CHAPTER 3

EXPERIMENTAL PROCEDURE

The modified barium titanate-Portland cement composites with 0-3, 1-3 and 2-2 connectivity were investigated. Piezoelectric-cement based composites were produced using barium zirconate titanate (BZT) ceramic and Portland cement (PC). The 0-3 modified barium titanate-Portland cement composites were fabricated by normal mixing, pressing and curing method. The 1-3 and 2-2 modified barium titanate-Portland cement composites were fabricated by the dice-and-fill method. The properties of composites were studied by using measuring instruments such as LCR-meter, d_{33} meter, impedance meter, ultrasonic thickness meter, LVDT dilatometer, SEM and EDS. The research plan, methodology and scope are represented in the flowchart (Fig. 3.1).

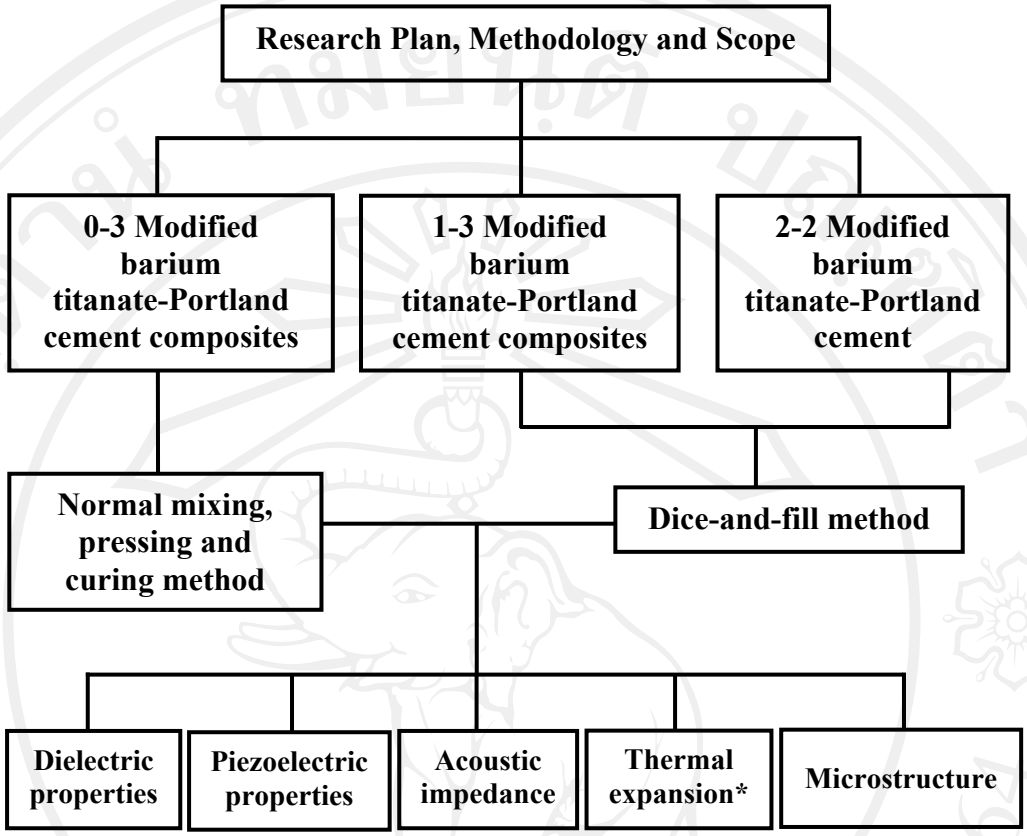

Fig. 3.1 Flow chart of research plan, methodology and scope.

Note: * thermal expansion measurement for 0-3 modified barium titanate-Portland cement composites

3.1 Materials and Fabrication

3.1.1 Modified barium titanate ceramic fabrication

Barium zirconate titanate; BZT

The starting materials used in producing BZT ceramic are listed in Table 3.1, along with the supplier, name and purities.

Table 3.1 Specifications of the starting materials for BZT ceramic.

