, n and m values (table 7.6) are slightly lower than the values obtained from the permittivity and  $d_{33}$ . In this case, as discussed previously in chapter 6, the low experimental values of p are due to the fact that the samples are too thick to be used as pyroelectric sensors (Dias 1994b). In thick samples, it will be difficult to ensure that the whole of the sample thickness is changing temperature at the same rate. The exterior layers will heat up faster than the interior leading to lower values of p in thick samples. The model does not consider that a large temperature gradient can occur.

Table 7.6: n and m parametercomposites derived from p coeff	s of the mixed co icient.	onnectivity cube mode	el for PTCa/PEKK
PTCa volume fraction (%)	n	m	$\phi_{par}^{c}$
30	0.14	0.67	0.009
40	0.15	0.74	0.011
50	0.24	0.79	0.04
60	0.29	0.84	0.06



Figure 7.7: p contour chart for the PTCa/PEKK composites using the mixed connectivity model.

### 7.3 Conclusions

In this chapter the advantages and limitations of the mixed connectivity model have been discussed. It has been shown that the mixed connectivity model fits well with the experimentally determined values of permittivity,  $\varepsilon'$  and d<sub>33</sub> piezoelectric coefficients. The model is also able to predict electromechanical properties of the composite, such as d<sub>31</sub> when the experimental set up does not gives the desired results. However, the results have to be considered as dependent on the poling conditions. In addition, the model showed some limitations since it does not consider other factors so important in composites, such as the ceramic grain size distribution and the limitations arising from the fabrication of relative thick samples.

## References

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# Chapter 8:

# Application to acoustic emission detection

## 8.1 Introduction

The ultimate goal of this project was to detect real acoustic emission (AE) using PTCa/PEKK sensors and to evaluate the potential for detecting damage using these sensors embedded in carbon fibre reinforced composite (CFRC) structures. For this purpose, the sensors were evaluated using simulated AE sources in two different composite structures, namely, S-glass fibre reinforced board (GFRB) and carbon fibre reinforced composite (CFRC) both in surface mounted and embedded modes. The best PTCa/PEKK sensor was then used in a surface mounted mode for detecting AE generated by crack growth in composite adhesive films.

## 8.2 Characterising the sensors

Two different artificial sources were used to excite acoustic emission in the panels, the first consisted of dropping a ball bearing from a known height onto the board, typically producing relatively large amplitude stress waves (Yan et al 2001) (figure 8.1). The second consisted of breaking a pencil lead which produce relatively low amplitude but both high and low frequency stress waves (a Hsu-Nielson source (Hsu et al 1977)). The main characteristics of these wave modes were discussed in chapter 2. The pencil lead break tests were carried out with the help of a Nielson shoe to hold the lead (Pentel, 2H, 0.5 mm) of a pencil at the correct angle of  $45^0$  to the plate surface (figure 8.2).

The AE source energy,  $E_S$  released upon an elastic impact of a bouncing ball against a stationary surface can be calculated as the loss of potential energy of the ball (Yan T. et al 2001), i.e.

$$\mathbf{E}_{\mathrm{s}} = \mathrm{mg}(\mathbf{h}_{1} - \mathbf{h}_{2}) \tag{8.1}$$

where m is the mass of the bouncing ball, g the acceleration due to gravity,  $h_1$  the height from which the ball is dropped and  $h_2$  the rebound height.

The energy of a transient AE signal,  $E_{AE}$  can be calculated from

$$E_{AE} = k \int_{0}^{T} V(t)^{2} dt$$
 (8.2)

where V(t) is the time dependent voltage signal from the AE transducer system output, k is a proportional constant and T the whole event duration over which the integral is performed. This energy is directly proportional to the AE energy source,  $E_S$  (Clough 1987). Therefore, the energies of two different AE events from the same source,  $E_S^1$  and  $E_S^2$  can be related to the energies of the transient AE signals,  $E_{AE}^{-1}$  and  $E_{AE}^{-2}$ , using the expression

$$\frac{E_{\rm S}^1}{E_{\rm S}^2} = \frac{E_{\rm AE}^1}{E_{\rm AE}^2}.$$
(8.3)

Using the AE signals from a pencil lead break and a known energy ball bearing impact the AE energy released by a pencil lead break was calculated by means of equations (8.2) and (8.3).

A Gould digital storage oscilloscope (4050) was used to collect the signal data from the sensors without any amplification or filtering. The experimental data reported, both from ball bearing drops and lead breaks, is the average of at least 5 measurements. Error bars show the dispersion of the measurements from the average.



*Figure 8.1*: Sketch of ball bearing drop experiment showing the AE wave propagating through the structure and detected by the sensors in either surface mounted or embedded mode.



Figure 8.2: Representation of a Hsu-Nielson source

#### 8.3 Sensor manufacture

All the sensors were produced using an identical fabrication process. The piezoelectric materials, i.e. PTCa/PEKK composites, PZT ceramic and PP porous polymer, were bonded to 50  $\mu$ m thick polyimide substrates (DuPont<sup>TM</sup>) using toughened epoxy. The substrate surface had a 25  $\mu$ m thick electro-deposited copper layer, which was spatially etched to produce the desired electrode shape. Conductive silver paint was applied to link the top electrode of the piezoelectric material to the copper layer completing the circuit. A 50  $\Omega$  impedance coaxial cable was soldered between the two copper electrodes. Embedded sensors had an additional 50  $\mu$ m polymide film on top to electrically isolate and protect the sensor from the panel. The construction of the low profile sensor is shown in Figure 8.3.



Figure 8.3: Illustration of a low profile sensor in the FFRC or GFRB panel.

#### 8.4 Sensor incorporation into test panels

Three different panels were used for the characterisation of the sensors; a 56 cm  $\times$  56 cm GFRB panel consisting of 25 plies with a stacking sequence of (0)<sub>25</sub> and two CFRC orthotropic panels with 16 ply and lay up (0,90,0,90)<sub>2</sub>, with dimensions 30 cm  $\times$  30 cm and 50 cm  $\times$  35 cm respectively. The fibre volume fraction in all panels was approximately 60%.

In the case of the GFRB panels, PTCa/PEEK sensors with 60, 50, 40 and 30% PTCa volume fractions were surface mounted, using toughened epoxy, in a 10 cm square array at the centre of the panel to avoid signal reflections (Figure 8.4).



Figure 8.4: GFRB Panel containing surface mounted PTCa/PEKK sensors.

In the case of the 30 cm  $\times$  30 cm CFRC panel, sensors were both surface mounted and embedded. Four sensors were surface mounted using toughened epoxy in a 10 cm square array at the centre of the panel (figure 8.5 a). The four sensors were PTCa/PEKK composites with 60 and 50 % ceramic volume fraction, a PZT ceramic and a PP porous polymer. In addition, a PZT ceramic and two PTCa/PEKK composites with 50 and 60% PTCa loading were embedded underneath their identical surface mounted sensors. These sensors were embedded 4 plies below the top surface. In the case of the 50 cm  $\times$ 35 cm CFRC panel an array of 4 sensors was surface mounted forming a 30 cm  $\times$  30 cm square (figure 8.5 b).



Figure 8.5a: CFRC Panel containing surface mounted and embedded sensors.



Figure 8.5b: CFRC Panel containing surface mounted sensors.

#### 8.5 Simulated AE detection

The use of simulated AE sources is necessary in order to evaluate and optimise the output of the sensors before they are used to detect real AE generated from damage in a structure. For that purpose the sensors were tested in both surface mounted and embedded modes in different panels

#### 8.5.1 Surface mounted sensors in GFRB panel

First of all, the different PTCa/PEKK composite sensors were tested in surface mounted mode in a GFRB since it was found that the attenuation of AE waves was lower in GFRB panels than CFRC panels (Wenger 1997).

Figure 8.6 shows the response of a surface mounted PTCa/PEKK 60/40% volume fraction sensor to a pencil lead break test on the GFRB panel. It is seen that the
PTCa/PEKK 60/40% volume fraction composite detects both propagation modes of the plate wave. The faster small amplitude and high frequency extensional mode is clearly identified from the slower large amplitude and lower frequency flexural mode. None of the other composites examined were able of detecting the extensional mode.



*Figure 8.6*: Response of the surface mounted PTCa/PEKK 60/40% vol. composite to a pencil lead break in the GFRB panel.

The frequency spectrum of the signal was obtained by means of a fast Fourier transform (FFT), a Hamming window being used to reduce the effects of the beginning and the end of the signal. Figure 8.7 shows the signal from a PTCa/PEKK 60/40 % vol. fraction composite sensor in the frequency domain. The two wave modes are clearly observed at significantly different frequencies. The flexural modes are observed at approximately 5 kHz and 100 kHz and the extensional mode is observed at approximately 330kHz. These results are in agreement with previous work with similar composites (Wenger 2000). Note that if a different AE sensor is used, the detected frequency can be different for a particular mode (Martin et al 2001). This will depend on factors such as the

acoustic match of the sensor to the panel and the mechanical quality factor of the sensor. Since the quality factor of the composite sensor is low, they have a broad frequency bandwidth (Dias et al 1993) and this suggests that the frequency response obtained with these composite sensors is reliable.



Figure 8.7: Graph showing the FFT of the response of the PTCa/PEEK 60/40% vol. surface mounted sensor to a pencil lead break in the FRB panel.

Figure 8.8 shows the response of the surface mounted PTCa/PEKK 60/40 %vol. sensor to a ball bearing drop of 0.22 mJ energy on an FRB panel. In this case only the flexural modes were detected, because the direction of the impact is normal to the plane of the panel.

The FFT frequency spectrum of the signal in figure 8.8 is shown in Figure 8.9. Flexural modes were observed near 3 kHz and 12 kHz.



*Figure 8.8*: Response of the surface mounted PTCa/PEKK 60/40% vol. composite to a ball bearing drop of 0.22mJ onto FRB panel.



Figure 8.9 : Graph showing FFT of the response of the surface mounted PTCa/PEEK 60/40% vol. sensor to a ball bearing drop of 2 mJ onto FRB panel.

Figure 8.10 shows the response of the PTCa/PEKK composite sensors with 30, 40, 50 and 60 % ceramic loading surface mounted on the GFRB panel to increasingly energetic AE events. The lowest energy AE events were produced by pencil lead breaks whereas the rest of the AE events were produced by ball bearing drops at different heights. All the AE events were generated at the centre of the panel.



*Figure 8.10*: Graph showing the response of the PTCa/PEKK sensors to a number low energy AE events on a GFRB panel. The symbol  $\blacktriangle$  represents pencil lead breaks and the symbol  $\bullet$ , ball bearing drops.

It can be observed that the peak-to-peak response increases with increasing content of PTCa in the composite. This expected result is due to the increase of the piezoelectric coefficient,  $d_{33}$  and the electromechanical coupling coefficient,  $k_t$  with the ceramic loading (table 8.1).

All the sensors show a deviation from a linear behaviour. In calculating the energy of the AE sources, elastic collisions were assumed, but the high impact velocities involved

in the experiment will create energy dissipating inelastic impacts (Buttle et al 1990) and the value of the calculated AE energy will be higher than the real value.

<b>Fable 8.1</b> : Values of $d_{33}$ , $k_t$ , $Q_m$ and $z_0$ for PTCa/PEKK composites, PP porous polyme and PZT ceramic.					
Property	k	Q <sub>m</sub>	z <sub>o</sub> (Mrayls)	d <sub>33</sub> (pC/N)	
PZT (*)	0.64	75	33.7	618	
PTCa/PEKK 60/40vol%	0.2	8.4	9.4	34	
PTCa/PEKK 50/50vol%	0.17	7	8.2	30	
PTCa/PEKK 40/60vol%	0.1	9	6.8	25	
PTCa/PEKK 30/70vol%				22	
PP (**)	0.06	3	0.03	200	

(\*)Dias 1994b, (\*\*) Neugschwandtneret al 2001.

Pencil lead break experiments were performed on the GFRB panel at different distances from the sensor to observe the velocities of the extensional and flexural modes. Figure 8.11 shows the time response of a surface mounted PTCa/PEKK 60/40% volume fraction sensor to a pencil lead break at different distances. The results clearly show the increasing time delay between the slower flexural mode and the faster extensional modes. This agrees with the classical plate theory described in the chapter 4 (Graff (1975)).

Table 8.2 shows the predicted and experimental values of the wave modes in the 0° and 90° directions. The equations (4.12, 4.13, 4.35 and 4.36) used to estimate the velocities neglect the effects of rotational inertia and shear and this introduces an error in the calculated velocities (Tang et al 1987; Prosser 1991). In addition, experimental error arises in identifying the arrival time of the modes since the times involved in the measurements were very small and any variation induces large error. The first peak of each mode was used to measure the time-of-flight.

Note that the ability of the PTCa/PEKK sensors with 60% of ceramic loading to detect both wave modes can be used to locate AE sources by means of modal analysis, which uses the time delay between the modes (Dunegan 1997, Watson et al 2001).



*Figure 8.11*: *Response of the surface mounted PTCa/PEKK 60/40% sensors to a pencil lead break at different distances in the GFRB panel.* 

**Table 8.2**: Theoretical and experimental values of the velocity of the extensional and flexural modes in a

 GFRB panel

<b>r</b>						
Angle	Experimental velocity	Experimental velocity	Theoretical velocity of	Theoretical velocity		
	of the extensional	of the flexural mode	the extensional mode	of the flexural mode		
	mode (m/s)	(m/s)	(m/s)	(m/s) (f=5 kHz)		
0 <sup>o</sup>	4800	1540	4200*	1600*		
90°	2440	1360	2200*	1400*		

(\*) Wenger 1997

### 8.5.2 Surface mounted and embedded sensors in CFRC panels

Once all the composite sensors had been tested in the GFRB panel, which was used as a sensor quality benchmark, the best ones i.e., PTCa/PEKK composites with 50 and 60% of ceramic loading, were used in surface mounted and embedded mode in the CFRC panels. The composite sensors were compared in surface mounted mode to the PZT ceramic and the PP porous polymer sensors whose advantage and disadvantages were discussed in Chapter 1. Figure 8.12 shows the response of the PZT, porous PP and PTCa/PEKK composites with 50 and 60% ceramic volume fraction to a 0.45 mJ energy ball bearing impact on the 30x30 cm<sup>2</sup> CFRC panel (figure 8.5 a).



*Figure 8.12*: Graph showing the response of PZT ceramic, porous PP and composite sensors to a 0.45 mJ energy AE event on the CRFC panel.

The peak to peak response of the composite sensors is seen to be significantly smaller than the response of the PZT ceramic and the porous PP sensors. The ratio of the PZT, PP and PTCa/PEKK 60/40% sensors to the PTCa/PEKK 50/50% is 90:1, 10:1, 4:1 respectively. This result was expected since the piezoelectric coefficient,  $d_{33}$  and the electromechanical coefficient,  $k_t$  of the composite are smaller than those of PZT and porous PP (table 8.1).

Pencil lead breaks were performed on the panel and it was found that only the embedded PTCa/PEKK composite with 60% ceramic loading was able to clearly detect the two components of the plate wave, i.e., the extensional and flexural modes. The rest of the composite sensors only detected the flexural mode.

Figure 8.13 shows the response of the surface mounted and embedded PTCa/PEKK 60/40% vol. sensors to a pencil lead break performed at 5 cm from the sensors in the carbon fibre direction (0°). It was observed that the embedded PTCa/PEKK 60/40% composite was capable of clearly detecting the two modes of the plate waves. There was difficulty in detecting the extensional mode with the surface mounted sensor because of the nature of the coupling. This is due to the coupling of the extensional mode. The coupling of the surface mounted sensors relies on shear stress transfer effects rather than direct stress transfer which occurs with embedded sensors. This shows one of the advantages of using embedded sensors rather than the surface mounted sensor (Wenger 1997).



*Figure 8.13*: Response of the PTCa/PEKK 60/40% sensors to a pencil lead break on the CFRC panel.

FFTs were performed on the signals and the frequency of each mode was established. The lead break test shows two peaks occurring near 20 kHz (flexural mode) and 500 kHz (extensional mode) for the embedded sensor but only one peak for the surface mounted sensor (figure 8.14). These results are in agreement with the values obtained by other workers (Martin et al 2001).



Figure 8.14: Graph showing FFT of the response of the PTCa/PEEK 60/40% sensors to a pencil lead break on the CFRC panel.

In order to estimate the minimum energy detectable by the sensors in the embedded mode, the response of the transducers as a function of impact energy was obtained. Figure 8.15 shows the response of PTCa/PEKK 50/50% vol. and PTCa/PEKK 60/40% vol. sensors to increasing energy AE events. The lowest energy AE events were produced by pencil lead breaks whereas the rest of the AE events were produced by ball bearing drops at different heights. All the AE events were generated at the centre of the 30 cm  $\times$  30 cm CFRC panel.

In the present experiment the noise level was 0.25 mV and in general it is necessary to have a 2:1 signal: noise ratio to detect AE events from the development of cracks and other structure faults. Damage growth such as fibre/matrix debonding and delamination, have typical energies an order of magnitude lower than that of pencil lead breaks (Martin et al 1999). These results predict that the minimum loading of PTCa/PEKK required to detect typical AE events is 60% by volume since the peak-to-peak response of the PTCa/PEKK 50/50% volume fraction to a pencil lead break is 0.5mV. As a results sensors containing 60% ceramic volume fraction were manufactured for the trials carried out to detect real AE events.



