Chapter 1

Introduction

Fore more than a decade, composite piezoelectric materials have yielded a rich trove of research ideas to enhance the performance of acoustic transducers. A variety of composite piezoelectric materials can be made by combining a piezoelectric ceramic with a passive polymer phase. These new piezoelectrics greatly extend the range of material properties offered by the conventional piezoelectric ceramic and polymer.

Recently, composite piezoelectrics have been fruitful for applications in transducers of pulse-echo medical ultrasonic imaging. These medical transducers are made from PZT-rod/polymer composite. There are several requirements for the piezoelectrics used in these transducers. First, for sensitive transducers, the piezoelectrics must efficiently convert between electrical and mechanical energy. Second, the piezoelectric must be acoustically matched with tissues so that the acoustic waves in the transducer and tissue couple well both during transmission and reception. Third, the electric properties must be compatible with the driving and receiving electronics. Composite piezoelectric gives their needs.

Combining PZT particles and a polymer matrix can give advantages of mechanical flexibility and low acoustic impedance while retaining useful pyroelectric and piezoelectric properties. Such materials have a considerable potential in sensor and transducer applications, due especially to the possibility of tailoring its properties to specify by a judicious selection of constituent components and of the volume ratio.

1. Literature Reviews

Piezoelectricity had been observed in 1880 and many types of materials had been investigated this properties ever since. A historical review of these measurements and some of theoretical principle of this effect clearly showed that piezoelectricity has continued to interest and puzzled the investigators for over a century. Newnham, Skinner and Cross were probably the first to propose the possibility of a piezo-and pyroelectricity in ceramic-polymer composites. They found that the connectivity is a critical parameter in composites design to use as piezoelectric transducers or as pyroelectric detectors. There are ten important connectivity patterns in diphasic solids, ranging from 0-0 unconnected checkerboard pattern to 3-3 pattern in which phases three-dimensionally self-connected. Their series and parallel models for composite piezoelectric and pyroelectric lead to several interesting results, such as a diphasic pyroelectric in which neither phase is pyroelectric. The models are also helpful in interpreting the structure-property relations in single-phase material where the crystal structures mimic certain connectivity pattern (Newnham, Skinner and Cross, 1978).

In 1989, Smith found that combining a piezoelectric ceramic and a passive polymer to form a piezocomposite allowed the transducer engineers to design new piezoelectrics that offer substantial advantages over the conventional piezoelectric ceramic and polymer. He shown that the rod composite geometry provided materials with enhanced electromechanical coupling and with acoustic impedance close to that of tissue; these advantages made transducers capable for medical ultrasonic imaging with high sensitivity and compact impulse response. A dice-and-fill technique was used to produce piezocomposites that easily formed into complex shapes to facilitate focusing the ultrasonic beam (Smith, 1989). In the same year, Chan and Unsworth presented a theoretical model for 1-3 composite materials to predict ultrasonic characteristics such as velocity, acoustic impedance, electromechanical coupling factor and piezoelectric coefficients. This model suggested the estimation of resonance frequencies of 1-3 composite transducers (Chan and Unsworth, 1989).

A few years later Smith presented a simple physical model of 1-3 composite piezoelectrics that advanced for the material properties relevant to thickness-mode oscillation (Smith, 1991). Expressions were derived for the composite's material parameters in terms of the volume fraction of piezoelectric ceramic and properties of the constituent piezoelectric ceramic and passive polymer. This model illustrated that the composite structure enhanced its hydrostatic charge coefficient, d_h, hydrostatic voltage coefficient, g_h and hydrostatic coupling factor, k_h, while three quantities falled short of their pure ceramic values in the modified PZT composites. The shortfall was due to a enhance composite d_{31} that arise from lateral stress on the polymer being transferred to a longitudinal stress along the ceramic rods by Poison effect in polymer, thus producing a charge through the ceramic's d_{33} (Smith, 1993).