Oxide	Manufacturer	Purity (%)
$BaCO_3$	Sigma-Aldrich*	≥ 99.0
ZrO_2	Riedel de Haën**	99.0
TiO_2	Sigma-Aldrich*	≥ 99.0

Note: * Sigma-Aldrich, INC, USA and Chemie GmbH, Germany

** Riedel deHaen Laborchemikalin GmbH&Co. KG, France

$Ba(Ti_{0.95}Zr_{0.05})O_3$, (BZT)

$$BaCO_3 + 0.95TiO_2 + 0.05ZrO_2 \longrightarrow Ba(Ti_{0.95}Zr_{0.05})O_3 + CO_2(g) \quad (3.1)$$

The conventional ceramic fabrication technique was used to prepare BZT ceramic. The powder of BaO, ZrO_2 and TiO_2 were used as starting raw materials. All of the materials were dried at 100 °C to remove any moisture, and then weighed according to the formulations. These materials were mixed by ball-milling in ethanol with zirconia balls for 24 h. The dried powders were calcined in alumina crucibles at ≈1,200 °C for 2 h. The polyvinyl alcohol (PVA) of 3 wt% binder were then added to the calcined powders and were pressed into disc-shape pellets with a diameter ≈ 12 mm and thickness ≈ 2 mm. After the binders have been burned out at 500 °C for 1 h and the green pellets were sintered at ≈1,450 °C for 2 h.

3.1.2 Composite fabrications

0-3 modified barium titanate-Portland cement composites

Barium zirconate titanate ceramic and cement (ordinary type: ASTM type I cement) were used to prepare 0-3 connectivity Barium zirconate titanate-Portland cement composites (0-3 BZT-PC composites). The particle size distributions of piezoelectric ceramic were measured by sieving techniques. BZT ceramic particles were then obtained by grinding the ceramics and sieved to a desired various particle sizes (75, 212 and 425 μm) content at 50% ceramic composite. For effect of volume fraction, ceramics particles of different ceramic content at 30%, 40%, 50%, 60% and 70% by volume were then mixed with normal Portland cement (PC) to produce 0-3 connectivity BZT-PC composites. The composites and ceramic size details can be seen in Table 3.2. The composites were pressed into the model disks (Fig. 3.2) of ≈12 mm in diameter and ≈1.5 mm in thickness using hydraulic press (Fig. 3.3). Thereafter, the composites were put in the curing chamber (Fig. 3.4) for 3 days in a controlled 60°C, 98% relative humidity (RH) chamber before measurements. The fabrication of 0-3 BZT-PC composites is represented in the flowchart in Fig 3.5.

Table 3.2 Composition of 0-3 BZT-PC composites.

Material	% Volume of ceramic	ceramic particle size (μm)
0-3 BZT-PC	0, 30, 40, 50, 60, 70 and 100	75, 212 and 425

Fig. 3.2 The model for fabricating 0-3 BZT-PC composites.

Fig. 3.3 The hydraulic press.

Fig. 3.4 The curing chamber.