Figure 8.15: Graph showing the response of the composite sensors to a number low energy AE events

The attenuation of the AE signal with distance was studied. In this experiment, ball bearing drops of 10 cm height were performed at different horizontal distances from the sensors in the 90° direction of the 30 cm  $\times$  30 cm CFRC panel (figure 8.5 a). Figure 8.16 shows how the PTCa/PEKK 50/50% and PTCa/PEKK 60/40% volume fraction sensor responses follow an exponential decay with distance. The composite with the higher ceramic loading detects at much greater distances. The attenuation coefficient was

calculated from the fitting giving a value of 9.1 m<sup>-1</sup>. This information can be used to decide the spacing between sensors in the design of smart CFRC structures.



Figure 8.16: Graph showing the response of the sensors to AE sources at different distances.

Lead break experiments were carried out at different orientations of the embedded PTCa/PEKK 60/40% vol. sensor for the 30 cm  $\times$  30 cm CRFC panel in order to study the propagation of the waves in an orthotropic plate (see figure 8.5 a). It was observed that in the fibre direction at 0° and 90° attenuation of the waves is less than in directions at other angles to the fibres i.e. +/- 45° (figure 8.17). This is due to the fact that the wave finds more matrix/fibre boundaries, with high acoustic mismatch, when travelling in the 45° direction than when it is travelling in the 0° and 90° directions. The wave transmission coefficient from a low acoustic impedance medium to a high impedance medium is low (Wood 1964) and therefore the attenuation in a epoxy/carbon fibre transmission is high. In addition, the visco-elastic effects in the epoxy matrix increase the attenuation in the panel (Corsaro et al 1990).



*Figure 8.17*: Graph showing the peak to peak response of the PTCa/PEKK 60/40 % vol. sensor to pencil lead breaks at different orientations on the CFRC panel.

The velocities of the extensional and flexural modes were measured and compared with the velocities predicted with the classical plate theory in the fibre directions. Pencil lead breaks were performed in the 30 cm  $\times$  30 cm CFRC panel and the embedded PTCa/PEKK 60/40% volume fraction composite was used to detect the AE signal. Lead breaks where performed at 0° and 90° angles at 7.5cm from the sensor. A commercial surface mounted sensor (WDI- Physical Acoustics ltd.) was placed close to the position of the lead break and the time-of-flight of the wave modes measured.

Table 8.3 summarises the theoretical and experimental results for both wave component velocities. Equations 4.12, 4.13, 4.35, and 4.36 were used to calculate the theoretical extensional and flexural velocities. Note that 20 kHz has been used as the frequency for the flexural wave (figure 8.14). Again discrepancies appear between the experimental

and theoretical values. These results suggests the need to measure the velocity of the waves in composites rather than predict them.

**Table 8.3**: Theoretical and experimental values of the velocity of the extensional and flexural modes in a

 CRFC panel

Angle I	Experimental velocity	Theoretical velocity of	Experimental velocity	Theoretical velocity
	of the extensional	the extensional mode	of the flexural mode	of the flexural mode
	mode (m/s)	(m/s)	(m/s)	(m/s) (f= 20 kHz)
0° and 90°	7140	8200	1150	805

Further pencil lead breaks were carried out on a CFRC panel of 50 cm  $\times$  35 cm (figure 8.5 b) in order to assess the ability of 60/40% PTCa/PEKK sensors to locate simulated AE sources (see figure 8.18). An algorithm based on a triangulation technique (Martin et al 1999) using the time-of-flight of the flexural wave was used to locate the AE sources. In a d  $\times$  d square array of 4 sensors (figure (8.18)) the relationship between the measured time-of-flight of the AE signal with three different sensors (t<sub>1</sub>, t<sub>2</sub> and t<sub>3</sub>) and the position of the AE source, (x, y) is given by the equations

$$y = \frac{d}{2} - \frac{d_1^2}{2d} + \frac{d_2^2}{2d}$$
(8.4)

$$x = \frac{d}{2} - \frac{d_3^2}{2d} + \frac{d_2^2}{2d}$$
(8.5)

where  $d_i=t_i\times c_f$ , been  $c_f$  the velocity of the flexural mode. Note that the fourth sensor can be used to measure the velocity but in this case the velocity was known beforehand (table 8.3).

The flexural mode was used to calculate the position of the AE source and therefore surface mounted sensors (which did not readily detect the extensional mode) would produce similar results to that of embedded sensors.



*Figure 8.18*: *d* × *d* square array of sensors used for the triangulation technique algorithm.

When the AE events occur centrally, the location of the event can be determined with a reasonable degree of accuracy +/- 1.5 cm. However, when the events occur off-centre significant errors occur in attempting to locate the event (figure 8.19). This is likely to be due to the dispersive nature of the flexural mode which introduces an error when the AE source is very close to one sensor but far from others.

There are many methods for calculating the location of AE sources from AE data and a full analysis of these techniques was beyond the scope of this project. Time-of-flight measurements are commonly used because of their simplicity but large errors are introduced in non-isotropic and real structures (Martin et al 1999).



Figure 8.19: Location of the origin of lead break signals on a CFRC panel using PTCa/PEKK 60/40% vol. sensors.

## 8.6 Real AE detection

In order to assess the ability of the composite sensors to detect real AE, a Double Cantilever Beam (DCB) test was performed. In the DCB experiment, see figure 8.20, delaminations are induced in a laminated CFRC beam by applying stresses in opposite directions at one end of the beam while the other end is free. The AE waves generated at the point of delamination are detected with a sensor located in the vicinity. The arrangement is shown in figure 8.21.



Figure 8.20: Diagram of the double cantilever beam experiment.



Figure 8.21: Picture of the double cantilever beam experimental arrangement.

In the present case a surface mounted PTCa/PEKK 60/40 %. composite sensor was used. The time response of the piezoelectric sensor to a DCB delamination is shown in figure 8.22. The wave components cannot be identified in the time domain response due to the proximity of the sensor to the AE source and Fourier frequency domain analysis was needed as shown in figure 8.23.



Figure 8.22: Response of the PTCa/PEKK 60/40% vol. sensor to a DCB delamination.

One sharp and clear peak is observed at 2kHz and secondary peaks are observed near 1kHz. The peak occurring at 2 kHz is likely to be due to the flexural mode whereas the secondary peaks are probably due to reflections at the surfaces. The extensional component of the wave is not observed because the composite sensors in surface mounted mode were not able to detect it (figure 8.13 and 8.14).



Figure 8.23: FFT of response of the PTCa/PEKK 60/40% vol. sensor to a delamination.

## 8.7 Conclusions

The Composite sensors were compared in a GFRB panel and the two best sensors, those with 50% and 60% volume fraction, were used for AE detection in CFRC panels. The composite sensors were shown to have less sensitivity than the low profile PZT ceramic sensor but the values of their mechanical quality factor and acoustic impedance were more suitable for AE detection in CFRC panels.

The embedded PTCa/PEKK 60/40% sensor was shown to be capable of detecting the two components of the plate waves in CFRC panels. This could potentially be used to locate AE sources by means of modal analysis. The attenuation of the AE waves in the CFRC panels was also studied and it was found that the better transmission occurs in

fibre directions. In addition, it has been shown that the surface mounted PTCa/PEKK composite sensors with 60% volume of ceramic loading can locate simulated AE with high accuracy using triangulation techniques. Finally, it has been shown that the sensors can detect real AE from fibre debonding in a CFRC beam.

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# Chapter 9: Conclusions

### 9.1 Conclusions

This thesis reports for the first time, the fabrication and characterisation of electromechanically active composites based on PTCa/PEKK.

In the work, novel flexible PTCa/PEKK composite films were fabricated using a hot pressing technique. During this stage of the fabrication process a vacuum was not used due to experimental limitations. The use of vacuum while pressing would help to remove air bubbles from the sample, although not much improvement is expected due to the high pressures involved. Another factor that would improve the sample quality would be to dissolve the PEKK polymer but the only solvent was found to be sulphuric acid, which was not used for safety reasons.

Aluminium electrodes were evaporated on both surfaces of the composite and samples were DC poled at high temperature. Different percentages of ceramic loadings were used for the composite fabrication with two different sets of PTCa powder. One set of PTCa was treated using titanate coupling agent whereas the other set was not treated.

It was observed by visual inspection that the quality of the chemically treated ceramic composites was much better than the non-treated ceramic composites since the sample surface significantly improved. In addition, the samples were less brittle. SEM images were obtained in order to study the microstructure of the composites and although it provided some indication of the amount of 1-3 connectivity present in the samples it did not supply any information about the ceramic/polymer interface quality.

Dielectric spectroscopy results showed that a relaxation peak occurring at low frequency in the non-treated ceramic composites was not present in the chemically treated ceramic composites. This relaxation peak was thought to arise from ceramic/polymer interfaces because its removal coincided with a reduction in air voids or moisture present in the interface owing to the treatment of the ceramic. However, some space charge might still be present due to other factors, such as impurities and oxidation. In addition, dielectric spectroscopy showed that the relative permittivity of the composites was frequency dependant and hence the piezoelectric and pyroelectric figures of merit, which are inversely proportional to the permittivity.

The measurement of the piezoelectric and pyroelectric coefficients revealed a superlinear dependence of the coefficients on the ceramic loading. This has been attributed to an increase in the 1-3 connectivity in the highly loaded composites. The  $d_{33}$  values obtained were comparable to other similar composites, but they are lower than for the ceramic alone. The values are also smaller than porous polypropylene but comparable with that for the electroactive polymer PVDF. The calculation of the elastic compliance showed that composites are much more flexible than the ceramic alone.

From the pyroelectric measurements it was found that although the p coefficient was comparable to that of other similar composites, it was very low in comparison with the ceramic p coefficient. This is believed to be due to the dielectric mismatch of the permittivities of the constituent phases and to the use of relatively thick samples.

Measurements of the electromechanical coupling coefficient,  $k_t$ , provided values for the mechanical loss,  $\psi$ , and the acoustic impedance,  $z_0$ , for the different composite sensors. The  $k_t$  values of the composites were less than half of the value of the ceramic. However, the value of  $\psi$  was higher in the composites than in the ceramic, thus providing a broader frequency bandwidth for the composites. In addition, the acoustic impedance of the composites was found to be closer to CFRC than the ceramic.

The mixed connectivity model was applied to the measured coefficients of the composites and the advantages and limitations of the model have been discussed. It was shown that the mixed connectivity model fits well with the experimentally determined values of permittivity,  $\varepsilon$ ' and piezoelectric coefficient, d<sub>33</sub>. The model was also able to predict the electromechanical properties of the composite, such as d<sub>31</sub>, when the

experimental set up does not gives the desired results. However, the obtained percentages of 1-3 connectivity were found to be dependent on the poling conditions. In addition, the model showed some limitations since it does not consider other important factors in composites such as the ceramic grain size distribution and the limitations arising from the fabrication of relatively thick samples.

The composite sensors were compared in different panels for their ability to detect AE in both surface mounted and embedded modes. The composite sensors were shown to have less sensitivity than the low profile PZT ceramic and porous PP polymer sensors, but they were found to have more suitable mechanical and thermal properties than the ceramic and polymer respectively for embedding in CFRC panels.

The embedded PTCa/PEKK 60/40% sensor was shown to be capable of detecting the two components of the plate waves in CFRC panels. This could potentially be used to locate AE sources by means of modal analysis. The attenuation of the AE waves in the CFRC panels was also studied and it was found that better transmission occurs in the fibre directions. In addition, it was shown that the surface mounted PTCa/PEKK composites with 60% volume of ceramic loading can locate simulated AE with high accuracy using triangulation techniques. Finally, it was shown that the sensors can detect real AE from fibre debonding in a CFRC beam. As far as the author is aware, it is the first time that composite sensors based on PTCa/PEKK have been used for AE detection.

### 9.2 Future work

In the final stages of the project it was found that the use of silicone oil when mixing the constituent phases resulted in better quality of samples. In addition, this helped to obtain thinner samples and eased the production of the composites. The piezoelectric properties of the composites prepared with silicone oil were comparable to the piezoelectric properties of the normal composites. Furthermore it was found that the response of this sensor to AE signals was significantly increased probably due to the improved mechanical quality of the samples.

Further work needs to be done to evaluate completely the electroactive and mechanical properties of the composites prepared with the use of silicone oil. The new system is not biphasic but triphasic and the structure of the new samples needs to be studied, in particular, the interfaces and the effects of the silicone oil on the PEKK polymer. Also, the amount of silicone oil remaining in the composite after pressing needs to be quantified.

In addition, this improvement could help in the fabrication of composites with higher ceramic loadings which will give significantly larger piezoelectric coefficient since its dependence on the ceramic volume fraction is super-linear. With the new fabrication method, ceramic loadings up to 70% can be expected. Other improvements could include the use of a solvent for the PEKK and the use of vacuum during the hot pressing stage.

Additional work can be done with the existing samples. For example, this could include mechanical measurements which can be compared with the calculated elastic compliance coefficient calculated. Also, bimorphs can be constructed for AE detection which have higher sensitivity since they enhance the detected signal. The sensors could be used to diagnose damage at different levels, namely, damage detection, damage location, damage classification and damage sizing. Finally, the composite sensors could be used as actuators driving signals to excite CFRC panels for location of defects in the structure using echo techniques.

## Papers published during the course of this work

Sakamoto W. K, Marin-Franch P. and Das-Gupta D. K., 'Characterisation and applications of PZT/PU and graphite doped PTZ/PU composite', Sensors and Actuators A, V 100 (2-3): 165-174, 2002.

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## Characterization and application of PZT/PU and graphite doped PZT/PU composite

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Received 23 July 2001; received in revised form 28 December 2001; accepted 10 January 2002

#### bstract

Composites, made of lead zirconate titanate (PZT) ceramic powder and castor oil-based polyurethane (PU), were prepared in the film form. The ilms were obtained in the thickness range 100–300 µm using up to 50/50 vol.% of ceramic. Another composite (PZT/C/PU) was obtained by dding a small amount (1.0 vol.%) of graphite (C) to the PZT/PU composite. By increasing the conductivity of PU-containing graphite, obtained of PZT could be carried out with better efficiency. A comparison of piezo- and pyroelectric activities and spatial distribution of bolarization between graphite doped and undoped composites reveal the advantages of using semiconductor filler. These composites were used as ensors to detect acoustic emission (AE). The detection was made using two simulated sources of AE, i.e., ball bearing drop and pencil lead break. ZT/C/PU composite was able to detect both flexural and extensional components of wave vibration.

Keywords: Piezoelectric composite; Acoustic emission sensors; Polarization distribution; Dielectric spectroscopy; Thermally stimulated current

#### . Introduction

Ferroelectric ceramic/polymer composites have been widely used as piezoelectric sensor [1--6] because they can combine the mechanical strength and flexibility of polymer with the high piezo- and pyroelectric activities of ceramic.

Although ceramic/polymer composites are a well-estabished alternative to a conventional ferroelectric material, he design of a composite with optimum properties is still a challenge. One difficulty with the ceramic/polymer composite is in achieving efficient polarization of ceramic dipoles. For a composite with 0–3 connectivity the electric field  $E_c$ acting on spherical grain is given by [7]

$$E_{\rm c} = \frac{3\varepsilon^{\rm p}}{\varepsilon^{\rm c} + 3\varepsilon^{\rm p}} E_0 \tag{1}$$

where  $\varepsilon^{c}$  and  $\varepsilon^{p}$  are the dielectric constant of ceramic and polymer, respectively,  $E_{0}$  is the external applied electric field. Because the dielectric constant of ceramic is, generally, much higher than that of the polymer, a large part of the

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applied voltage is wasted across the polymer phase (the analog electrical circuit is two resistances in series for the composite). By introducing a small amount of semiconductor filler a resistance is created in parallel with that of polymer, thus reducing the resistance of the polymer phase and the poling of the composite becomes easier because more voltage will now be available to polarize the ceramic phase. The importance of the reduction of the resistance is explained by Maxwell–Wagner interfacial mechanism [8].

The present paper reports the results of the dielectric and electrical characterization of PZT/PU composite with 50/50 vol.% composition and PZT/C/PU composite with 49/1/50 vol.%. The effect of semiconductor phase on the poling conditions, dielectric loss and piezo- and pyroelectric activities and the spatial distribution of polarization of the composite are discussed. Furthermore, some results of acoustic emission (AE) detection are presented to show that the later composite may be used as a sensor to detect structural damages in a non-destructive manner.

#### 2. Experimental

#### 2.1. Sample preparation

Commercial PZT (American Piezo Ceramic-APC) powder with grains ranged in diameter from 3 to 10 µm and

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fine-grained graphite were used as ferroelectric ceramic and semiconductor fillers, respectively. A vegetable-based ester, obtained from a native plant in Brazil, was used to produce the polyurethane (PU) by mixing the ester with di-isocyanate (MDI).

To prepare the composites without semiconductor phase, the PZT powder was mixed with PU by hand with spatula and pressed at room temperature at 20 MPa. The composites with graphite were made in the similar way by mixing ceramic grains and semiconductor filler first. Aluminum electrodes with 1 cm of diameter were vacuum evaporated onto both sides of the sample. The PZT/PU composites in the thickness range 100–200  $\mu$ m, were poled at 373 K at a DC field of 10<sup>7</sup> V/m in silicone oil bath on a temperature-controlled plate for 1 h. The PZT/C/PU composites, in the thickness range 200–300  $\mu$ m, were poled at 5 × 10<sup>6</sup> V/m DC field for 30 min at 373 K in silicone oil bath.