In 1994, Taunaumang and Guy studied the fabrication and electromechanical properties of the piezoelectric 1-3 ceramic/polymer composites. The composites were prepared by both layering and dice-and-fill techniques. The electromechanical properties of the composites were measured and compared with a modeling result. It was found that the composite properties agreed with the model predictions, with exception of the piezoelectric coefficients, which were significantly lower than predicting (Taunaumang and Guy, 1994). Dias and Das-Gupta presented the piezo-and pyroelectric properties exhibition by composites with 0-3 connectivity type. A review of the electroactive properties predicting model of 0-3 composites was presented together with a proposal for a new mixed connectivity cubes model to be applicable in the case of high ceramic loading and/or when the ceramic grain size incorporated in the polymer matrix was comparable to the thickness of the sample. They also presented the experimental results of the piezo-and pyroelectric properties of various ferroelectric composite materials (Dias and Das-Gupta, 1994).

Kwok et al. fabricated 1-3 composites of PZT in the P(VDF-TrFE) copolymer by embedding pre-sintered PZT rods in a pre-poled copolymer matrix. The following were observed (Kwok, Chan and Choy, 1995):

1. The characteristic resonance of the individual PZT rods were clearly observable. The copolymer matrix did not significantly modify the characteristic resonance of the individual PZT rods, because the soft copolymer matrix did not impose an appreciable clamping on the rods.
2. The thickness resonance of the poled copolymer matrix was very weak and, in the sample geometry, merged with the PZT resonance to form a broad resonance peak.
3. The resonance characteristics of the composites with PZT and copolymer poled in the same direction and oppositely were quite similar. Higher electromechanical coupling constant, k_t, is obtained if the two phases were poled in the same direction.

4. The radial mode resonance of the 1-3 composites depended only on the diameter of the sample but independent of sample poling history.

Kwok, Chan and Choy evaluated the elastic, dielectric and piezoelectric constants of four piezoelectric materials, including polyvinylidene fluoride (PVDF), vinylidene fluoride-trifluoroethylene copolymer (P(VDF-TrFE)), PZT/epoxy 1-3 composite, and lead metaniobate ceramic using five different methods: the IEEE Std. 176 method, the method of Smits, the method of Sherrit et al., a software package "Piezoelectric Resonance Analysis Program (PRAP)", and a nonlinear regression method. The IEEE Std. 176 method was strictly valid only for lossless materials. They have found that it was applicable to material with moderate loss, in agreement with generally accepted practice. However, for high-loss materials such as PVDF, the k_t value evaluated using this method was much higher than the value determined by the nonlinear regression method (Kwok, Chan and Choy, 1997).

Levassort and Lethiecq presented a model for prediction the effective electroelastic moduli of a piezocomposite according to its connectivity (Levassort and Lethiecq, 1998). Geng, Ritter and Shung fabricated 1-3 PZT/polymer composites using a polymer possessing a high glass transition temperature and low loss. They found that the composites could be used as high power ultrasonic transducer materials for high intensity focused ultrasound (HIFU) application (Geng, Ritter and Shung, 1999).

In 1999, Chan, Ng and Choy fabricated 0-3 composite PZT/P(VDF-TrFE) by incorporating PZT powder into a P(VDF-TrFE)copolymer matrix. In this work, original experimental results on the properties of 0-3 composite PZT/P(VDF-TrFE) poled under different condition were reported and possible reasons behind the reinforcement and cancellation of piezoelectric and pyroelectric properties were reported (Chan, Ng and Choy, 1999). In same year, Lau et al. measured the piezoelectric coefficient of the 0-3 composite PZT/P(VDF-TrFE) using laser interferometric technique. The composites poled in the opposite direction is order to enhance the piezoelectric activity. A needle type hydrophone for calibration of medical ultrasonic transducers was fabricated using the nanocomposite as the sensing element and its performance was evaluated (Lau et al., 1999).