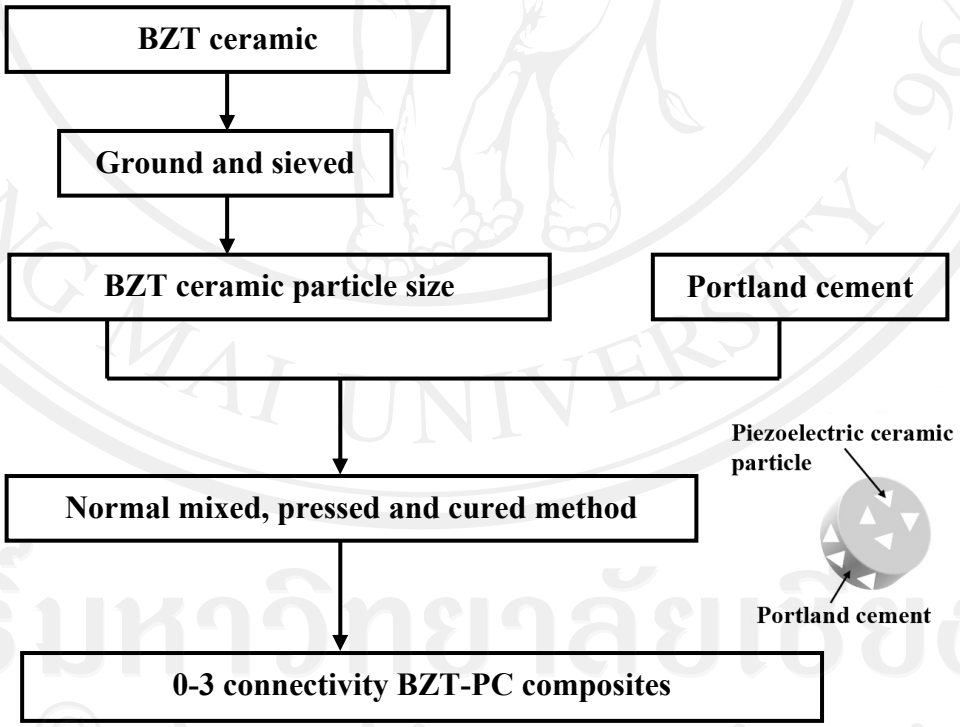

Fig. 3.5 Flow chart of 0-3 BZT-PC composites fabrication.

1-3 modified barium titanate-Portland cement composites

The 1-3 connectivity barium zirconate titanate-Portland cement composites (1-3 BZT-PC composites) were fabricated by the dice- and-fill technique [7] with different BZT ceramic contents at 30±2%, 40±2%, 50±2%, 60±2% and 70±2% by volume. First, the piezoelectric ceramic (disk samples of ≈ 12 mm diameter and ≈ 1.3 mm thickness) was put into moulds (≈ 16 mm diameter and 7 mm thickness) and the mould was filled with cement paste (water/cement ratio = 0.5). After that, the samples were removed from the moulds and the samples were cured at a temperature of 60 °C for 5 days under a condition of 98% relative humidity.

Fig. 3.6 The diamond saw (Buehler ISO- MET Low speed saw).

A diamond saw (Buehler ISO- MET Low speed saw) was then used to cut the sample in one direction (y axis) first. Fig. 3.6 shows the diamond saw (Buehler ISO-MET Low speed saw). The grooves were then filled with cement paste (water/cement ratio = 0.5) and the samples were cured at a temperature of 60 °C for 5 days under a condition of 98% relatively humidity and cut in the second direction (x axis). After filling the second direction of cuts with cement paste, the composites were cured at a temperature of 60 °C and 98% relative humidity for 5 days. Excess cement was polished using silicon carbide abrasive papers. The composition of 1-3 BZT-PC composites are shown in Table 3.3. The fabrication process of 1-3 BZT-PC composite is represented in the flowchart (Fig. 3.7).

Table 3.3 Composition of 1-3 BZT-PC composites.

Material	**% Volume of ceramic**
1-3 BZT-PC composites	0%, 30±2%, 40±2%, 50±2%, 60±2%, 70±2% and 100%