#### 2.2. Measurements

The dielectric data were taken in the wide range of frequency from  $10^{-5}$  to  $10^5$  Hz using time domain and bridge techniques. The pyroelectric currents were measured using a direct method [9]. In this method of measuring pyroelectric coefficient, a pre-poled sample is heated at a constant rate with its electrodes shorted and the short circuit current is monitored with an electrometer. The first run provides irreversible current due to the space charge injected during the poling process. This current is subsequently reduced by subsequent TSDC. When no appreciable reduction is observed the reversible and repeatable pyroelectric current is established.

The spatial distribution of polarization in the composite was measured using the laser-intensity-modulation method (LIMM) [10]. The composite film was mounted in an evacuated chamber with optical window. Each electrode of two surfaces of the sample, in turn, was exposed to a He-Ne beam ( $\lambda = 0.633$  mm, 1.0 mW), which was intensity-modulated by an electromechanical chopper. The heat of a laser beam was absorbed by sample. The sinusoidal modulation of the laser beam causes a sinusoidal fluctuation in temperature of the front electrode and these results in the propagation of temperature waves into the sample. The interaction of the fluctuating temperature and the spatially distributed polarization produces a complex sinusoidal pyroelectric current [11].

The real and imaginary parts of this current were measured with a lock-in amplifier (Model EG&G 5206) whose reference phase is provided by the same frequency generator that drives the electro-mechanical chopper. The frequency modulation was varied from 20 to 3 kHz. The temperature fluctuations penetrate successively to shallower depths, as the frequency of the modulation is increased [10].

AE tests were carried out by using simulated AE sources, i.e., ball bearing drop and pencil lead break. Two different composites of PZT/PU (33/67 vol.%, 50/50 vol.%) and PZT/C/PU 49/1/50 vol.% were used for comparison in simulated AE detection. For the production of the sensors the samples were bonded to 50  $\mu$ m polyamide substrate (Du Pont) using toughened epoxy. The substrate contained a 25  $\mu$ m thick electro-deposited copper layer, which was spatially etched to produce the desired electrode shape. A conductive paint was applied to the top surface of the sensors to complete the electrical circuit. For the characterization of the piezoelectric transducer, the sensors were surface mounted on a 56 cm  $\times$  56 cm fiberglass reinforced board (FRB). The location of the sensors on the panel surface is shown in Fig. 1.



Fig. 1. FRB containing the surface mounted sensors.

#### . Results and discussion

The complex permittivity of both (PZT/PU 50/50 vol.% nd PZT/C/PU 49/1/50 vol.%) composites were measured a the frequency range  $10^{-5}$ – $10^{5}$  Hz. The low-frequency ata of dielectric loss ( $\epsilon''$ ) were calculated from the transient ischarge current measurement with subsequent Hamon 12] approximation. In the medium and high frequency anges a lock-in amplifier and a general radio bridge were used to obtain experimentally both dielectric loss and pernittivity ( $\epsilon'$ ).

The dielectric loss data were combined for the entire requency range using the "Universal" relaxation law [13]. The low-frequency permittivity was calculated using the Gramers-Kronig relation [14], which is

$$\ell'(\omega) = \varepsilon_0 + \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\varepsilon''(\omega)}{x - \omega} \, \mathrm{d}x \tag{2}$$

Fig. 2 shows the behavior of the complex permittivity ( $\epsilon$ ). It ian be seen that the presence of a semiconductor phase in the composite increases the dielectric loss mainly in the requency range  $10^{-1}-10^5$  Hz. The enhancement in the lielectric loss is, of course, related with the increase of the electrical conductivity of the composite. The peak in the medium frequency range  $(10^{-1}-100 \text{ Hz})$  may be attributed to impurities in the polymer matrix. This peak was observed in PU [15] and also in LDPE [14]. The quasi-DC contribution arising from ionic space charge at low frequency (< $10^{-1}$  Hz) is not significantly different in the two amples.

Fig. 3 shows the nature of the reversible pyroelectric current in the temperature range 300–353 K. A pre-poled cample was placed in a temperature-controlled chamber at a

$$p(T) = \frac{1}{A} \frac{I_{\rm p}}{dT/dt}$$
(3)

where A is the electrode area,  $I_p$  the pyroelectric current and dT/dt the heating rate.

The values of p(T) were found to be 5.6  $\mu$ C/m<sup>2</sup> K for PZT/ PU and 10.7  $\mu$ C/m<sup>2</sup> K for PZT/C/PU samples at 303 K. Despite an increase in the dielectric loss, the pyroelectric activity is almost twice for the composite-containing graphite at this temperature in spite of the lower poling electric field and time.

The  $d_{33}$  piezoelectric coefficient were measured using a  $d_{33}$  Piezo-Tester (APC) and Fig. 4 shows the variation of the piezo activity as a function of the carbon contents in the composite. The samples were poled with  $5 \times 10^6$  V/m electric field at 100 °C for 30 min. By adding 1.0 vol.% of carbon to PZT/PU composite the  $d_{33}$  coefficient was increased 25% in comparison with the composite without carbon phase. The values are the average of four measurements took during a week.

For PZT/PU (without carbon) composite poled with  $10^7$  V/m electric field at 100 °C for 1.0 h, the  $d_{33}$  was found near 13 pC/N. These results suggest that with the inclusion of a semiconductor filler, in small amount (1.0 vol.%) in the composite the poling can be carried out easier and



Fig. 2. Complex permittivity of PZT/PU 50/50 vol.% and PZT/C/PU 49/1/50 vol.% composites, fitted by using "Universal" relaxation law and Kramers-Kronig relation.

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Fig. 3. Pyroelectric current obtained by direct method. The composites were poled at 100 °C for 1 h. PZT/C/PU at 5 × 10<sup>6</sup> V/m and PZT/PU at 10<sup>7</sup> V/m.

consequently the piezo- and pyroelectric activities are increased. It might be because the carbon particle could create a continuous electric flux path between PZT grains. When the amount of carbon in the composite exceeds 1.0 vol.% the piezo activity is reduced, possibly because the electrical conductivity has increased so much. Similar results were obtained by Sa-Gong et al. [7], using PZT composite with epoxy-based polymer as matrix.

In order to verify the validity of the results obtained, some fittings with existing models were carried out. The model proposed by Yamada et al. [16] can be used to determine the dielectric and piezoelectric properties of the composite. This model considers the composite as a binary system consisting of ellipsoidal ceramic particles dispersed on the continuous medium. The dielectric constant of the composite is given by [16]:

$$\varepsilon = \varepsilon^{p} \left[ 1 + \frac{\eta \phi^{c} (\varepsilon^{c} - \varepsilon^{p})}{\eta \varepsilon^{p} + (\varepsilon^{c} - \varepsilon^{p})(1 - \phi^{c})} \right]$$
(4)

where  $\varepsilon^{c}$  and  $\varepsilon^{p}$  are the values of dielectric constant of the ceramic and the polymer respectively,  $\phi^{c}$  the volume fraction of the ceramic in the composite and  $\eta$  a parameter dependent on the shape of the particles and their orientation in relation to the composite film [16].

In Fig. 5 the experimental values of dielectric constant of 33/67 and 50/50 vol.% PZT/PU composites have been fitted with Yamada's model [16] using different shape factors. A shape factor of  $\eta = 8.5$  was found to be the best-fit. This value agrees with results for other composites containing similar ceramic particles, i.e., PTCa [16,17].



Fig. 4. Variation of the piezoelectric coefficient  $d_{33}$  with the carbon contents in the composite film.



Fig. 5. Theoretical plot of the permittivity for three values of the Yamada shape factor in a PZT/PU composite together with the experimental data for this composite.

(9)

Considering that some degree of 1-3 connectivity can be found in a highly loaded ceramic composite, the mixed connectivity model [17] has also been used. This model was proposed to overcome the difficulty arising from Banno's modified cube model [18]. In Banno's model when the height of the self-connected ceramic particle approaches that of the sample thickness the electroactive properties change abruptly, which makes a difficulty to calculate the 1-3 connectivity percentage. Mixed connectivity model considers that both parallel and series connectivity exist in the composite, giving a tri-phasic system. In the mixed connectivity model [17] the properties depend on two parameters n and m, which are related to the connectivity of the composite. The expression for the dielectric constant given by this model, applies to this particular case and is

$$\epsilon = \phi_{\text{par}}^{\text{c}} \epsilon^{\text{c}} + (1 - \phi_{\text{par}}^{\text{c}}) \epsilon^{\text{p}} + \phi_{\text{ser}} \epsilon_{\text{ser}}$$
(5)

and

$$\frac{1}{\varepsilon_{eer}} = \frac{\phi^{c}}{\varepsilon^{c}} + \frac{1 - \phi^{c}}{\varepsilon^{p}}$$
(6)

$$\phi_{\rm ser} = m^2 (1 - n^2) \tag{7}$$

$$\phi_{\rm par} = m^2 n^2 \tag{8}$$

$$\phi^{c} = m$$

where the subscript "par" and "ser" means parallel and series, respectively.

In this model the composite properties are represented in contour charts as a function of the constituent phases properties and the connectivity parameters n and m [17]. These connectivity parameters provide the percentage of 1– 3 connectivity in the composite. This model can also predict the electroactive properties of the composite, thus indicating in advance the expected efficiency of the transducer. Fig. 6 shows a contour chart for the permittivity of PZT/PU composites using the mixed connectivity model. The constant volume fraction curves have also been included. Each measured point is located in the intersection of the known value of volume fraction of the composite and the corresponding value of the permittivity. The *n* and *m* values can be found and the percentage of 1–3 connectivity can be calculated using Eq. (8). The experimental data for the 50/50 vol.% of ceramic composite show an *n* value of 0.14, which result in a 2% of 1–3 connectivity. This result suggests that the composite sample is predominantly of 0–3 connectivity which may explain the low value of  $d_{33}$  in comparison with other 50/50 vol.% composite [19].

A determination of the electromechanical coupling coefficient  $(k_t)$  was obtained from the measurement of the complex impedance around the resonant peak of the composite material acting as a free resonator. A network analyzer, Model HP8702A, was used to measure the real part of the complex impedance of the PZT:PU 50:50% composite around its resonant peak. The experimentally determined impedance can be fitted using the theoretical equation of optimization of some parameter [17]. The optimized  $k_t$  value is given by the expression

$$k_t^2 = \frac{1}{2}\pi^2 R_{\max} f_0 C_0 (\psi^2 + 4)^{1/2} \tanh\left(\frac{\pi\psi}{4}\right) \tag{10}$$

where  $C_0$  is the sample capacitance,  $\psi$  the mechanical loss,  $f_0$  the resonance frequency and  $R_{\text{max}}$  the amount of increase of the real part of the impedance in the resonance frequency from the base line. The fit of the real part of the complex impedance around the resonance peak provides a value of  $\psi = 0.13$ ,  $f_0 = 6$  MHz and  $R_{\text{max}} = 3$ , being  $C_0 = 106$  pF. These values used in Eq. (10) result in  $k_t = 0.04$  (see Fig. 7).



Fig. 6. Permittivity contour chart for the PZT/PU composite using the mixed connectivity model.

This low value of  $k_t$  may be due to the small PZT grain size used in this composite [20].

The film may contain a combination of polarization and space charge. One method of solution for the unknown polarization distribution is to represent the polarization as truncated polynomial series, as Fourier cosine series:

$$P(y) = \sum_{m=0}^{M} P_m \cos\left(\frac{m\pi y}{L}\right) \tag{11}$$

where the series is truncated after the Mth term. The complex pyroelectric current can be written [21], considering that the composite film containing no space charge,

$$P(y) = \sum_{m=0}^{M} P_m \frac{2D^2 + j(m\pi/L)^2}{(m\pi/L)^4 + 4D^4}$$
(12)



with  $B_P = Aq_0\eta[(\alpha_P + \alpha_x - \alpha_s)/2kL]$ , where  $q_0$  is the beam intensity, A the electrode area, k the thermal diffusivity,  $\eta$  the

Fig. 7. Experimental and theoretical real impedance of PZT/PU 50/50 vol.% composite around resonant peak, k<sub>1</sub> = 0.04.



Fig. 8. Spatially distributed polarization through the composite film obtained by LIMM measurement.

bsorptivity of the electrode,  $\alpha_{P}$ ,  $\alpha_{x}$  and  $\alpha_{e}$  are the relative emperature dependence of the polarization, thermal expanion and permittivity, respectively, and  $D = (\omega/2k)^{1/2}$ , where  $\omega$  is the angular frequency. This equation becomes exact solution for the current as M approaches infinity. Eq. (12) is the basis for the determination of the polarization listribution as a function of frequency. A mathematical leconvolution technique is used for transformation of the current-frequency distribution data to polarization distribuion [22].

Fig. 8 shows the nature of spatial distribution of polarization P (C/m<sup>2</sup>) for the undoped and carbon–graphite doped composite samples. The fundamental LIMM equations are 21]:

$$\frac{L}{0} = 1 + C_1 \int_0^1 P(y) \left[ \frac{v \cosh v y}{\sinh v} \right] dy + C_2 \int_0^1 \rho(y) \left[ \frac{\sinh v y}{\sinh v} - y \right] dy$$
(13)

$$\frac{c}{c_0} = 1 + C_1 \int_0^1 P(y) \left[ \frac{v \cosh[v(1-y)]}{\sinh v} \right] dy - C_2 \int_0^1 \rho(y) \left[ \frac{\sinh[v(1-y)]}{\sinh v} - (1-y) \right] dy$$
(14)

where 
$$v = [\omega/2k]^{1/2}L(1+j)$$
,

$$C_1 = \frac{\alpha_P + \alpha_x + \alpha_\varepsilon}{p}$$

ind

$$C_2 = \frac{\alpha_x - \alpha_\varepsilon}{p} L$$

 $_0$  is the current at zero frequency. L is the sample thickness,  $_L$  is the pyroelectric current when laser beam is incident on

the sample face x = L,  $I_z$  is the current when the laser beam is on the face x = 0, p is the pyroelectric coefficient. The values of  $\alpha_P$ ,  $\alpha_x$ ,  $\alpha_e$  and k are:  $8.08 \times 10^{-4}$ ,  $1.4 \times 10^{-4}$ ,  $6.76 \times 10^{-3}$  K<sup>-1</sup> and  $9.9 \times 10^{-7}$  m<sup>2</sup> s<sup>-1</sup> [23], respectively. The samples were poled in the same conditions as described above, i.e.,  $E = 10^7$  V/m for PZT/PU and  $E = 5 \times 10^6$  V/m for PZT/C/PU. The polarization is very uniform through the sample and the presence of graphite phase allows a more efficient poling of the samples than that for samples without graphite.

In order to characterize the surface mounted composites as AE detectors, the FRB panel was excited using two different simulated AE sources, i.e., ball bearing drop, typically producing relatively large amplitude and low frequency stress waves and pencil lead breaks (Hsu-Nielson source), producing relatively low amplitude with higher frequency stress waves. A digital storage oscilloscope (Gould Model 4050) was used to collect the data from the sensors. No pre-amplification or filtering of signals was applied to the signals.

To predict the minimum energy detectable by the sensor, the signal/noise response of the transducer, as a function of impact energy, was plotted. Fig. 9 shows the response of the three sensors to increasing energy impacts. In general a signal/noise of 2/1 is required to allow suitable amplification of the output signal, and this was set as a cut-off point for AE detection. Taking a noise level of 2 mV, from Fig. 9, by extrapolation it can be predicted that the cut-off energy for 33/67 vol.%, 50/50 vol.% PZT/PU and 49/1/50 vol.% PZT/C/PU composites were 0.02, 0.004 and 0.003 mJ, respectively. As expected, with increasing content of PZT in the composite the peak to peak response increases significantly. Additionally, it can be pointed out that the composite doped with graphite is a better sensor as it can detect lower energy AE events than with the undoped sensor. W.K. Sakamoto et al. / Sensors and Actuators A 100 (2002) 165-174



Fig. 9. Response of the sensors to simulated AE tests for different energies.

The energy of the pencil lead break was estimated by comparing it with the energy of AE events recorded for a 2 mJ impact. For reference, a mean value of 0.03 mJ was defined as an estimated energy of a pencil lead break. The variability in pencil break energy was calculated to be 0.01 mJ for the tests carried out.

The sensors were also compared for their ability to detect AE at different distances. Ball bearing drops from fixed height (5 cm) were used. Fig. 10 shows that the sensor responses follow an inverse law with distance. Again it can be noticed that the composite containing 1 vol.% of graphite gives a better response. By extrapolation it can be seen that the maximum distance in which the 0.25 mJ ball bearing impact can be detected is 132, 615 and 821 cm for the 33/67, 50/50 vol.% PZT/PU composition and 49/1/ 50 vol.% PZT/C/PU composites, respectively.

The pencil lead break experiment is a well-established technique that can show the ability of the sensor to detect the components of a plate wave. Fig. 11 shows the time response of the PZT/C/PU sensor to a lead break test. The extensional and flexural modes can be clearly observed.