Burianova and Prokopova measured piezoelectric coefficient of PZT ceramic and the ceramic-polymer 0-3 composites by resonance and laser interferometric methods. The obtained results d_{33} coefficients by the both methods were in good agreement (Burianova and Prokopova, 2001). Ng, et al. showed that 0-3 composites of lead zirconate titanate particles dispersed in a polyvinylidene fluoride-trifluoroethylene copolymer matrix may have a good potential for pyroelectric sensor application (Ng, et al., 2001). Table 1.1 gives the value of the material parameter of the composites as reported in the literatures.

Table 1.1 Values of the material parameter of the composites as reported in the literatures

Reference	Type	value	Method
Chan, 1989	1-3 composite PZT/epoxy	$d_{33} = 163 - 167\ pm/V$ $k_p = 0.29 - 0.33$	Resonance
Taunaumang and Guy, 1994	1-3 composite PZT/P(VDF-TrFE)	$d_{33} = (-7) - (-29.6)\ pC/N$ $d_h = (-2) - (-11)\ pC/N$ depend on poling direction	Resonance
Kwok, et al., 1995	1-3 composite PZT/P(VDF-TrFE)	$k_t = 0.13 - 0.45$ depend on poling direction	Quasi-static
Lau et al., 1999	0-3 composite PZT/epoxy	$d_{33} = 1.8 - 8\ pm/V$ depend on poling direction	Mach-Zehnder Interferometer
Burianova et al., 2001	0-3 composite PZT/P(VDF-TrFE)	$d_{33} = 7.8\ pm/V$	Interferometer

In 1971, Fabel and Henisch presented a technique which could be used for the pyroelectric coefficients determination in polar crystals. Their procedure was based on a simple relationship derived from an equivalent circuit which regarded the material as a constant current generator. The measured coefficient was free from contributions arising from tertiary pyroelectricity when special precautions were taken, by the proper design and adjustment of the specimen heaters to minimize non-uniform heating (Fabel and Henisch, 1971). Byer and Roundy described a direct method for measuring pyroelectric coefficient in 1972. Their method was more straightforward that eight the charge distribution technique or dynamic method (Byer and Roundy, 1972).

Ploss and Domig measured the pyroelectric coefficient of the PVDF under quasistatic and dynamic conditions. They found that the quasistatic measured pyroelectric coefficient was higher than the dynamic one, with a quotient of both quantities up to three (Ploss and Domig, 1994).

Chan, et al. showed that the changes in the pyroelectric and piezoelectric coefficients of the poled 0-3 composites PT/P(VDF-TrFE) with increasing ceramic volume fraction could be described by modified linear mixture rules. In 2000, Ng, Chan and Choy showed that the pyroelectric activities of the 0-3 composite PZT/P (VDF-TrFE) will reinforce and the piezoelectric activities will partially cancel if the ceramic and copolymer phases were poled in the same direction. On the other hand, when the ceramic and copolymer phases were poled in opposite directions, their piezoelectric will reinforce while their pyroelectric activities will partially cancel (Ng, Chan and Choy, 2000).

A technique based upon heating of one surface of the sample to obtain the thermal diffusivity of the sample was first proposed by Ångström as described by Parrott and Stuckes. Contemporary implementations of the technique used samples in the form of long rods with incandescent lamp or thermojunction joint. Cowan applied the periodic heating method to thin plates using electron beam. Lang developed a modification of the technique with intensity-modulated laser beam and measurement of the phase lag in the test sample by means of a polyvinylidene fluoride (PVDF) pyroelectric detector. But PVDF is difficult to pole uniformly making it a less desirable pyroelectric detector for this type of measurement. Muensit and Lang presented more sophisticated model for thermal analysis. Litium tantalate was selected in their work because of its uniformly polarization and great stability (Muensit and Lang, in press).

2. Objectives

The overall objective of this dissertation is to carry out the piezoelectric measurement on the composites. It also our aim to study the pyroelectric response of the composite. These goals will be achieved by:

1. Preparing the composite materials of PZT and polymer.
2. Studying the piezoelectric response of the composites using interferometric technique.
3. Studying the possibility of the pyroelectric response in the composite.