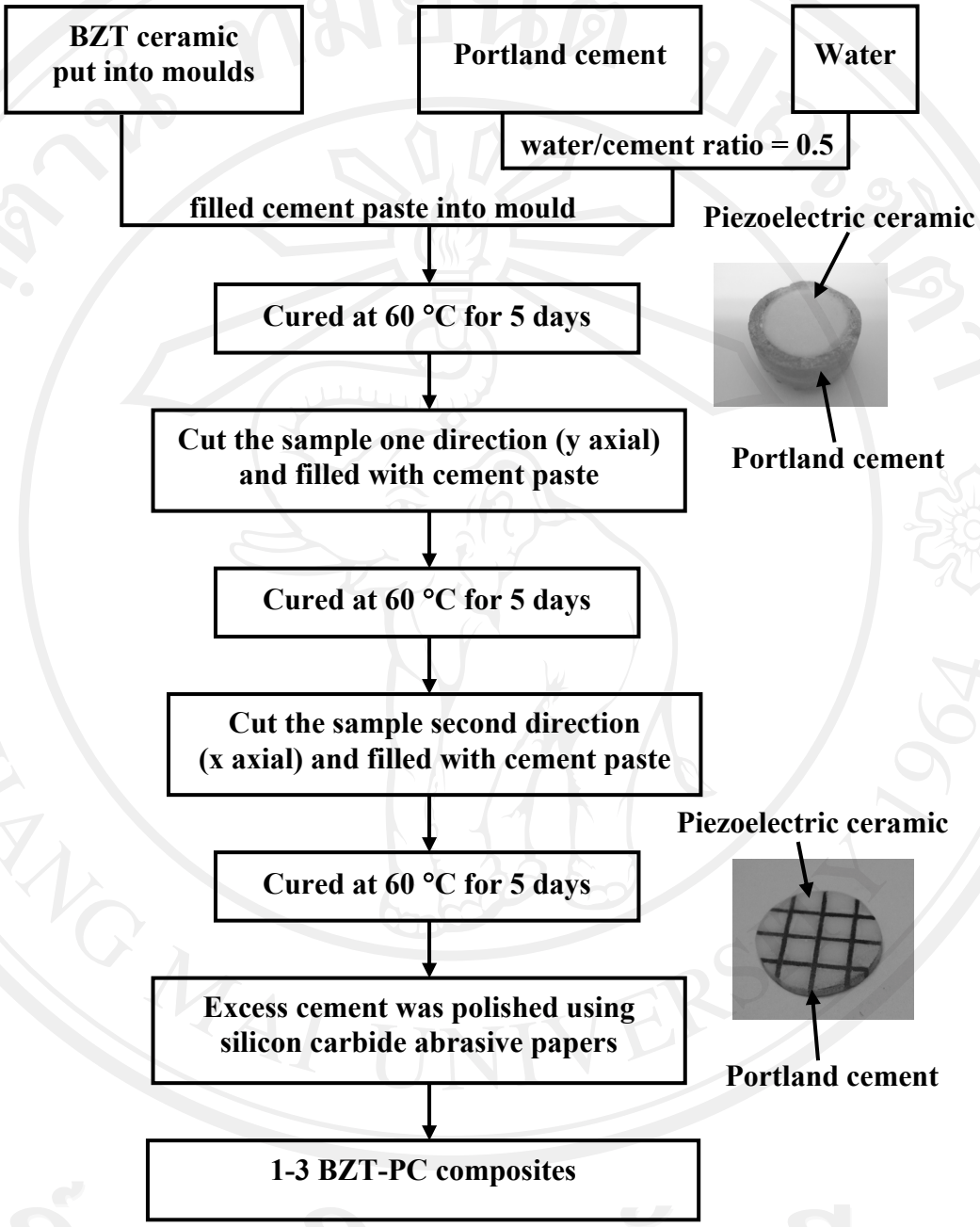

Fig. 3.7 Flow chart of 1-3 BZT-PC composites fabrication.

2-2 modified barium titanate-Portland cement composites

The 2-2 connectivity barium zirconate titanate-Portland cement composites (2-2 BZT-PC composites) were fabricated by the dice- and-fill technique [7] with different ceramic contents at 30±2%, 40±2%, 50±2%, 60±2% and 70±2% by volume. First, the piezoelectric ceramic (disk samples of ≈ 12 mm diameter and ≈ 1.3 mm thickness) was put into moulds (≈ 16 mm diameter and 7 mm thickness) and the mould was filled with cement paste (water/cement ratio = 0.5). After that, the sample was removed from the moulds and the sample was cured at a temperature of 60 °C for 5 days under a condition of 98% relatively humidity. A diamond saw (Buehler ISO-MET Low speed saw) was used to cut the sample in one direction. The grooves were then filled with cement paste (water/cement ratio = 0.5) and the samples were cured at a temperature of 60 °C for 5 days under a condition of 98% relatively humidity. Excess cement was polished using wet silicon carbide abrasive papers. The details of composition of 2-2 BZT-PC composites can be seen in Table 3.4. The fabrication process of 2-2 BZT-PC composites is represented in the flowchart (Fig. 3.8).

Table 3.4 Composition of 2-2 BZT-PC composites.