Fast Fourier transform (FFT) of the data of Fig. 11, in Fig. 12, shows evidence of a peak occurring at 5 kHz due to the flexural mode, and two peaks due to the extensional mode at 25 Hz being the fundamental mode and at 75 Hz, being the third harmonic. As expected for symmetrical plate wave, only odd harmonics appear [24]. Wenger using 60/40 vol.% PTCa/epoxy composite reported similar result for the flexural mode range but for the extensional mode he reported just one peak at about 300 Hz [24]. It could be due to quite different property of the polymer matrix used that may provide different mechanical matching with the FRB panel.



Fig. 10. Response of the sensors at different distances from AE sources.



Fig. 11. Response of the PZT/C/PU 49/1/50 vol.% composition to a lead break test.



Fig. 12. FFT of the response of the PZT/C/PU composite to a lead break test.

#### 4. Conclusion

Adding 1.0 vol.% of graphite the PZT/C/PU sample shows high polarization than that for samples without semiconductor phase, indicating that the poling process becomes more effective. This result can explain the higher pyroelectric coefficient for PZT/C/PU composite in comparison with that for PZT/PU as shown in Fig. 3. This composite has ability to detect both extensional and flexural modes of AE and can detect a signal at a distance of 8 m from the source, thus indicating that it may be use for damage detection in structures in a non-destructive manner.

The increases in the dielectric loss and the possibility of an electrical breakdown at lower electric field for carbon doped composite could be a disadvantage. Further studies related with this problem are in progress.

#### Acknowledgements

The authors express their gratitude to Dr. Gilberto O. Chierice for providing the PU polymer. One of the authors (WKS) gratefully acknowledges the financial support from Fundacao de Amparo a Pesquisa do Estado de Sao Paulo— FAPESP, Brazil for the pos-doctoral fellowship. Another author (PMF) expresses his gratitude to BAE Systems for the maintenance. The authors express their gratitude to Dr. D. Tunnicliffe of BAE Systems for valuable discussion.

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## PTCa/PEKK piezo-composites for acoustic emission detection

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Received 8 August 2001; received in revised form 30 November 2001; accepted 1 December 2001

#### Abstract

Piezoelectric ceramic/polymer composites with mixed connectivity combine the high values of piezoelectric coefficients of the ferroelectric ceramics and the formability and flexibility of the polymer, making them suitable for in situ acoustic emission (AE) sensors. The present paper reports a study of the piezoelectric and dielectric properties of the ceramic/polymer composite films composed of the calcium modified lead titanate (PTCa) ceramic and the thermoplastic polymer, polyetherketoneketone (PEKK). The mixed connectivity model is used to calculate the percentage of 1–3 connectivity in each composite. Additionally, the sensors were embedded in a carbon fibre reinforced composite (CFRC) and were able to detect simulated AE. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Sensors; Piezoelectric composites; Piezoelectric coefficients; Mixed connectivity model; Acoustic emission

#### 1. Introduction

Health and usage monitoring system (HUMS) is one of the areas of ongoing research in aerospace structure applications. In order to monitor damage in structures some methods are needed. There are several potential methods for HUMS; however, acoustic emission (AE) is one of the key inspection techniques with the potential to both detect and locate damage sites continuously in a non-destructive manner. An AE transducer senses the dynamic stress waves propagating through a structure, which have been generated by the release of energy as a result of a failure mechanism.

The use of piezoelectric ceramics as low profile sensors for detecting AE has been made. Low profile sensors are that due to their size, can be either surface mounted flush with the structure or even embedded within it. This can potentially improve their response and resistance to environmental effects. However, the potential applications of piezoelectric ceramics as embedded sensors for structural damage detection are restricted due to their relatively high stiffness and low toughness. In order to overcome this problem the use has been made in recent years of ceramic/polymer thin film composite sensors, which combine the high piezoelectric properties of ferroelectric ceramics and the viscoelastic properties of polymers. In this work, calcium modified lead

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titanate/polyetherketoneketone) (PTCa/PEKK) ceramic/ polymer composite sensors have been fabricated, characterised and embedded in a carbon fibre reinforced composites (CFRC) and tested for simulated AE detection.

PTCa (supplied by GEC-Marconi Materials Research Laboratory at Caswell, UK) is obtained from the perovskite ceramic PT by doping with  $Ca^{2+}$ . The composition of the PTCa used in this work is (Pb<sub>0.76</sub> Ca<sub>0.24</sub>)[(Co<sub>0.5</sub> W<sub>0.5</sub>)<sub>0.05</sub> Ti<sub>0.95</sub>]O<sub>3</sub> [1].

The doping of PT with calcium by substituting 24% of the lead atoms with Ca<sup>2+</sup> atoms on the A sites, reduces the tetragonality of the crystal structure of the ceramic, which results in an enhancement of the electromechanical anisotropy, thus decoupling  $d_{31}$  and  $d_{33}$  coefficients (note: the first suffix denotes the direction of the measured electrical signal and the second suffix is the direction of the applied stress). The electromechanical anisotropy of PTCa ceramic leads to a high value of  $d_{\rm h}$  coefficient. This doping process also lowers the permittivity (from 230 to 200) and the Curie temperature of the ceramic (from 490 to 260 °C) [2], which makes PTCa a material easier to pole than PT or PZT at a reduced temperature which is suitable for the polymer matrix in ceramic/polymer composite. PTCa is also a material that does not tend to fracture when cooled through its Curie temperature. Additionally, the low permittivity of this ceramic, with respect to PZT, gives PTCa high values of piezoelectric g coefficients. These two properties provide a high piezoelectric figure of merit (FOM) which makes PTCa a good material for ceramic/polymer composite transducers.

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PEKK, supplied by Du Pont laboratories, has excellent chemical resistance (viz. 1,1,1-trichloroethane, Skydrol B4, MEK jet fuel and toluene), low moisture absorption, low flammability and high temperature stability ( $T_g = 154$  °C and  $T_m = 304$  °C) combined with good processability. As PEKK has a melting point of 304 °C, it makes PTCa/PEKK a high temperature sensor, which also enables PTCa/PEKK suitable for embedding in CFRC panels which require a curing temperature of 130 °C. The above reasons make PTCa/PEKK composite sensor quite attractive for aerospace applications. In particular, these sensors can be embedded in aircraft wings to detect structural damages.

In this paper, the fabrication method of PTCa/PEKK composites with different volume fraction, i.e. 30, 40, 50 and 60% is reported. Furthermore, the results of the determination of dielectric constant ( $\varepsilon$ ), piezoelectric coefficients ( $d_{31}$ ,  $d_{33}$ ) and the electromechanical coupling coefficient ( $k_i$ ) are given. Additionally, the mixed connectivity model [3] is used in order to evaluate the percentage of 1–3 connectivity. Finally, the result of simulated AE detection tests are reported in order to evaluate the ability of the sensors to detect AE.

#### 2. PTCa/PEKK composite fabrication

Before mixing the ceramic with the polymer, the PTCa ceramic grains (with 10  $\mu$ m size) were chemically treated with a titanate coupling agent supplied by Kenrich Petrochemicals Inc. This chemical treatment improves the compatibility between the inorganic ceramic and the organic polymer [4]. The aim of this treatment was to modify the surface properties of the ceramic particles and hence to strengthen the connection of the ceramic with the polymer.

Four different ceramic volume fractions were used to prepare the composite samples, i.e. 30, 40, 50 and 60%. The required amounts of PTCa and PEKK in the composite are calculated for a desired ceramic volume fraction  $\phi^c$  from

$$M_{\rm c} = M_{\rm p} \frac{\rho_{\rm c}}{\rho_{\rm p}} \left( \frac{\phi^{\rm c}}{1 - \phi^{\rm c}} \right) \tag{1}$$

where *M* is the mass,  $\rho$  the density, and the subscripts p and c denote the polymer and ceramic, respectively. After suitably mixing the two phases the mixture is placed in a hot press. Thin films of 250 µm are obtained after applying a pressure of 15 MPa for 3 h at a temperature of 345 °C, which is 40 °C above the polymer melting point (305 °C). These parameters were found to be optimum in order to allow the ceramic to spread evenly within the polymer matrix. The thickness of the film is reduced to 180 µm after further pressing of the samples. Circular aluminium electrodes of 10 mm of diameter were deposited by evaporation in vacuum. After the electrodes were evaporated on each surface of the thin film, the samples were poled in a glass beaker containing insulating silicone oil using a TREK high voltage power supply. For the dc poling process a 10 MV/m field was applied to

the composite at 150 °C (below  $T_g = 155$  °C of the polymer) for 30 min, which was found to be appropriate to obtain a high piezoelectric strain coefficient,  $d_{33}$ .

For the production of the surface mounted and embedded sensors, the piezoelectric composites were bonded to 50- $\mu$ m polymide substrates (Du Pont) using toughened epoxy (RS components). The substrate contained a 25  $\mu$ m thick electrodeposited copper layer, which was spatially etched to produce the desired electrode shape. A conductive paint was applied to the top surface of the sensors to complete the circuit. Only the sensors PTCa/PEKK 50/50 and 60/40 vol.% were both surface mounted and embedded on a 30 cm  $\times$  30 cm CFRC panel.

#### 3. Mixed connectivity model

A key concept to describe electromechanical properties of composites is that of connectivity introduced by Newnham et al. [5]. Connectivity describes the interspatial relationships in a multiphase material. The phases in the composite materials may be spatially self-connected in one or more dimensions. In a two-phase system, there are 10 different ways or connectivity patterns of self-connections of the constituent phases. This can be expressed with two digits, denoting the connectivity of the filler and that of the matrix respectively. The case of a composite made of particles of ceramic powder embedded in a polymer matrix and separated from each other will be indicated as a 0–3 composite.

During the present work the mixed connectivity model proposed by Dias and Das-Gupta [3] has been used to explain the electromechanical properties of the composites. This model was proposed to overcome the difficulty arising from Banno's modified cube model [6]. Banno, who improved Pauer's model [7], describes 0-3 composites based on a unit cube representing the volume of the composite material containing within it a smaller parallelepiped of base dimensions m and height n representing the ceramic (Fig. 1a). The electromechanical properties of the composite will depend upon these two parameters. In this model a difficulty arises when n has values close to 1. In this case, the electromechanical properties change rapidly making difficult to identify the dimensions of the ceramic parallelepiped. The mixed connectivity model considers that both parallel and series connectivity exist in the composite, whereas in Banno's model only one of the two cases could exist at the same time. The ceramic is now represented as a cube of dimensions m where a fraction of it n, in the form of a parallelepiped, which connects both electrodes resulting in a triphasic system (Fig. 1b). Therefore, the composite is viewed now as having mixed connectivity of 0-3 and 1-3. Now the ceramic volume fractions are given by

$$\phi^{c} = m^{3} + (nm)^{2}(1-m), \qquad \phi^{c}_{ser} = m,$$
  
$$\phi_{ser} = m^{2}(1-n^{2}), \qquad \phi^{c}_{par} = (nm)^{2}$$
(2)



Fig. 1. Cube models for 0-3 connected composites.

(4)

(9)

where  $\phi_{par}^{c}$  is the fraction of the ceramic with parallel connectivity.

The properties of the cube, and therefore the composite, are given by considering the series branch in parallel with the ceramic phase and with the polymer phase. In this work  $\varepsilon$  and  $d_{33}$  properties have been studied, and their equations describing the composite are [8]

$$\frac{d_{33}}{s_{33}} = \frac{\phi_{par}^{c} d_{33}^{c}}{s_{33}^{c}} + \frac{\phi_{par}^{p} d_{33}^{p}}{s_{33}^{p}} + \frac{\phi_{ser} d_{33}^{ser}}{s_{33}^{ser}}$$
(3)  

$$\varepsilon = \phi_{par}^{c} \varepsilon^{c} + \phi_{par}^{p} \varepsilon^{p} + \phi_{ser} \varepsilon_{ser} - \frac{(d_{33}^{c} - d_{33}^{p})^{2} s_{33} \phi_{par}^{c} \phi_{par}^{p}}{s_{33}^{c} s_{33}^{p}} - \frac{(d_{33}^{e} - d_{33}^{p})^{2} s_{33} \phi_{par}^{ser} \phi_{par}^{p}}{s_{33}^{c} s_{33}^{ser}} - \frac{(d_{33}^{ser} - d_{33}^{p})^{2} s_{33} \phi_{par}^{ser} \phi_{par}^{p}}{s_{33}^{c} s_{33}^{ser}} - \frac{(d_{33}^{ser} - d_{33}^{p})^{2} s_{33} \phi_{par}^{ser} \phi_{par}^{p}}{s_{33}^{ser} s_{33}^{p}} - \frac{(d_{33}^{ser} - d_{33}^{p})^{ser} s_{33}^{p}} - \frac{(d_{33}^{ser} - d_{33}^{p})^{ser} \phi_{par}^{p}}{s_{33}^{ser} s_{33}^{p}}} - \frac{(d_{33$$

where

$$\frac{1}{s_{33}} = \frac{\phi_{\text{par}}^{\text{c}}}{s_{33}^{\text{c}}} + \frac{\phi_{\text{par}}^{\text{p}}}{s_{33}^{\text{p}}} + \frac{\phi^{\text{ser}}}{s_{33}^{\text{ser}}}$$
(5)

$$\frac{1}{\varepsilon^{\text{ser}}} = \frac{\phi^{\text{c}}_{\text{ser}}}{\varepsilon^{\text{c}}} + \frac{\phi^{\text{p}}_{\text{ser}}}{\varepsilon^{\text{p}}}$$
(6)

$$\frac{d_{33}^{\text{ser}}}{\varepsilon^{\text{ser}}} = \frac{\phi_{\text{ser}}^{c} d_{33}^{c}}{\varepsilon^{c}} + \frac{\phi_{\text{ser}}^{\text{p}} d_{33}^{\text{p}}}{\varepsilon^{\text{p}}}$$
(7)

$$s_{33}^{\text{ser}} = \phi_{\text{ser}}^{\text{c}} s_{33}^{\text{c}} + \phi_{\text{ser}}^{\text{p}} s_{33}^{\text{p}} + \left[ \frac{(d_{33}^{\text{c}} - d_{33}^{\text{p}})^2 \phi_{\text{ser}}^{\text{c}} \phi_{\text{ser}}^{\text{p}}}{a_1} + 2 \frac{((d_{33}^{\text{c}} - d_{33}^{\text{c}})a_3 - (s_{13}^{\text{c}} - s_{13}^{\text{c}})a_1) \phi_{\text{ser}}^{\text{c}} \phi_{\text{ser}}^{\text{p}}}{a_2 a_1 - 2 a_3^2 a_1} \right]$$
(8)

$$a_1 = \varepsilon_0(\phi^{\mathrm{c}}\varepsilon^{\mathrm{c}} + \phi^{\mathrm{p}}\varepsilon^{\mathrm{p}})$$

$$a_{2} = \phi^{p}(s_{12}^{c} + s_{12}^{c}) + \phi^{c}(s_{11}^{p} + s_{12}^{p})$$
(10)  
$$a_{3} = \phi^{c}d_{31}^{p} + \phi^{p}d_{31}^{c}$$
(11)

where  $s_{ij}$  is the elastic compliance,  $d_{ij}$  the piezoelectric coefficient and  $\varepsilon$  the permittivity. The superscripts c and p

refer to ceramic and polymer phases, respectively, whereas the subscripts 'ser' and 'par' denote series and parallel connected phases respectively. The subscripts *i* and *j* refer to the direction of the response and applied stimulus, respectively. The composite properties are represented in contour charts as a function of the connectivity parameters *n* and *m* [3]. These connectivity parameters provide the percentage of 1–3 connectivity in the composites.

#### 4. Experimental

In order to characterise the piezoelectric composite sensor, the dielectric constant ( $\varepsilon$ ) the piezoelectric coefficients ( $d_{33}$  and  $d_{31}$ ) and the electromechanical coupling coefficient ( $k_t$ ), were measured. For dielectric measurements the use was made of a general radio bridge (model 1616). Capacitance measurements, which provided the values of the dielectric constant ( $\varepsilon'$ ) were performed at 1 kHz at room temperature in a vacuum chamber.

The  $d_{33}$  coefficient was measured applying a stress in the direction of the thickness of the samples and the voltage produced was measured in the electrodes using a Pennebaker model 8000 piezo  $d_{33}$  tester. Prior calibration of the instrument needs to be undertaken with a known ceramic. The  $d_{31}$  coefficients for the composites were measured by suspending a weight from the lower end of a sample, measuring  $3.5 \text{ cm} \times 1 \text{ cm}$ , which was rigidly clamped at its upper end. The weight was almost instantaneously removed by means of a solenoid lift and the charge developed across the sample electrodes was recorded on a store oscilloscope. The  $d_{31}$  coefficient is then given by [9]

$$d_{31} = \frac{CVd}{lmg} \tag{12}$$

where C is the standard capacitance, V the developed voltage, d the thickness, l the length of the electrode and mg the force applied by the weight (Table 1).