Material	% Volume of ceramic
2-2 BZT-PC composites	0%, 30±2%, 40±2%, 50±2%, 60±2%, 70±2% and 100%

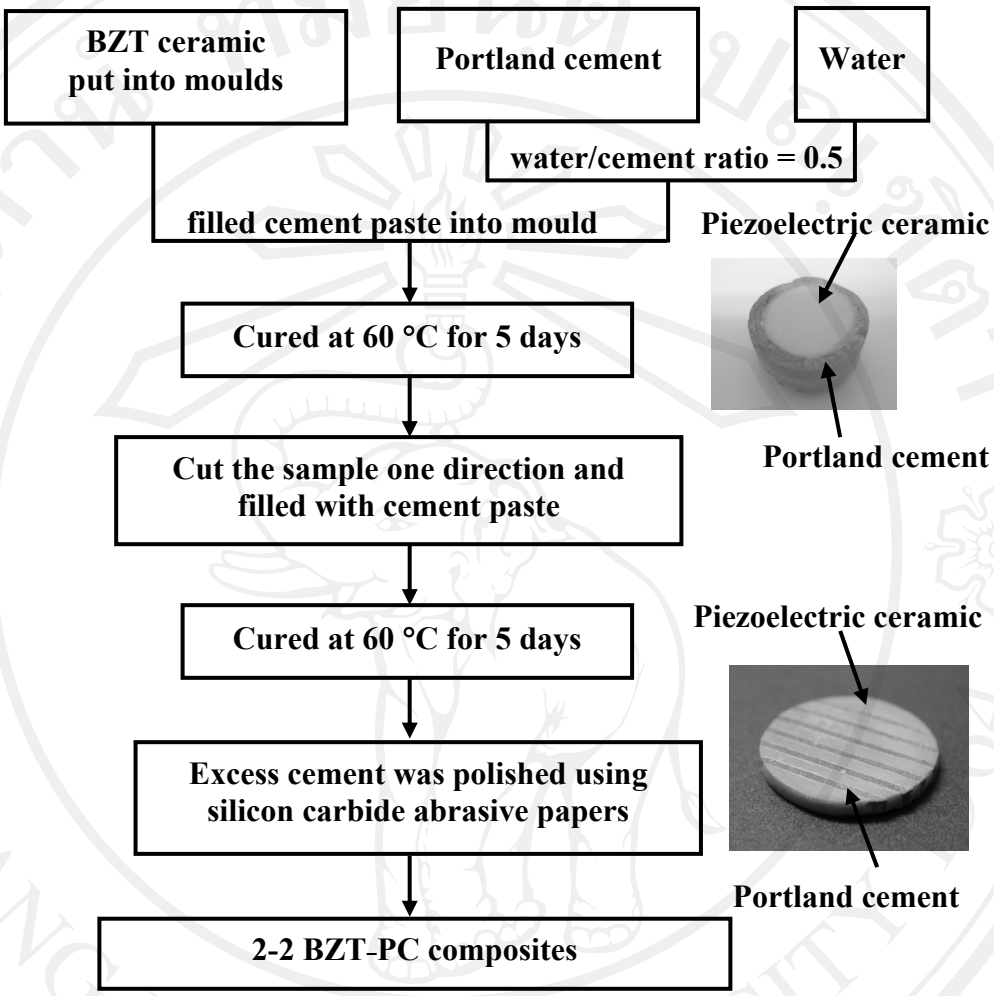

Fig. 3.8 Flow chart of 2-2 BZT-PC composites fabrication.

3.2 Physical, acoustic impedance and microstructure characterization measurements

The density, porosity and thermal expansion measurement were carried out. The acoustic impedance properties were also measured in this work. Morphology and the microstructure as well as the interface and elemental analysis of modified barium

titanate-Portland cement composites were characterized using scanning electron microscopy and energy dispersive X-ray spectrometry.

3.2.1 Density and porosity

The density of piezoelectric ceramic-cement based composite was obtained using the Archimedes method which was described using the following equation:

$$\rho(density) = \frac{W_d}{W_d - W_w} \tag{3.2}$$

The dried composites were used for the porosity test. Porosity measurements were made using Archimedes' principle. The porosity was calculated using the following formula [85]:

$$P(porosity) = \frac{(W_s - W_d)}{(W_s - W_w)} \times 100 \tag{3.3}$$

Where W_s is the weight in the air of the composites saturated with water; W_d is the dry composites weight in air; W_w is the weight of composites saturated of water suspended in water.