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Table 1 Piezo and dielectric properties of PTCa/PEKK composites and its single phases						
Property	РЕКК	PTCa/PEKK 30/70 vol.%	PTCa/PEKK 40/60 vol.%	PTCa/PEKK 50/50 vol.%	PTCa/PEKK 60/40 vol.%	PTCa
Dielectric constant, $\varepsilon'$ (at 1 kHz)	3.6	15	19	24.8	36.3	230
Piezoelectric, $d_{33}$ coefficient (×10 <sup>-12</sup> C/N)	0	22	25	28	34	68
Piezoelectric $d_{31}$ coefficient(×10 <sup>-12</sup> C/N)	0	Not observed	-0.1	-0.4	-3.4	-3.1
Electromechanical coupling factor, $k_i$	No peak observed	No peak observed	0.1	0.17	0.20	0.47

# The electromechanical coupling coefficient $(k_t)$ can be obtained from the measurement of the complex impedance Z(f), of the transducer vibrating as a free resonator around its resonant peak [10]. A network analyser, model HP8702A, was used to measure the real and imaginary part of the complex impedance around the resonant peak of the composite materials (Table 1).

For AE measurements, the sensors were tested by exciting the FRB and CFRC panels using two different artificial sources, i.e. ball bearing drops, typically producing relatively large amplitude and low frequency stress waves and pencil lead breaks (Hsu-Nielson source), producing relatively low amplitude, higher frequency stress waves. The pencil lead break tests were carried out with the help of a Nielson shoe to hold the lead (Pentel, 2H, 0.5 mm) of a mechanical pencil at the correct angle to the plate surface (45°). A Gould digital storage oscilloscope (4050) was used to collect the data from the sensors. No pre-amplification or filtering of signals was applied to any of the signals.

#### 5. Results and discussion

#### 5.1. Characterisation

The permittivity  $(\varepsilon')$ , was measured for different ceramic volume fraction PTCa/PEKK poled composites at 1 kHz and room temperature ( $\sim 25$  °C). The values are given in Table 1. As expected, the values of permittivity increase, with increasing ceramic content in the composite. Fig. 2 shows a contour chart for the permittivity of PTCa/PEKK composites using the mixed connectivity model [3]. The constant volume fraction curves have also been included. Each measured point is located at the intersection of the known value of volume fraction of the composite and the corresponding value of the permittivity. Then the n and m values can be found and the percentage of 1-3 connectivity can be calculated using Eq. (2). The values of n and m increase with the ceramic concentration and this will result in a higher percentage of 1-3 connectivity in the composites with higher ceramic loading. For instance, in the case of 50%



Fig. 2. Permittivity contour chart for the PTCa/PEKK composites using the mixed connectivity model.

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Fig. 3. The d<sub>33</sub> contour chart for the PTCa/PEKK composites using the mixed connectivity model.

of ceramic composite, n = 0.31 and m = 0.78 and therefore the ceramic phase has a 12% of 1–3 connectivity (Eq. (2)). The percentage of 1–3 connectivity in the ceramic phase increases from 9% in the 30 vol.% ceramic volume fraction case to 16% in the 60 vol.% composite. This value is lower than that the obtained by previous workers [3,8] in similar composites (20–25%). This may be due to the fact that a higher poling field was used in their cases, thus producing a higher apparent 1–3 connectivity.

In Table 1 are displayed the values of  $d_{33}$  coefficient obtained for the different volume fraction composites. The

values of  $d_{33}$  increase with the ceramic loading. Fig. 3 shows an *n*-*m* plane where the  $d_{33}$  values for the different ceramic volume fraction composites have been plotted. The  $d_{33}$ contour plots were calculated considering the *d*-coefficients of the PEKK polymer as 0. The *m* and *n* values obtained from this contour chart are very close to those gained from the permittivity case (Fig. 2). Now, the percentage of 1–3 connectivity in the ceramic phase increases from 10% in the 30 vol.% ceramic volume fraction case to 17% in the 60 vol.% volume fraction case, which is close to the value obtained for the case of permittivity.



Fig. 4. Graph showing the response of the sensors to a number low energy AE events.

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Fig. 5. Graph showing the response of the sensors to a different distance AE sources.

#### 5.2. Applications

An acoustic wave is considered as a lamb wave when the wave propagates in a plate-like manner where the two dimensions of the plate are much larger than its thickness [11–14]. There are two general types of lamb waves depending on the particle motion within the material as the wave propagates through the plate. These are the extensional (symmetrical) and flexural (asymmetrical) modes. The extensional plate waves propagate faster and with higher frequencies than the slower and lower frequency flexural plate waves. Another difference is that the extensional plate wave velocities are non-dispersive (independent of frequency) whereas the flexural plate wave velocities are dispersive in nature with a square root dependence on the

frequency of the wave. The use of simulated AE sources is necessary in order to evaluate and optimise the output of the sensors before they are used to detect AE generated from damage in a structure. The two PTCa/PEKK sensors, i.e. 50/ 50 and 60/40 vol.% were evaluated by embedding them in the CRFC panel. In order to estimate the minimum energy detectable by the sensors, the response of the transducers as a function of impact energy is plotted. Fig. 4 shows the response of the embedded sensors of PTCa/PEKK to increasing energy impacts of the ball bearing source, additionally with the pencil lead break. As expected, with increasing content of PTCa in the composite the peak to peak response increased significantly.

In the present experiment the noise level was 0.25 mV. In general, it is necessary to have a 2:1 signal:noise ratio to



Fig. 6. Response of the PTCa/PEKK 60/40 vol.% sensors to a pencil lead break.



Fig. 7. Graph showing FFT of the response of the PTCa/PEEK 60/40 vol.% sensors to a pencil lead break.

detect AE energy on development of cracks and other structure faults, viz. debonding and delamination, which energy is an order of magnitude lower than pencil lead break. The embedded PTCa/PEKK 60/40 vol.% composite satisfies above condition for both methods of simulated AE and it is expected that it will be able to detect real AE. The sensors were also compared for their ability to detect AE at different distances. For this, the ball bearing was dropped from a fixed height (10 cm). Fig. 5 shows how the sensors follow an inverse law to distance. As expected, the composites with higher ceramic loading will detect at further distances.

Finally, lead break experiments at different distances from the sensor were carried out with the two different sensors, i.e. PTCa/PEKK 60/40 and 50/50 vol.%, both surface mounted and embedded. In Fig. 6 the response of the surface mounted and embedded PTCa/PEKK 60/40 vol.% to a pencil lead break is shown. From the figure, it can be observed that only the embedded PTCa/PEKK 60/40 vol.% was capable of clearly detecting the two wave modes of the plate waves, i.e. extensional and flexural mode and the surface mounted has difficulties to detect the shear mode. This shows the advantage of using embedded sensors against the surface mounted sensor.

Furthermore, fast Fourier transforms (FFT) was performed to the signals and the frequency of each mode was established. The FFT of the lead break test was performed showing two peaks occurring around 15 kHz (flexural mode) and 500 kHz (extensional mode) (Fig. 7). These results are in agreement with the values obtained by other workers [12].

#### 6. Conclusions

The electroactive characterisation of the PTCa/PEKK composites shows that these materials have good sensing properties in comparison with similar sensors, viz. PTCa/Epoxy and PTCa/P(VDF-TrFE). It has been shown that, the mixed connectivity model fits well with the experimentally determined values of permittivity and  $d_{33}$  piezoelectric coefficient.

An increase of the response of the sensors with the increase of ceramic loading has been observed. The embedded PTCa/ PEKK 60/40 vol.% sensor was shown to be capable of detecting the two components of the plate (lamb) waves making it a good candidate to detect real AE.

#### Acknowledgements

Acknowledgements are due to Professor W.K. Sakamoto for his valuables comments in the data analysis. One of the authors (P. Marin-Franch) is grateful to BAE Systems for his maintenance grant.

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# NOVEL SENSORS FOR DAMAGE DETECTION

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Keywords: Acoustic Emission, composites, HUMS, damage detection.

# Abstract

In the present work Calcium Modified Lead Titanate (PTCa) and Polyetherketoneketone (PEKK) ceramic/polymer sensors have been produced and characterised for their electroactive and dielectric properties. Thin films of these composites have been surface mounted on isotropic and orthotropic plates and their frequency response and ability to detect Acoustic Emission (AE) have been evaluated and compared with other sensors, i.e., Lead Zirconate Titanate (PZT) and PTCa/Epoxy and PTCa/P(VDF-TrFE) composites. Furthermore, PTCa/PEKK embedded sensors in Carbon Fibre Reinforced Composites (CFRC) have also been examined for the detection of simulated AE and have been shown suitable for acoustic emission sensors.

#### 1 Introduction

It is likely that future requirements for aerospace structures will include the integration of a Health and Usage Monitoring System (HUMS). Operational Load Monitoring (OLM) has already been incorporated into aerospace structures [1] but in order to move towards damage tolerant structures it is essential that there is some means of detecting damage initiation and growth. There are several potential methods for HUMS and it is widely accepted that no single method will satisfy all of the requirements. However, Acoustic Emission (AE) is still seen by many workers [2,3,4,5] as a key inspection technique with the potential to both detect and locate damage sites. The use of piezoelectric materials in sensors for detecting AE is not new and there are many commercially available transducers available. In general, these sensors have very high sensitivities and are relatively robust and for most applications these transducers are suitable. However, for many aerospace applications we need to limit the size, mass and cost of sensors especially for large area coverage. One practical solution is to use low profile sensors. Low profile sensors are that due to their size can be either surface mounted flush with the structure or even embedded within it. This potentially can improve their response and resistance to environmental effects which is a clear advantage over the commercial sensors which can not be embedded.

Currently most piezoelectric sensors incorporate ceramic PZT. However the potential applications of piezoelectric ceramics as embedded sensors for structural damage detection are restricted due to their relatively high stiffness and low toughness. New challenges have arisen for designing novel sensors which can be embedded, the mechanical properties of the sensors being identical to their surroundings in order to avoid the inclusion matrix problems. To achieve more compliant sensors, ceramic-polymer composites are attractive as Acoustic Emission (AE) detectors in thin film form as they posses high piezoelectric properties of ferroelectric ceramics and the viscoelastic properties of polymers. In addition, these sensors have low acoustic impedance, comparable to those of water and blood, and broad electrical bandwidth which make them suitable for diverse applications including hydrophone and biomedical technology. The two components of the biphasic ferroelectric ceramic/polymers composites and their respective volume fractions need to be chosen carefully to obtain an optimum advantage.

Typical electroceramics, viz. Barium Titanate (BaTiO3) and Lead Zirconate Titanate (PZT), have high values of dielectric permittivity which make them more suited for applications as actuators rather than sensors. Lead Titanate (PT), on the other hand has a lower value of permittivity and larger value of hydrostatic (d<sub>b</sub>) coefficient than those of BaTiO3 and PZT. However, calcium doped lead titanate (PTCa) is preferred over PT as the doping reduces the anisotropy and the Curie temperature, thus improving the sinterability and the poling efficiency respectively. For the polymer of the biphasic composite, thermoplastics with as high as possible values of melting  $(T_m)$  and glass transition (T<sub>g</sub>) temperatures are desirable for wide temperature range applications. Polyetherketoneketone (PEKK) is such a polymer with  $T_m$  and  $T_g$  values of 304 °C and 153 °C respectively. Work at Bangor University has been carried out in the production of high temperature (150 °C) tough polymer-piezo composites. In particular PTCa/PEKK sensors have been fabricated with different volume fractions of ceramic, i.e., 30% and 40% volume fraction. After calculating the dielectric and piezoelectric properties, the response of these sensors have been compared with other sensors, i.e., PZT, PTCa/Epoxy, PTCa/P(VDF-TrFE) and AE commercial sensors. The aim of this study was to measure the response both in the amplitude and frequency domain in order to determine their ability to detect AE generated by real damage in structures. This was achieved by exciting both Carbon Fibre Reinforced Composites (CFRC) and aluminium panels with artificial AE and detection was carried out using both surface mounted and in the case of the CFRC panel embedded sensors.

# 2 Experimental

#### 2.1 PEKK polymer

Poly(ether ketone ketone) has excellent chemical resistance, low moisture absorption and high temperature stability combined with good processability. PEKK polymers consist of either all paraphenylene linkages (PEKK(T)), one meta-phenylene linkage (PEKK(I)) or alternating T and I isomers(PEKK(T/I)). A PEKK with all para-phenylene linkages (T) has the chemical structure of



The chemical structure for a PEKK with one meta-phenylene linkage (I) is



Different compositions of T and I in the synthesis lead to different PEKK(T/I) copolymers and therefore to a different structure, morphology and properties of the polymer. The PEKK(T/I) used in this work has T/I rate of 60/40. Additionally, from a Differential Scanning Calorimetric (DSC) test the PEKK(T/I) polymer used was found to be mostly amorphous in structure.

#### 2.2 PTCa/PEKK composite preparation with 0-3 connectivity

The mechanical and electrical properties of the sensor will depend on the ceramic concentration of the composite; in this work PTCa/PEKK composites with 30% and 40% volume fraction of ceramic have been prepared. In the 0-3 composites the ceramic powder is randomly distributed in the polymer matrix. When the desired amount of ceramic and polymer are combined, the mixture is placed in a hot press. This was found to be the more important and difficult step in the composite fabrication. This part of the process is divided in 3 different stages in which the pressure and temperature are changed in order to obtain an even distribution of the ceramic filler within the polymer phase. In the final stage, a pressure of 15 MPa and a temperature of  $320^{\circ}C$  are

applied for 2 hours and the sample is then cooled down under the stress of the press in order to obtain thin films of 150 to 200  $\mu$ m. Sometimes this process has to be repeated in order to obtain an even distribution of the ceramic and reduce the thickness of the composite. Figure 1 shows the hot press apparatus. Once the thin films are produced, aluminium electrodes of 10 mm diameter are deposited in both surfaces of the film by evaporation in vacuum.

Finally, the composites were poled. For the DC poling process a 10MV/m field was applied to the composite at  $150^{\circ}$ C of temperature (below T<sub>g</sub> of the polymer) for 30 minutes, which was found to be appropriate poling conditions in order to obtain a high piezoelectric strain coefficient, d<sub>33</sub>. For this purpose the samples were placed in a glass beaker containing silicone oil to prevent breakdown across the surface and were heated. A magnetic stirrer was used to circulate the hot oil and provide an even distribution of the temperature. In order to prevent damaging the sample, the voltage applied through the TREK high voltage power supplier was increased gradually until a poling field of 10 MV/m was reached. The field was applied for 30 minutes holding the temperature constant, and the sample was then cooled down under the action of the field. Finally the field was removed and the samples cleaned in an ultrasonic bath.



Figure 1: Schematic of the pressing operation

After the samples were prepared dielectric and piezoelectric characterisations were made. The dielectric constant and the dielectric loss were calculated from Bridge measurements (General Radio Bridge model 1621). The  $d_{33}$  coefficient was measured using a Pennebaker Model 8000 Piezo  $d_{33}$  tester. The electromechanical coupling coefficient ( $k_t$ ) was obtained from the measurement of the complex impedance Z(f), of the transducer vibrating as a free resonator around its resonant peak (6,7). A network analyser, Model HP8702A, was used to measure the complex impedance. All the properties, discussed above, are reported in Table 1. It may be noted that the values of  $d_{33}$  for the PTCa/PEKK composites are comparable to 0-3 composites produced in the past using more ceramic concentration, i.e., 60% (6,8).

Property	PTCa/PEKK 30/70 vol%	PTCa/PEKK 40/60 Vol%	PEKK
Density, $\rho$ (kg/m <sup>3</sup> )	2977	3536	1300
Dielectric constant, Er (at 1 kHz)	10.5	19	3.6
tanð % (at 1 kHz)	1.3	0.6	0.28
Piezoelectric d <sub>33</sub> coefficient (×10 <sup>-12</sup> C/N)	28	36	not measurable
Electromechanical coupling factor, k.	No peak observed	0.1	No peak observed

Table 1: Pyro-, piezo and dielectric properties of PTCa/PEKK composites.

# 2.3 Sensor manufacture

Apart from the commercial off-the-shelf (COTS) transducers all the sensors were produced using identical constructions. The piezoelectric materials were bonded to 50 micron polyimide substrates (DuPont) using toughened epoxy. The substrate contained a 25 micron thick electro-deposited copper layer which was etched away to produce the base electrode. A conductive paint was applied to the top surface of the sensors to complete the circuit and a 50 Ohm impedance coaxial cable was soldered to the two electrodes. A silicone based coating was applied to the surface of the sensors. The construction of the low profile sensors is shown in Figure 2.



Figure 2: Illustration of the low profile sensor geometry.

2.4 Incorporating sensors into test panels



Figure 3: Panel 1 (CFRC) and panel 2 (aluminium) containing surface mounted and embedded sensors.

Two types of panels were used for the characterisation of the sensors. A 25 cm by 25 cm quasiisotropic 16 ply CFRC (orthotropic) panel and a 50 cm by 30 cm aluminium (isotropic) panel. Note that the composite lay up was: T300/920 CFRC (+45,-45,0,90,+45,-45,0,90)2 and the fibre volume fraction is approximately 60 %. With reference to Figure 3 the sensors attached or embedded in the CFRC panel were:

- 30:70 PTCa/PEKK- One sensor surface mounted using toughened epoxy and one sensor embedded between the middle plies.
- A Commercial-Off-The-Shelf (COTS) sensor attached to the surface using vacuum coupling grease.
- 40:60 PTCa/PEKK- One sensor surface mounted using toughened epoxy and one sensor embedded between the central plies.
- 4) 40:60 PTCa/PEKK- One sensor surface mounted using toughened epoxy and one sensor

- 5) Low profile PZT (LP PZT)- One sensor surface mounted using toughened epoxy and one sensor embedded between the central plies.
- 6) 30:70 PTCa/PEKK- One sensor surface mounted using toughened epoxy and one sensor embedded between the central plies.

With reference to Figure 3 the sensors attached to the aluminium panel were:

- 1) PTCa/Epoxy.
- 2) 40:60 PTCa/PEKK.
- 3) PTCa/P(VDF-TrFE).
- 4) Low profile PZT (LP PZT).
- 5) R50 (Physical Acoustics Ltd) COTS.
- 2.5 Characterising the sensors

The sensors were characterised by exciting the CFRC and Aluminium panels using artificial sources. These sources were:

- 1) Ball bearing drops- typically producing relatively large amplitude, low frequency stress waves with a range of impact energies.
- 2) Pencil lead breaks (Hsu-Nielson source) with the help of a Nielson shoe to hold the lead (Pentel, H, 0.5 mm) of a mechanical pencil at the correct angle to the plate surface (45°) -typically producing relatively low amplitude, higher frequency stress waves.
- A driven PZT element linked to a calibrated AE emitter (AE-Cal 2- Physical Acoustics Ltd.)allows defined stress wave patterns to be excited in the panel with defined amplitude, frequency, rise time and decay time.

The AE sources were generated in the centre of the panels. The driven PZT sensor was located in position 4 of the aluminium panel (Figure 3). All the sensors were connected to one of four channels on a Gould DataSys Digital Storage oscilloscope. No pre-amplification or filtering of signals was applied to any of the signals.

#### **3 Results**

3.1 Response of sensors to artificial AE

The use of artificial AE sources is necessary in order to evaluate and optimise the output of the sensors before they are used to detect AE generated from damage in a structure. Three sources of AE were used for the evaluation for the sensors in both panels (Figure 3) and the results are described in the following subsections. In general dropping a steel ball bearing onto a panel produces relatively high energy stress waves of relatively low frequency. Figure 4 shows the response of a commercial sensor, a low profile PZT (LP PZT) and two PTCa/PEKK sensors. The two PTCa/PEKK sensors contained 30 and 40 % PTCa by volume respectively.

The response of each sensor indicates detection of the 2 mJ impact, although the different volts per division of each sensor should be pointed out. An FFT was performed on the response of each sensor type shown in Figure 5. The results indicate similar frequency spectrum for the LP PZT and the 40% PTCa/PEKK sensor. The commercial sensor was not optimised for low frequency signals, due to its construction. The FFT of the 30 % PTCa/PEKK sensor indicates limited detection of the higher frequencies.



Figure 4: Graph showing response of all four sensors to 2mJ ball bearing drop.

A comparison of the frequency spectrum from a surface mounted and embedded 40 % PTCa/PEKK sensor indicates a slight increasing shift of frequency response (see Figure 6). It is possible that the detected modes within the panel will dither from those on the surface and in addition it would be expected that extensional modes would be coupled more strongly into fully integrated sensors. These issues are being investigated further.



Figure 5: FFT of a 2mJ ball bearing



Figure 6: FFT of the response of a surface mounted and embedded 40:60 PTCa/PEKK sensor to a 2 mJ ball bearing drop.

Pencil lead breaks generally produce higher frequency, low amplitude stress waves. Figure 7 shows the time response of the four surface mounted sensors in the CFRC plate, note the different scale of the voltage for each sensor. The FFT represented in Figure 8, shows a peak at 4-5 kHz. These peaks may be due to the flexural mode of the acoustic wave. Only the COTS sensor seems to be able to detect the extensional mode of the wave showing a peak at about 37 kHz. It is also important to note that the PTCa/PEKK 30% sensor picks a very small signal, this is due to the small concentration of ceramic in the sensor.



Figure 7: Graph showing the response of four sensors to a pencil lead break.



Figure 8: FFT of the response of the four sensors to a pencil lead break.

# 3.2 Effect of AE energy

In most AE systems the signal from the sensor is filtered and amplification is applied to the signal; therefore, the key to detection is the signal:noise of the signal. In order to predict the minimum energy detectable of the sensor the signal:noise response of the sensor as a function of impact energy is plotted. Figure 9 shows the response of four types of sensors to increasing energy impacts. In general a signal:noise of 2:1 is required to allow suitable amplification to be applied to the output signal, therefore this was set as a cut off point for AE detection. From Figure 9, by

extrapolation, it can be predicted that the cut off energy for 30:70 and 40:60 PTCa/PEKK was 0.05 mJ and 0.02 mJ respectively. As expected, the increase of ceramic concentration result in an improvement of sensitivity in the sensor. Independent data (not reported) have indicated that typical damage generated AE events from CFRP panels can be an order of magnitude lower than that of the pencil lead break. This suggests that the sensitivity of the PTCa in PEEK sensors still require improvements in order to detect low energy AE events. This can be done by increasing the ceramic content in the composite. Note that, the energy of the pencil lead break was estimated by comparing it with the energy of AE events recorded for a 2 mJ impact. For reference a mean value of 0.03 mJ was defined as an estimated energy of a pencil lead break. The variability in pencil lead break energy was calculated to be 0.01mJ for the tests carried out.



Figure 9: Graph showing the response of four types of sensors to a number low energy AE events.

Surface mounted	COTS	LP PZT	30:70 PEKK	40:60 PEKK
Noise level	2.5 mV	4 mV	2 mV	1 mV
2 mJ peak FFT	2.22 V +/-0.46 3,6,11,34 kHz	1.49 V +/-0.17 3,5,11 kHz	46 mV +/- 5.3 2,5,10 kHz	85 mV +/-10.1 5,10, kHz
1 mJ peak FFT	1.48 V +/-0.18 3,6,11,34 kHz	1.12 V +/-0.28 3,5,11 kHz	29 mV +/-3.6 2,5,10 kHz	72 mV +/-9 5, 10 kHz
0.5 mJ peak FFT	1.24 V +/-0.17 3,6,11 kHz	0.88 V +/-0.16 3,5,11 kHz	23 mV /- 3 2,5,10 kHz	50 mV +/- 6 5,10 kHz
0.02 mJ peak FFT	88 mV +/-23 4,14,39,50kHz	78 mV +/-24 3,16, 34 kHz	2 mV +/- 0 3,7,11,16 kHz	5 mV +/- 1 3,5,16 kHz
Embedded Sensors			A TAN	
Noise level	No data	4 mV	2 mV	l mV
2 mJ	No data	1.40 V +/-0.09	6 mV +/- 1	19 mV +/- 1
1 mJ	No date	0.94 V +/-0.06	4 mV +/- 0.8	14 mV +/- 1
0.5 mJ	No data	0.71 V +/-0.03	3 mV +/- 0.4	10 mV +/- 0.8
0.02 mJ	No data	56 mV +/- 11	0.5 mV +/- 0.2	3 mV +/- 1.1
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Table 2: Summary of test data for a series of sensors in the CFRP panel.

The results, however, show a number of features for all of the sensors. Firstly, the peak response increased logarithmically with increasing energy. FFT analysis, refer to Table 2, showed no significant variation in the frequency of the AE generated (with the exception of the pencil lead breaks) and therefore the effects may be due to damping effects in the CFRP panel. Secondly as stated above with increasing content of PTCa in the composite the peak response increased significantly. For an increase from 30 to 40 % PTCa in PEKK the response more than doubled. It was however seen that the response of the 30:70 PTCa/PEKK was weak with some of the higher frequencies not detected. This suggests that the concentration of the PTCa was close to the lower limit required for the composite to exhibit a piezoelectric response. The third feature of the results is that the peak response of the embedded sensors was lower than for the surface mounted sensors. This was expected as the AE sources were generated on the surface of the panel, however, this also suggest that some polarization is lost in the sensors during embedding. The data is summarised in Table 2.

#### 3.3 Frequency response of sensors

The peak response of the sensors for a given impact energy indicates sensitivity at a particular frequency. However in order to be able to determine whether a sensor could detect AE generated AE it is also necessary to know the frequency response of the sensors. By using a calibrated AE source connected to a wide band PZT transducer the CFRC panel was excited at four frequencies, 60,150, 300 and 500 kHz. The drive signal to the transducers, refer to Figure 10, was designed to simulate typical AE by having a short rise time (50 $\mu$ s) and a relatively long decay time (500 $\mu$ s). Figure 10 also shows the response of a 40:60 PTCa/PEKK sensor to a driven 60 kHz event. As an example the FFT of its response confirmed detection of a the PTCa/PEKK 40% composite to the 60 kHz signal is shown in Figure 11.







Figure 11: FFT of the response of a 40:60 PTCa/PEKK sensor to a driven 60 kHz pulse.

Table 3 summarises the data obtained from these trials. It should be noted that all the sensors detected AE events and the frequency of the response correlated with the drive frequency of the piezo-ceramic transducer. Figure 12 shows the amplitude response of the surface mounted PTCa/PEKK 40%, PTCa/Epoxy and PTCa/Copolymer sensors at different frequencies. It can be observed that both the PEKK and copolymer based sensors have a peak in amplitude at 300 kHz while the epoxy based sensor showed a peak at 150 kHz. In comparison the COTS sensor showed a

peak around the 150 kHz (not shown). As the ceramic used for each sensor is the same these results indicate that the polymer in which they are blended will have a significant effect on the response of the sensor due to damping or coupling effects. Therefore selection of host material for the ceramic particles can have a significant effect on the performance of the sensors. This area needs to be investigated in more detail.

Surface mounted	COTS (V)	Epoxy	40:60 PEKK	Co-polymer	
Noise level	2.5 mV	2 mV	2 mV	2 mV	
60 kHz peak FFT	0.38 60 kHz	5.5 60 kHz	0.31 60 kHz	0.04 60 kHz	
150 kHz peak FFT	1.34 150 kHz	7.8 150 kHz	2.01 150 kHz	1.80 150 kHz	
300 kHz peak FFT	230 302 kHz	3.8 302 kHz	6.0 301 kHz	7.6 302 kHz	
500 kHz peak FFT	45 504 kHz	4.6 503 kHz	4.5 503 kHz	4.2 502 kHz	

Table 3: Frequency response of four types of sensors mounted on the aluminum panel.



Figure 12: Frequency response of the PTCa/PEKK 40%, the PTCa/Epoxy and PTCa/Copolymer sensors.

#### **4** Conclusions

The aim of this study was to evaluate whether PTCa/PEKK sensors could be used to detect AE generated during loading of damaged composite and metallic structures. Due to the complex nature of AE generation and high attenuation in CFRC this was set as the benchmark for the sensors to achieve adequate sensitivity of detection. The observed improvement in the response of the 40:60 sensor compared to the 30:70 indicates that further improvements can be made by increasing the concentration of PTCA up to 60%. Work is currently being carried out in the sample preparation with more ceramic concentration. This study has also shown that the sensors can be successfully embedded and cured (at  $125^{\circ}C$ ) and still detect AE. However it may be noticed that some

polarisation can be lost during the curing process and repolarisation of the sample may be needed in order to improve the sensor response.

#### Acknowledgements

One of the Authors (P. Marin-Franch) would like to acknowledge the financial support of BAE Systems for his PhD studentship.

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**ORIGINAL ARTICLE** 

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# Dielectric properties and spatial distribution of polarization of ceramic + polymer composite sensors

Received: 6 November 2000 / Reviewed and accepted: 7 November 2000

Abstract Thin films ceramic + polymer composite sensors with mixed connectivities possess high values of piezo- and pyroelectric coefficients and the formability and flexibility which are not attainable in a single-phase ferroelectric material, i. e., an electroceramic or a polymer. The efficiency and the piezo- and pyroelectric figure of merit (FOM) are influenced by the temperature dependence of the dielectric properties and the nature of the spatial distribution of polarization of the composite material. We report the results of a study of dielectric properties of calcium - modified lead titanate (PTCa) and a polar copolymer, polyvinylidene fluoride and trifluoroethylene P(VDF-TrFE) and PTCa and epoxy in a wide frequency range. Each of the two composites was fabricated with two different volume fractions of the constituent phases. Furthermore, the spatial distribution of polarization was determined by the laser intensity modulation method (LIMM) for each composite sensor in order to assess the polarization distribution of the sensors. These results are also reported in this work.

Keywords Sensors · Composites · Dielectric relaxation · Polarisation distribution · Space charge distribution · LIMM

# Introduction

Ferroelectric material may be used as smart piezo- and pyroelectric sensors for diverse applications. The properties of these dielectric materials such as pyroelectric and piezoelectric responses, thermal behavior and other properties are dependent of their dielectric behavior over

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BAE Systems, Advanced Technology Centre-Sowerby, PO Box 5, Filton. Bristol BS34 7QW, UK a wide frequency range and over an appropriate temperature range. Dielectric relaxation study in polar materials using dielectric spectroscopy in a certain frequency range allows characterising these materials. In this report, dielectric spectroscopy in a wide frequency range has been studied for PTCa+Epoxy and PTCa+P(VDF-TrFE) composite samples at different temperatures.

PTCa is obtained from the perovskite ceramic PbTiO<sub>3</sub> by doping with Ca2+. The doping of PT with calcium by substituting 24% of the lead atoms with Ca2+ atoms on the A sites, reduces the tetragonality of the crystal structure of the ceramic, which results in an enhancement of the electromechanical anisotropy, thus decoupling  $d_{31}$  and  $d_{33}$  coefficients. This doping process also lowers the Curie temperature of the ceramic from 490 °C to 260 °C, which makes PTCa a material easier to pole than PT at a reduced temperature which is suitable for the polymer matrix in ceramic + polymer composite. PTCa is also a material that does not tend to fracture when cooled through its Curie temperature. The electromechanical anisotropy of PTCa ceramic leads to a high values of  $d_h$  coefficient. Additionally, the low permittivity of this ceramic, with respect to PZT, gives PTCa high values of piezoelectric g coefficients. These two properties provide a high piezoelectric figure of merit (FOM) which makes PTCa a good material for ceramic + polymer composite transducers.

The copolymer P(VDF-TrFE) is synthesised by the polymerization of the monomers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) in the liquid phase. The copolymer tends to crystallize in the polar form when cooled from the melt. A crystallinity of 80% can be achieved after annealing the copolymer at 135 degres centigrade for an hour. The lattice structure is the same for both the copolymer and homopolymer (PVDF). The copolymer containing 20–50% TrFE is of special interest as there is a clear indication of a Curie temperature with such compositions. P(VDF-TrFE) used in this work, has a nominal 24% by weight of TrFE which is 19.8% in terms of molar percentage and its Curie temperature is 120 degrees centigrade. The coploymer was supplied in powder form from PiezoTech S. A. of France.

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The epoxy is Epikote 828 which is a thermo setting lium viscosity epoxide resin produced from bisphe-A and epichlorohydrin, the curing agent being 2, 4, cris((dimethyl amino)methyl) phenol tri(2-ethyl hexate). The epoxy resin and the curing agent were supd by Shell Chemicals and Anchor Chemicals respecly.

Different methods are used for the measurement of ectric properties, depending on the frequency range sidered. Bridge measurements provide the data in the juency range of 20 Hz to  $10^{6}$  Hz, whereas the dielecdata in the frequency range of  $10^{-5}$  Hz to  $10^{-2}$  Hz is culated from the data of the discharge current measurement. The dielectric data in the frequency gap been  $10^{-2}$  Hz and 20 Hz were not measured due to techal limitations. However, the dielectric information in gap was determined using a fitting function, i.e., scher 'universal' law [1].

Since the recognition that the Debye model [2] is not formed for most solids, empirical models were subsently developed, such as Cole-Cole function [3], the oss-Kirkwood function [4], the Davidson-Cole funcin [5], the Williams-Watts function [6], the Havriliakgami function [7] and the Jonscher 'universal' funcin [1]. The models mentioned above have been iewed recently [8]. In this work, Jonscher 'universal' was used to fit the experimental data, but the Havril--Negami function can also be used giving the same ults.

One of the major problems in the study of the piezol pyroelectric materials is to know the mechanism of poling process and its relationship with the dielectric l electroactive properties of the material. Therefore, determination of the spatial distribution of polarizan and the space charge are very useful in this matter. e spatial distribution of dipoles and space charges in id materials can be probed using non-uniform thermal l mechanical forces.

In this paper, the polarization distribution profile of poled composite samples was studied using the laser ensity modulation method (LIMM). The LIMM [9,10] thod is a thermal wave method where a non-uniformdistributed thermal force interacts with the spatially tributed polarization or space charge to produce a sisoidal pyroelectric current. This pyroelectric complex rent is a unique function of the modulation frequency I the polarization and space charge distribution. In this e, only dipole polarization is assumed [11]. A suitable nputer program is used to analyse the experimental a [12] using the fundamental LIMM equations plained in the discussion section.