3.2.2 Thermal expansion measurement

When a solid material is subjected to a change of temperature, there is a small change in the dimension of that solid i.e. a thermally induced strain is generated. For a homogeneous isotropic solid, this thermal strain is often proportional to the temperature change [36].

$$\frac{\Delta L}{L} = \alpha[\Delta T] \tag{3.4}$$

Where ΔL is change in length, ΔT is change in temperature and α is the coefficient of thermal expansion (CTE). Dilatometric thermal expansion measurements are generally employed to determine the thermal strain generated during the course of heating. The use of this technique has mainly been confined for the study of ceramic, alloys and composites. The information about phase transitions in materials, sintering behavior, thermal expansion coefficients and their anisotropies have been obtained from this technique. For thermal expansion measurement, the samples were cut to give rectangular bars with dimension 5mm×1mm×1mm, placed inside a fused silica holder, heated and cooled at a rate of 2 °C/min and range of temperature at -100 to 250 °C and the thermal expansion was measured as a function of temperature using a linear voltage-differential transformer (LVDT) dilatometer in Fig. 3.9. The LVDT has an advantage over the other transformers as it gives a linear output for every unit displacement [34].

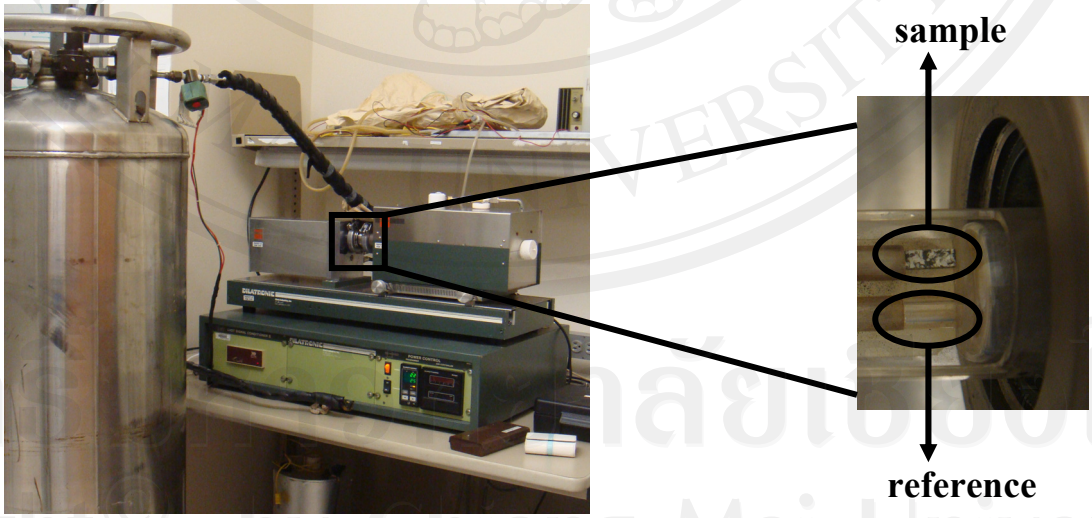

Fig. 3.9 Photograph of the dilatometer used for the thermal strain measurements.

3.2.3 Acoustic impedance

The acoustic impedance of a material has been measured for the purpose of fundamental understanding of acoustic property. Sound travels through materials under the influence of sound pressure. Because molecules or atoms of a solid are bound elastically to one another, the excess pressure results in a wave propagating through the solid [37]. The following applet can be used to calculate the acoustic impedance for any material, as long as its density (ρ) and acoustic velocity (V) are known. In this work, the acoustic velocity of composites (V_c) was measured using an ultrasonic thickness meter (TM-8812) in Fig. 3.10. The experimental values of the acoustic impedance (Z_c) were obtained by multiplying the densities of composites (ρ_c) with the velocities. The acoustic impedance (Z_c) of the composite can be obtained by the following equations [3]:

$$Z_C = \rho_C V_C \tag{3.5}$$

Fig. 3.10 Ultrasonic thickness meter (TM-8812).

3.2.4 Scanning electron microscopy, SEM

In modern material science research, microstructural study is widely used as a powerful tool for prediction of many properties of the materials. It produces micrographs by scanning the surface of a specimen with a small electron probe (a beam of electron) synchronous with an electron beam from a source. Scanning electron microscopy (SEM) is a very popular technique used in materials and biological sciences as well as in industry for microstructural analysis at high magnification. In the SEM, two of interesting signals are the secondary and backscattered electrons, since these vary according to differences in surface topography as the electron beam sweeps across sample. Other signals may be used to measure different properties, e.g. Auger electrons or characteristic X-ray is normally used to determine chemical composition of sample [86].

Fig. 3.11 Scanning electron microscope (SEM; JEOL JSM-5910LV).

In this experimental, SEM; JEOL JSM-5910LV (Fig. 3.11) was used to analysis the morphology and interfacial zone of the composites. The sample for SEM was prepared by fixing the samples on a brass stub. Then, the sample on the stub was coated with gold for making the electrode. Element composition of the selected area was quantified by using an energy dispersive X-ray spectrometry (EDX).

3.3 Electrical and acoustic impedance measurements

The preparation sample, dielectric and piezoelectric measurements are explained in this part.

3.3.1 Sample preparation

Prior to poling process, dielectric and piezoelectric measurements, the samples were polished to obtain smooth and parallel surfaces. The close adhesion of electrode is important since most piezoelectric have high permittivity and a large fraction of any applied potential will therefore occur across any low permittivity gap between an electrode and the material surface. Electrodes are therefore usually formed by applying a silver or Ag_2O suspension. As considering the thermal properties of cement material, a special silver paint with very low firing temperature is chosen to deal with the composite samples.

3.3.2 Dielectric measurement

The dielectric properties of specimen were examined by LCR meter at room temperature. The LCR-meter (HP 4194A, Hewlett-Packard Inc.) in Fig. 3.12

measured the capacitance (C) and loss tangent ($\tan\delta$) of the samples. Dielectric constant can then be obtained using the following equation:

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \qquad (3.6)$$

where, C is capacitance of the sample, ε_r is the dielectric constant of the sample, ε_0 is the permittivity of vacuum (8.854×10^{-12} F m^{-1}), A is the area of the electrode of the sample and d is the thickness of the sample.

Fig. 3.12 The LCR-meter for dielectric properties measurements at room temperature.

3.3.3 Piezoelectric measurement

Poling process

Potentially piezoelectric materials can be forced to be piezoelectric by a process called poling. In a newly fabricated piezoelectric-cement based composite, the

crystallites, and hence the polar axis, can lie in a large number of directions. This is because the material have only a quasi-isotropic response in its electrical, piezoelectric and other characteristics. This process can only be carried out at temperatures below the curie point, when the crystal structures cause an electric dipole to be created. In perovskite structures the dipole is created by movement of the central ion in the structure. Above the curie point the central ion is on average in the plane of the structural ions, but below the curie temperature the central ion moves out of the plane of the structural ions and so the charges no longer balance and give a dipole [87].

The process of poling involves aligning all of these individual dipole moments, so that they all point in the same general direction. For polar axis orientation is done by a poling technique, which consists of applying a D.C. voltage for a sufficient time to the material. The amplitude and duration of the voltage required for poling very substantially between materials. Some material will pole easily and if used in large-signal switching applications may not even require a preliminary poling cycle. Other can only be poled near their curie point where the coercive field of the material is small. The maximum poling voltage that can be applied is limited by breakdown and arcing in the material. Hence poling is often done in a silicon oil bath [29, 87]. The detail of poling condition in this experiment can be seen in Table 3.5. After polarization the specimen were placed in room temperature for 24 hours to maintain the status of polarization.

Table 3.5 Poling condition of the BZT-PC composites.

System	Poling condition		
	Poling field (kV/mm)	**Poling temperature (°C)**	**Poling time (min)**
0-3 BZT-PC	1	40, 50, 60	45
1-3 BZT-PC	1.5	50	30
2-2 BZT-PC	1.5	50	30

Piezoelectric coefficient

The piezoelectric coefficient or piezoelectric constants relating the mechanical strain produced by an applied electric field are termed the strain constants, or the "*d*" coefficients.

Fig. 3.13 The d_{33} meter model PM25.

The piezoelectric *d* constant is a measure of the charge density per unit stress or the strain per unit field. The d_{33} applies when the force is in the 3 direction (along the polarization axis) and is impressed on the same surface on which the charge is collected. The piezoelectric coefficient (d_{33}) was then measured at 24 h after poling using a d_{33} meter (piezometer system model PM25) in Fig. 3.13.