#### perimental

e dielectric spectroscopic study for the unpolarized and polard cases was made over a wide frequency range at three differtemperatures i.e., room temperature (RT), 50 °C and 70 °C for omposites samples, i.e., PTCa+Epoxy 50+50% and 60+40% PTCa+P(VDF-TrFE) 50+50% and 65+35% for both polarized For dielectric measurements in the frequency range of 20 Hz to 10<sup>6</sup> Hz a Wayne Kerr Bridge and a General Radio Bridge were used. Capacitance and conductance measurements were performed as a function of frequency at room temperature using the Wayne Kerr Bridge and a General Radio Bridge was used for the measurements at 50 °C and 70 °C. For the General Radio bridge the composites were located in a vacuum chamber at a pressure of 1.3 Pa. An ac voltage of 3 V was applied between the electrodes of the sample. The values of the real ( $\varepsilon$ ) and the imaginary parts ( $\varepsilon$ ") of the complex permittivity were calculated as:

$$\varepsilon' = \frac{Cd}{A\varepsilon_0} \tag{1}$$

$$\varepsilon'' = \frac{Gd}{\omega A \varepsilon_0} \tag{2}$$

where  $\omega$  is the angular frequency ( $\omega = 2\pi f$ ), *C* and *G* are the capacitance (F) and conductance (S) of the sample respectively, *d* is the thickness of the sample (m), *A* is the area of the electrode (m<sup>2</sup>) and  $\varepsilon_0$  is the permittivity of the vacuum. For measurements in the frequency range of  $10^{-5}$  Hz to  $10^{-2}$  Hz discharge current process is used. For this, the dielectric sample is placed in a temperature controlled vacuum chamber at an appropriate and constant temperature. Then a field of  $10^5$  V/m is applied for 27 hours and then the sample is sort-circuited for 3 hours and the discharge current, I(t), is monitored using a Keithley 617 programmable electrometer. It is important to notice that the charging time has to be approximately 1 order of magnitude greater than the discharging time in order to have an error lower than 18% [15]. The values of  $\varepsilon''(\omega)$  were calculated using the Hamon approximation [16]

$$\varepsilon'' = \frac{I(t)d}{2\pi f A \varepsilon_0 V} \tag{3}$$

where V is the applied voltage (v), f the Hamon frequency (f=0,1/t), I(t) the magnitude of the discharge current (Amps) at a time t after the removal of the voltage and the rest of the parameters have the usual meaning.

In the present work, the LIMM [9, 10] technique was used at room temperature for four polarized samples, i.e., PTCa+Epoxy 50+50% and 60+40% ceramic+polymer volume fraction composites and PTCa+P(VDF-TrFE) 50+50% and 65+35% ceramic + polymer volume fraction, in order to determine their spatial distribution of polarization. For the LIMM measurements the composite sample was located in a sample holder, which in turn was mounted in a vacuum chamber, possessing a quartz window. The use of the vacuum chamber was required to provide thermal insulation around the sample to be tested. For this purpose a rotatory pump is sufficient. A Spectra-Physics 159 He-Ne laser, with a 2 mm beam diameter, was used to provide the heat source on the sample. An electromechanical chopper was used to modulate the intensity of the beam. The frequency was controlled by a computer, giving a sinusoidal modulation of the heat intensity at the desired frequency. The pyroelectric current generated, was converted into ac voltage using an inverting current amplifier (Keithley 428). The pyroelectric current of the samples was measured over the frequency range of 10 Hz to 3000 Hz by a lock-in amplifier, whose reference input was provided by the same frequency generator, which drove the electromechanical modulator. The frequency sweep was controlled by the computer, which was also interfaced with the lock-in amplifier to act as a data logger. Once the pyroelectric current was collected, the computation of the polarization distribution can be performed.

# **Results and discussion**

As stated before, a fitting calculation may be carried out to combine the data of  $\varepsilon''(\omega)$  in the frequency ranges of 10-5 to 10-2 Hz and 20 to 106 Hz using the Jonscher 'universal' law [1]. After the fitting of  $\varepsilon''(\omega)$  is obtained, the Kramers-Kroning relation [1], is used to calculate the values of  $\varepsilon'(\omega)$  in the frequency range of 10<sup>-5</sup> Hz to 10<sup>6</sup> Hz. It will be observed that this fitting agrees with the experimental data obtained by means of bridge measurements for  $\varepsilon'(\omega)$  in the frequency range of 20 Hz to 106 Hz.

The Jonscher 'universal law has the form [1],

$$\varepsilon^{\prime\prime}(\omega) \propto \frac{1}{\left(\omega / \omega_p\right)^{-m} + \left(\omega / \omega_p\right)^{1-n}} \tag{4}$$

where 0 < m < 1 and 0 < n < 1 are fitting parameters,  $\omega_n$  is the peak frequency and all the other parameters have been already defined. The Kramers-Kroning equation [1] is given by

$$\varepsilon'(\omega) = \varepsilon'_{\omega} + P \int_{-\infty}^{\infty} \frac{\varepsilon''(x)}{(x-\omega)} dx$$
(5)

where  $\varepsilon'_{\infty}$  is the value of  $\varepsilon'(\omega)$  at frequencies which is too high for the permanent dipoles to follow. The  $\varepsilon''(x)$ function is known in the whole frequency range and the poles,  $\omega$ , are the experimental data. Therefore, the integral has to be performed for each of the data points.

Figures 1, 2, 3, 4, 5 and 6 show the dielectric behavior of the real  $\varepsilon'(\omega)$  and imaginary  $\varepsilon''(\omega)$  part of the complex permittivity in the frequency range of 10-5 Hz to 106 Hz of the PTCa+Epoxy and PTCa+P(VDF-TrFE) composites for different cases. It is important to notice

that the epoxy is a non-polar polymer [13] and the P(VDF-TrFE) 75+25 mol % is ferroelectric polar polymer [14] which has higher electrical conductivity, particularly at low frequency, due to ions and localised space charges in contrast to the former case. The PTCa ceramic has its loss peak in the Gigahertz range [17], and so the observed peaks in the composites discussed are due to ionic impurities and moisture containing dissolved ions in the polymer phase [8].

Figure 1 represents the behavior of the dielectric properties of the polarized PTCa+Epoxy with temperature. It may be observed that with the increase of temperature, the composites have higher values of the loss component at low frequencies as a result of conductive processes, which are enhanced when the sample is heated. The loss peak appearing at medium frequencies, due to ionic impurities [8], shifts to higher frequencies when the temperature is increased which can be expected. At high frequencies, the peak due to adsorbed water containing dissolved ions [8] also shifts to higher frequencies when the samples are heated.

Figure 2 represents the temperature dependence of the polarized PTCa+P(VDF-TrFE) composite. It may be observed that the thermal activation process is similar to that of the PTCa+Epoxy case, however, the medium frequency peak arising form the ionic impurity, is absent for the present case. It is suggested that the enhanced quasi DC conduction (QDC) in this composite masks the relaxation process. It should be noted that the dielectric behavior as a function of temperature of the unpolarized composites, was observed to be similar to that of the polarized case.

Figures 3 and 4 show the comparison of the dielectric behavior of the polarized and unpolarized composites for



Fig. 1 Dielectric spectroscopic data for the polarized (poled with a field of 20 MV/m at 80 °C during 30 minutes) PTCa+Epoxy 60+40% at different temperatures

Fig. 2 Dielectric spectroscopic data for the polarized (poled with a field of 10 MV/m at 90 °C during 30 minutes) PTCa+P(VDF-TrFE) 65+35% at different temperatures

5 6



ig. 3 Dielectric spectroscopic data for the unpolarized and polared (poled with a field of 20 MV/m at 80 °C during 30 minutes) TCa+Epoxy 50+50% at RT



**g. 4** Dielectric spectroscopic data for the unpolarized and polared (poled with a field of 10 MV/m at 90 °C during 30 minutes) Ca+P(VDF-TrFE) 65+35% at RT

e PTCa+Epoxy and PTCa+P(VDF-TrFE) cases respec-/ely. It can be observed in both figures that the poling ocess increases the quasi dc conductive (QDC) prosses due to the injection of charges. In Figure 3, the agnitude of the peak in the medium frequency range is creased with the poling process without any shift of the



Fig. 5 Dielectric spectroscopic data for different volume fractions of the polarized (poled with a field of 10 MV/m at 90 °C during 30 minutes) composite PTCa+P(VDF-TrFE) at RT

peak frequency,  $\omega_p$ . This increase is due to the injection of charges during the poling process.

In Figure 4 the ionic impurity peak shows a different behavior from that of the previous case. During the poling process charges are injected into the sample. The injected charges can neutralise the ions, and thus shielding the ionic peak occurring at medium frequencies. These processes indicate that the ionic charges are of opposite polarities in the two composites.

Figure 5 shows the dielectric spectroscopic data for different volume fractions of ceramic content in the PTCa+P(VDF-TrFE) composite. It can be observed that the conductive processes are enhanced for higher concentration of ceramic in the composite, thus masking the relaxation peak of the polymer.

In the PTCa+Epoxy case (Figure 6), no shift in frequency in the medium frequency peak and no change in the QDC process is observed.

For the LIMM measurements the distribution of polarization is obtained from the mathematical deconvolution of the experimental complex pyroelectric current for each side of the sample. The spatial distribution obtained by the present calculation assumes a mean value of the polarization of 0.1 Cm<sup>-2</sup> and calculates the deviation from this value. The fundamental LIMM equations are [11],

$$\frac{I_i}{I^0} = 1 - \int_0^l \left\{ \frac{\sinh[\nu(i-y)]}{\sinh(\nu)} - (i-y) \right\} \phi dy$$
(6)

$$\phi = C \frac{dP}{dy} \tag{7}$$



Fig. 6 Dielectric spectroscopic data for different volume fractions of the polarized (poled with a field of 20 MV/m at 80 °C during 30 minutes) composite PTCa+Epoxy at RT

$$v = \left(\frac{\omega}{2k}\right)^{1/2} d(1+j)$$

$$C = \frac{-(\alpha_P + \alpha_x - \alpha_\varepsilon)}{p}$$
(9)

where y=x/d is the normalized position along the thickness direction,  $I^0$  the current at zero frequency, P the polarization, measured from the mean value  $P_0$ , i is equal to 0 for the side x=d and i is equal to 1 for the sample side x=0,  $k(=4\times10^{-8} \text{ m}^2/\text{s})$  is the thermal diffusivity of the sample,  $\alpha_p$  (=-2.5×10<sup>-4</sup> k<sup>-1</sup>),  $\alpha_x$ (=1.4×10<sup>-4</sup> k<sup>-1</sup>),

and  $\alpha_{\varepsilon}(=-1.8\times10^{-3} \text{ k}^{-1})$  are the relative temperature dependence of the polarization, the thermal expansion coefficient and the permittivity respectively and  $p(=6\times10^{-6} \text{ Cm}^2/\text{K}, =10\times10^{-6} \text{ Cm}^2/\text{K}, =30\times10^{-6} \text{ Cm}^2/\text{K}$ and  $=45\times10^{-6} \text{ Cm}^2/\text{K}$  for the PTCa+Epoxy 50+50%, 60+40%, PTCa+P(VDF-TrFE) 50+50\% and 65+35%cases respectively) is the pyroelectric coefficient. It has been shown that a 10% variation of the diffusion coefficient does not produce a significant difference in the spatial distribution of polarisation of polarisation and space charge [9].  $I_0$  and  $I_1$  are the pyroelectric currents when the laser beam impinges on the surfaces x=d and x=0 respectively and the other parameters have been already defined.

Equation 6 can be calculated by numerical integration. For this, the range of integration is divided into m intervals of size h=1/m, with m=25, within which  $\phi$  is assumed to be constant( $=\phi_j$ ). Then approximations for each side are given by the expression,

$$\frac{I_i}{I^0} \cong 1 + (-1)^i \sum_{j=1}^m \phi_j \left[ \frac{\cosh(vy)}{v\sinh(v)} - \frac{y^2}{2} \right]_{y=\frac{(-1)^i j + i(m+1) - 1}{m}}^{y=\frac{(-1)^i j + i(m+1) - 1}{m}}$$
(10)

To match the experimental values to the model it is necessary to choose the set  $\{\phi_i\}$ , which minimises

$$\sum_{\omega} \left\{ \left| \frac{(I_1)_{\exp}}{I^0} \right| - \left| \frac{I_1}{I^0} \right| \right\}^2 + \sum_{\omega} \left\{ \left| \frac{(I_0)_{\exp}}{I^0} \right| - \left| \frac{I_0}{I^0} \right| \right\}^2 + \lambda \sum_{j=2}^m (\phi_j - \phi_{j-1})^2 \right\}^2$$
(11)

Finally, the polarization, P, can be found by numerical integration of the set  $\{\phi_j\}$  using the trapezoidal rule. The last term in Equation 11 is a smoothing term, and has to be chosen small but non-zero such that the computed solution does not contain any numerically induced violent oscillation. The minimization of Equation 11 was carried out using a computer minimization routine from the





G library [12]. Note that the x=d side of the sample s connected to the positive polarity of the poling volt-. It may be expected that hole injection can occur, the charge location will occur close to the surface ion.

In Figure 7 is shown the spatial distribution of polarion for all the samples. For the Epoxy samples the ribution is very close to the assumed mean value (0.1 n<sup>2</sup>). Near the surfaces some deviation is observed due surface properties. In the P(VDF-TrFE) composites re deviation from the mean value is observed. It uld be noted that P(VDF-TrFE) has piezoelectric d<sub>33</sub>,

fficient which has an opposite polarisation to that of PTCa ceramic. Secondly, it is established [18] that efficiency of the hole injection in this polymer is ater than that of the electrons. It is suggested that the erved asymmetry of the polarisation distribution for two cases of PTCa+P(VDF-TrFE) composites (in ticular the 65+35% case) may be explained by the ve observations.

mowledgement Acknowledgements are due to Mr J. Hornsby his help in the LIMM data analysis. One of the authors Marin-Franch) is grateful to British Aerospace (BAE) Systems his maintenance grant.

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Ferroelectric thin films of ceramic/polymer composite sensors with mixed connectivities possess high values of piezo- and pyroelectric coefficients and the formability and flexibility which are not attainable in a single-phase ferroelectric material, i.e., an electroceramic or a polymer. The present paper reports a study of the pyro-, piezoelectric and dielectric properties of the ceramic/polymer composite films composed of the calcium modified lead titanate (PTCa) ceramic and the non-polar thermoplastic polymer, polyetherketoneketone (PEKK). The pyroelectric coefficient has been measured both by a direct method and the thermal step technique. Dielectric spectroscopy measurements were carried out in the frequency range of 10<sup>-5</sup> Hz to 10<sup>6</sup> Hz at room temperature. Additionally, the magnitude of the piezoelectric coefficient d<sub>33</sub> and an estimation of the k<sub>t</sub> coefficient are also reported. Furthermore, Scanning Electron Microscope (SEM) pictures are included in order to show the inner structure. i.e., mixed connectivity of the ceramic/polymer reported.

# THEORETICAL INTRODUCTION

PTCa/PEKK composites may be used as smart piezoand pyroelectric sensors for diverse applications. In these electroactive polar composites, the dielectric, piezo- and pyroelectric properties are interrelated. The present paper provides information on the nature of behavior of these properties.

#### **Dielectric spectroscopy**

Dielectric relaxation study in polar materials using dielectric spectroscopy in a wide frequency range allows characterising PTCa/PEKK composites. Capacitance and conductance measurements provide the values of permittivity ( $\epsilon$ ') and dielectric loss ( $\epsilon$ '') in the frequency range of 10 Hz to 10<sup>6</sup> Hz.

$$\varepsilon' = \frac{Cd}{A\varepsilon_0}$$
(1)  
$$\varepsilon'' = \frac{Gd}{2\pi f A\varepsilon_0}$$
(2)

where C and G are the capacitance (F) and conductance (S) of the sample respectively,  $\varepsilon_0$  the permittivity of the free space (F/m), d the thickness of the sample (m), A the area of the electrode (m<sup>2</sup>) and f the frequency (Hz). Additionally, the discharge current measurements provide the values of dielectric loss ( $\varepsilon$ '') in the

frequency range of  $10^{-5}$  Hz to  $10^{-2}$  Hz by means of the Hammon approximation (1), which has the form,

$$\varepsilon'' = \frac{I(t)d}{2\pi f A \varepsilon_0 V}$$
(3)

where V is the applied voltage (v), I(t) the magnitude of the discharge current (A) at a time t (s) after the removal of the voltage f the Hammon frequency (f=0.1/t), and the rest of the parameters have the usual meaning. A fitting calculation of the dielectric loss can be carried out in order to combine the dielectric loss data using the universal 'law' proposed by Jonscher (2), which has the form,

$$\varepsilon''(f) \propto \frac{1}{(f/f_p)^{-m} + (f/f_p)^{1-n}}$$
 (4)

where  $0 \le m \le 1$  and  $0 \le n \le 1$  are arbitrary fitting parameters and  $f_p$  is the peak frequency. In addition, Jonscher pointed out that carrier dominated systems exhibit a low frequency dispersion (LFD) (1). This dispersion occurs at very low frequencies. Below a certain critical frequency  $f_c$ , no loss peak is observed, instead the response rises steadily towards low frequency, obeying a power law, with a small value of n (1). The LFD process add an additional term to the Jonscher function of the form,

 $\varepsilon'' \propto f^{n-1}$  (5)

Using the Krammer-Kronning relations (2),  $\varepsilon'(f)$  can be obtained from  $\varepsilon''(f)$ 

$$\varepsilon'(f) = \varepsilon'_{\infty} + P \int_{-\infty}^{\infty} \frac{\varepsilon''(x)}{(x-f)} dx$$
(6)

where P is Cauchy principal value and  $\varepsilon_{\infty}$  is the value of  $\varepsilon'(f)$  at frequencies which are too high for the permanent dipoles to follow. This provides the values of  $\varepsilon'(f)$  in the frequency range of 10<sup>-5</sup> Hz to 10<sup>6</sup> Hz. It will be observed in the discussion section that this fitting agrees with the experimental data obtained by means of bridge measurements for  $\varepsilon'(f)$  in the frequency range of 10 Hz to 10<sup>6</sup> Hz.

# **Pyroelectric coefficient**

Pyroelectricity and Piezoelectricity refer to changes in the internal charge distribution in a material arising from small changes in temperature and stress respectively. Pyroelectric coefficient can be either measured using direct or dynamic methods. Both methods are reported in this work. In the direct method (3), the change of the dielectric displacement D ( $C/m^2$ ), with temperature gives an expression for the pyroelectric responses. The relationship between

where E is the electric field (V/m) and P is polarisation  $(C/m^2)$ . For a poled sample with the shorted electrodes, i.e., E=0,

 $D = \varepsilon_0 E + P$ 

$$\begin{pmatrix} \frac{\partial D}{\partial T} \end{pmatrix}_{E=0,X} = \left( \frac{\partial P}{\partial T} \right)_{E=0,X}$$

$$= \left( \frac{\partial (Q/A)}{\partial T} \right)_{E=0,X} \approx \frac{1}{A} \left( \frac{\partial Q}{\partial T} \right)_{E=0,X}$$
(8)

where Q is the liberated charge (C) and X the stress  $(N/m^2)$ . It is assumed an electrode area A constant for changes in temperature. The pyroelectric coefficient p (C m<sup>-2</sup> K<sup>-1</sup>), may be expressed,

$$p = \frac{1}{A} \left( \frac{\partial Q}{\partial T} \right)_{E=0,X} = \frac{1}{A} \frac{\partial Q}{\partial T} \frac{\partial t}{\partial T} = \frac{1}{A} I \frac{\partial t}{\partial T}$$
(9)

where I is the current through the sample when the electrodes are short circuited and  $\partial T/\partial t$  is the rate of rise of sample temperature. In the dynamic method, an input step heat is applied to the sample. This generates a transient current, which has the form (4),

$$I(t) = \frac{F_0 Ap(T)}{\rho c_p d} \left[ exp(-t/\tau_{th}) - exp(-t/\tau_e) \right]$$
(10)

where  $F_0$  is the radiation power absorbed per unit area of the electrode material (W/m<sup>2</sup>),  $\rho$  is the density (Kg/m<sup>3</sup>),  $c_p$  is the specific heat (J Kg<sup>-1</sup> K<sup>-1</sup>),  $\tau_e$  and  $\tau_{th}$  are the electrical and thermal time constants (s) respectively and the other parameters have the usual meaning. It can be shown (4) from equation 10 that the maximum value of the intensity I<sub>p</sub>, is,

$$I_{p}(t) = \frac{F_{0}Ap(T)}{\rho c_{p}d} \theta \left[ \theta / (1-\theta) \right]$$
(11)

where  $\theta$  is  $\tau_c/\tau_{th}$ . From equation 11 the pyroelectric coefficient may be obtained.

# **Piezoelectric coefficients**

The piezoelectric strain coefficient  $d_{ij}$  (C/N) may be defined from the change of the dielectric displacement with the stress. The piezoelectric coefficient can be defined in a similar way as has been defined the pyroelectric coefficient, i.e.,

$$d_{ij} = \frac{1}{A} \left( \frac{\partial Q}{\partial X} \right)_{E=0,T}$$
(12)

where i= 1, 2 and 3, j= 1, 2, 3, 4, 5 and 6 and the other parameters have the usual meaning. The electromechanical coupling factor  $k_t$ , is an important quantity to characterise a piezoelectric transducer and it is defined as,

$$k_t^2 = \frac{\text{output electrical energy}}{\text{input mechanical energy}}$$
(13)

A high value of  $k_t$  is desirable in order to have a good piezoelectric transducer. A  $k_t$  value may be obtained from the measurement of the complex impedance Z(f),

of the transducer vibrating as a free resonator around its resonant peak. It may be showed that the expression for the complex impedance, can be expressed in the form (5, 6 and 7),

$$Z(f) = R + \frac{A}{f^{\alpha}} - i \frac{B}{f^{\beta}} + i \frac{R_{max}}{(1 + if\psi/f_0)^{1/2}} \left(\frac{f_0}{f}\right)^2 \tanh\left(\frac{\pi\psi}{4}\right) \tan\left(\frac{\gamma l}{2}\right)$$
(14)

where  $\gamma = \pi f/(f_0(1+i\psi f/f_0))$  is the wave number,  $\psi$  is the mechanical loss,  $f_0$  is the resonance frequency,  $R_{max}$  is the amount of increase of the real part of the impedance in the resonance frequency from the base line, R is the value of the real part of the impedance at high frequencies, A and  $\alpha$  are related with the real part slope and B and  $\beta$  are related with the imaginary part slope. The experimentally determined impedance can be fitted using equation 14 upon optimisation of these parameters. The optimised  $k_t$  value, after some manipulations, is given by the expression (7),

$$k_t^2 = \frac{1}{2} \pi^2 R_{\max} f_0 C_0 \left( \psi^2 + 4 \right)^{1/2} \tanh(\pi \psi / 4)$$
 (15)

where  $C_0$  is the sample capacitance. Other material properties can also be calculated from these fitted parameters, such as the velocity of sound  $v_s$ , mechanical loss  $\psi$ , etc.

# PTCa/PEKK COMPOSITE FABRICATION

The aim in the development of these materials is to obtain a combination of properties, which are not available in a single-phase material. Making a composite by combining a ceramic and a polymer means not only choosing the right materials to be processed, but also coupling them with the best possible design structure. There is a trade off between the properties of the materials involved in the process. It is clear that the fabrication method will influence the final properties of the material. In that sense, the relative amounts of the constituent phases and the spatial connectivity of the phases will affect the dielectric and electroactive properties. Connectivity describes the interspatial relationships in a multiphase material. The phases in the composite materials may be spatially selfconnected in one or more dimensions. In a two-phase system, there are ten different ways or connectivity patterns of self-connections of the constituent phases. This can be expressed with two digits, denoting the connectivity of the filler and the connectivity of the matrix respectively. The ten cases represented in figure 1 are: 0-0, 0-1, 0-2, 0-3, 1-1, 1-2, 1-3, 2-2, 2-3, and 3-3, where a cube represents the composite block. The first digit refers to the connectivity of the filler and the second that of the host material. The case of a composite made of particles of ceramic powder embedded in a polymer matrix and separated from each other will be indicated as a 0-3 composite, whereas the composite consisting in a filler of fibres implanted on a matrix will be denoted as 1-3 composite. In the composite preparation, the appropriate volume fraction

of the ceramic (PTCa) is added to the polymer (PEKK) and mixed with the help of a solving agent. After that, the mixture is placed in a hot press, and is heated under stress above the melting point of the polymer. Finally, the sample is allowed to cool down to room temperature and the stress is removed then. With this process, thin films of 180 microns thick are obtained. The reported composite in this work has a 30% of volume fraction of ceramic. Due to the low concentration of ceramic, the resulting composite has 0-3 connectivity. From the SEM picture (figure 2) can be observed how the polymer surround the ceramic grains avoiding contact between them and therefore giving a 0-3 connectivity.



Figure 1: Ten different connectivity patterns of diphasic materials (8).

Aluminium electrodes of 1cm of diameter were deposited on the samples by evaporation at  $1200^{\circ}$ C under a vacuum of  $10^{-5}$  torr. After the completion of the electroding process the composite samples were poled under a high field, which had maximum value of 10 MV/m. In the poling process, the composites were heated to  $150^{\circ}$ C of temperature, which is just bellow the polymer glass transition temperature T<sub>g</sub>. The desired poling field is then applied. The current is monitored during the poling process to avoid an electrical breakdown of the sample. The field was applied for 30 minutes holding the temperature constant and the sample was then cooled down under the action of the field.



Figure 2: SEM micrograph of PTCa/PEKK 30/70 %vol composite showing a 0-3 connectivity. The large bar indicates 10 µm.

# MEASUREMENTS AND DISCUSSION

#### **Dielectric measurements**

For dielectric measurements in the frequency range of 10 Hz to 10<sup>6</sup> Hz, the use was made of a General Radio Bridge. Capacitance and conductance measurements were performed as a function of frequency at room temperature in a vacuum chamber. The values of the real  $\varepsilon$ ', and the imaginary parts  $\varepsilon$ '', of the complex permittivity were calculated using equations 1 and 2. For measurements in the frequency range of 10<sup>-5</sup> Hz to 10<sup>-2</sup> Hz discharge current process is used. For this, the dielectric sample was placed in a vacuum chamber and a field of 10<sup>5</sup> V/m was applied for 27 hours. Then, the sample was sort-circuited for 3 hours and the discharge current, I(t), was monitored using a Keithley 617 programmable electrometer. Dielectric loss e", values were calculated from equation 3. As stated before, the high and low frequency values of the dielectric loss were fitted with the universal 'law' (2). Finally, Krammer-Kronning relation (2) were used to obtain ɛ' values in the frequency range of 10<sup>-5</sup> Hz to 10<sup>6</sup> Hz. It may be observed from figure 3 that this fitting agrees with the experimental data obtained by means of bridge measurements for  $\varepsilon$ '(f) in the frequency range of 10 Hz to 10<sup>6</sup> Hz.



Figure 3: Dielectric spectroscopy of the PTCa/PEKK 30/70 %vol for the case of polarised and unpolarised composites.

Figure 3 shows the comparison of the dielectric behaviour of the polarised and unpolarised PTCa/PEKK 30/70 %vol composites cases. As stated before it may be observed that the fitted  $\varepsilon$ ' data agrees with the experimental data. Two peaks are observed in the frequency range of 10<sup>-5</sup> Hz to 10<sup>6</sup> Hz. Also, at very low

frequencies, a steady increase of the loss is observed. Dielectric relaxation peaks are difficult to interpretate due to the complex morphology of the composites. The peaks do not shift with the poling process. PTCa ceramic has a relaxation peak at the GHz range (9) and the relaxation of clustered water has been shown to occur in the MHz region (10); so the peaks observed are due to space charge and ionic impurities. The low frequency peak may be attributed to space charge trapped at the interfaces of the composite. It can be observed that the magnitude of the peak increases after the poling process. This may be due to the injection of charges and subsequent trapping occurring during the poling process. The relaxation peak occurring around 1 Hz is due to ionic impurities. It may be noticed that this peak has been reduced with the poling process. In this case, the injected charges neutralise the dopant ions, thus the ionic peak is reduced. The increase of the dielectric loss at low frequencies is due to mobile charges. The main contribution to this conductive process is due to the ceramic. Also can be pointed out that the permittivity is not substantially improved in the poled composite. This is due to the fact that a DC poling field in 0-3 composites is only partially effective.

#### **Pyroelectric measurements**

Pyroelectric measurements were carried out using both Direct and Dynamic methods.

Direct method. In the direct method, the sample is placed in a vacuum chamber provided with a temperature controller. The sample electrodes are shortcircuited through an electrometer and the temperature is risen at constant rate  $\partial T/\partial t$ , and the pyroelectric current in measured. Thus, the pyroelectric coefficient is obtained using equation 9. In this method a linear heating rate of 1 K/min was used. The value of the pyroelectric current was determined after four thermal runs. In each thermal run, the sample was heated up from room temperature to 130°C and then cooled down again to ambient temperature. This was made in order to remove the trapped charges and obtain the reversible pyroelectric current. The first run shows a large increase of current with no peak up to 130°C. This increase is due to the fact that a peak occurs around the glass transition temperature of the polymer, i.e.T<sub>g</sub>=150 °C. The subsequent runs have a significant reduction of current. In the fourth run no appreciable change occurs in comparison with the previous run (see figure 4). Therefore, the reversible pyroelectric current was achieved after the third run. The dependence of the pyroelectric coefficient with the temperature is obtained from the reversible pyroelectric current using equation 9. The results are represented in figure 5. The observed pyroelectric coefficient at room temperature is  $1.2 \times 10^{-6}$  C/m<sup>2</sup>K. This low value in comparison with other composite materials (5 and 11) is mainly due to the low concentration of ceramic, only 30% volume fraction. Current work in the production of composites with higher concentration of ceramics is in progress.



Figure 4: Thermally stimulated currents in PTCa/PEKK 30/70 %vol composite (E=10MV/m, T=150<sup>o</sup>C).



Figure 5: PTCa/PEKK 30/70 %vol pyroelectric coefficient dependence with time.

Dynamic Method. In the dynamic method, the sample is placed in a vacuum chamber with a quartz window. An input heat step is applied to the short-circuited sample shinning the sample electrode with a He-Ne laser through the vacuum chamber window. The transient current is measured with the programmable electrometer, which store the data. As stated in equation 10, a peak is observed as a consequence of the subtraction of two exponentials decays as can be observed in figure 6. One exponential decay gives the electric response governed by the electrical time constant  $\tau_{e}$ , and the other gives the response governed by the thermal time constant  $\tau_{Th}$ . The fitting of the experimental data with equation 10 gives the optimised parameters of  $\tau_{Th}$  and  $\tau_e$ . The used values for the fitting were:  $F_0=45W/m^2$ ,  $\rho=2.95\times10^3$ Kg/m<sup>3</sup>,  $c_p=1380.3$ J Kg<sup>-1</sup> K<sup>-1</sup>, d=185  $\mu$ m and A=7.854×10<sup>-5</sup>m<sup>2</sup>. This gives a value of  $\theta = \tau_e / \tau_{th} = 0.386$ . Thus, from equation 11 with  $I_p=9.5\times10^{-13}$ A, the resulting value of the pyroelectric coefficient at room temperature is  $10^{-6}$ C/m<sup>2</sup>K, which agrees with that obtained using the direct method, thus indicating the consistency of the results.



Figure 6: Pyroelectric transient response separated into thermal and electrical components.

#### **Piezoelectric measurements**

A measurement of  $k_t$  may be obtained from the measurement of the complex impedance around the resonant peak of the composite material acting as a free resonator. A network analyser, Model HP8702A, was used to measure the real and imaginary part of the complex impedance around the resonant peak of the composite materials. Measurements were made with existing samples of the PTCa/Epoxy 50/50 %vol. The fit of the real and imaginary parts of the complex impedance around the resonance peak gave the values of  $\psi$ =0.096, f<sub>0</sub>=13.25MHz, R<sub>max</sub>=27.65 and C<sub>0</sub>=98.5pF which used in equation 15 result in k<sub>t</sub>=0.16, see figure 7.



Figure 7: Experimental and theoretical real and imaginary impedance of PTCa/Epoxy 50/50% composite around resonant peak, with  $k_t=0.16$ .

In the case of the PTCa/PEKK 30/70 %vol composite. no resonance peak was observed. This is due to the low concentration of ceramic of the composite, which will have the resonance peak at too high frequencies for the network analyser to measure. An estimation of the kt coefficient was then performed with information available in bibliography (6, and 12). Values of kt were plotted against different volume fraction of the PTCa ceramic with the thermoplastic copolymer P(VDF-TrFE). From the extrapolation for the 30 % vol of ceramic case, an estimated value of 0.16 was obtained for the PTCa/PEKK 30/70 %vol. The d<sub>33</sub> coefficient was measured applying a stress in the direction of the thickness of the samples and the produced voltage was measured in the electrodes using a Pennebaker Model 8000 Piezo d<sub>33</sub> tester. Prior calibration of the instrument needs to be undertaken with a well-aged known ceramic. Values of 23 pC/N, 12pC/N and 8 pC/N were obtained for the PTCa/PEKK 30/70 %vol poled with a 10MV/m, 5MV/m and 1MV/m of poling field, respectively. This indicates a good piezoelectric response of the transducer, which can be improved with higher concentration of the ceramic. The composite properties studied in this work are reported in table 1.

<u>Table 1: PTCa/PEKK 30/70 vol% properties at room</u> temperature. Poling field E=10MV/m.

ρ	2.95 gr cm <sup>3</sup>
$k_t$	0.16
ε'(IkHz) polarised	10.46
ε''(1kHz) polarised	0.14
<i>d</i> <sub>33</sub>	23 pC/N
p	$1.2 \ \mu Cm^{-2}K^{-1}$

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# DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF THE PTCa/PEKK COMPOSITE SENSORS

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Ferroelectric thin films ceramic/polymer composite sensors with mixed connectivities possess high values of piezo- and pyroelectric coefficients and the formability and flexibility which are not attainable in a single-phase ferroelectric material, i. e., an electroceramic or polymer.

The results of a study of dielectric and piezoelectric properties of calcium modified lead titanate (PTCa) and a non-polar polymer, polyetherketoneketone thermoplastic resin (PEKK) for different volume fractions of ceramic/polymer is reported in this paper. Dielectric spectroscopy measurements were carried out in the frequency range of  $10^{-5}$  Hz to  $10^{6}$  Hz. Additionally the calculations of several piezoelectric properties such as  $d_{33}$ ,  $d_{31}$  and  $k_t$  will also be reported.

Furthermore, Scanning Electron Microscope (SEM) pictures are included in order to show the inner structure, i.e., mixed connectivity of the ceramic/polymer composite and its contribution to the piezoelectric response.

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