Electromechanical coupling coefficient

The resonance properties of the poled specimens were measured using an impedance meter (Hewlett Packard 4194A) See Fig. 3.14. The electrical properties of a piezoelectric vibrator are dependent on the elastic, piezoelectric, and dielectric constants of the vibrator materials. Thus, values for these constants can be obtained from resonator measurements on a suitably shaped and oriented specimen, provided the theory for the mode of motion of that specimen is known. The measurements basically consist of determining the electrical impedance of the resonator as a function of frequency. A specific frequencies at which the impedance of a resonator reaches a minimum or a maximum are termed the minimum-impedance frequency f_m and the maximum-impedance frequency f_n respectively.

The thickness electromechanical coupling coefficient (K_t) was then calculated from the electric impedance graph plotted against the frequency and using the following formula:

$$K_t^2 = \frac{\pi}{2}\frac{f_s}{f_p}\tan\left(\frac{\pi}{2}\frac{f_p - f_s}{f_p}\right) \qquad (3.7)$$

where f_s and f_p are the series frequency and the parallel resonance frequency, respectively, and K_t can be approximated as follows:

$$K_t^2 = \frac{\pi}{2}\frac{f_m}{f_n}\tan\left(\frac{\pi}{2}\frac{f_n - f_m}{f_n}\right) \tag{3.8}$$

where f_m and f_n are the frequency at the minimum and maximum electric impedance respectively, which can be approximately replaced by frequency f_m and f_n, that is, $f_s \approx f_m, f_p \approx f_n$ [33].

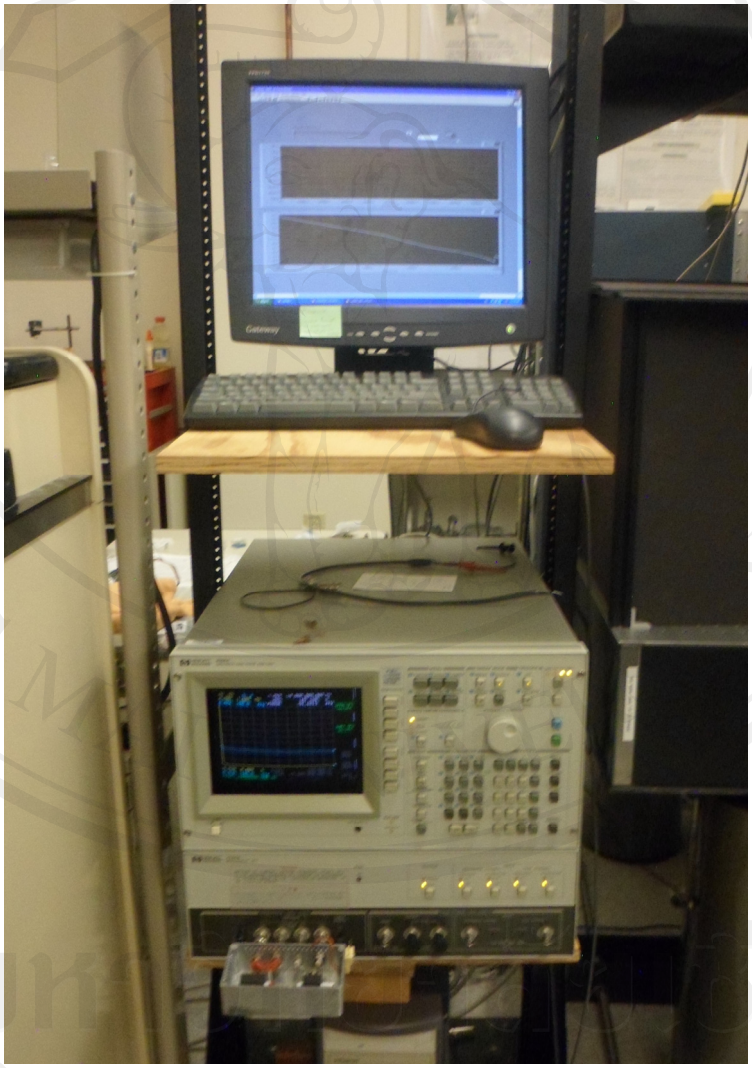

Fig. 3.14 The impedance meter (Hewlett Packard 4194A).