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Dielectric and piezoelectric properties of 1–3 non-lead barium zirconate titanate-Portland cement composites

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Abstract

Non-lead barium zirconate titanate (BZT)-Portland cement (PC) composites have been seen as promising new non-lead composites. This paper reports research work on the dielectric and piezoelectric properties of 1–3 non-lead barium zirconate titanate (BZT)-Portland cement (PC) composites. The 1–3 non-lead composites with different BZT contents at 40–70% by volume were fabricated by the dice-and-fill method. The results show that the dielectric loss of the 1–3 non-lead composite was lowest at 0.08 at 70% BZT composites. The models are applied for the calculation with the dielectric constant, piezoelectric coefficient and piezoelectric voltage constant and the results were found to fit closest to that of the parallel model. At 70% BZT content or higher, piezoelectric coefficient was found to have values higher than 130 pC/N. In addition, the new 1–3 non-lead composites can be tuned to an ideal compatible value that match the requirement of concrete structure.

Keywords: B. Composites; C. Dielectric properties; C. Electrical properties; C. Piezoelectric properties

1. Introduction

The traditional piezoelectric smart materials, such as piezoelectric ceramic and piezoelectric polymer may not be applicable in civil engineering due to the distinct differences in the properties between the smart materials and the concrete structures such as acoustic impedance and hydration reaction of cement [1,2]. Therefore, the energy transfer between the traditional smart materials and the host concrete would be degraded by such mismatching [1,2]. Li et al. [1] first developed a 0–3 PZT-white Portland cement composite in 2002. Their research indicates that, when the 40–50% PZT composites, the acoustic impedance of the 0–3 composite can match that of concrete ($Z_c \approx 9 \times 10^6\ \mathrm{kg\,m^{-2}\,s^{-1}}$). Recently, piezoelectric cement-based 1–3 composites was proposed by Lam et al. [3] and 1–3 cement-based piezoelectric composite also showed that the piezoelectric properties of the composite were better than those of 0–3 cement-based piezoelectric composite.

Lead-based piezoelectric ceramic such as PZT has been used with cement to form piezoelectric cement-based composites [1–3], but PZT ceramic cause pollution and environmental problems due to lead oxide toxicity [4,5]. Therefore, it is desirable to produce environmental friendly non-lead piezoelectric ceramic with equivalent properties, which could be used as an alternative to lead-based ceramics. It is well-known that barium titanate (BT) ceramic is one of the most widely studied non-lead piezoelectric materials [6]. Moreover, doping the ceramic is one of the ways to improve BT material performance in electroceramics. Barium zirconate titanate ($BaTi_{1-x}Zr_xO_3$) ceramics were extensively investigated and show promising piezoelectric/electrostrictive properties [5]. The $BaTi_{1-x}Zr_xO_3$ ceramics at $x=0.05$ showed good piezoelectric properties [7] and this material is of interest for applications in the field of environmental protection.

The type of smart materials suitable for applications in civil engineering structures should have good piezoelectric properties as well as good compatibility concrete and environmental friendly lead-free composites. Thus, this study examines the dielectric and piezoelectric properties of new functional 1–3 non-lead barium zirconate titanate-Portland

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cement composites for smart structure applications. The experimental results of new non-lead composites are presented and compared with several models.

2. Experiment

2.1. Fabrication of 1–3 non-lead piezoelectric composites

Barium zirconate titanate ($BaZr_{0.05}Ti_{0.95}O_3$) ceramic particles were produced using BZT powder sintered at 1,450 °C. The 1–3 non-lead barium zirconate titanate-Portland cement composites were fabricated by the dice-and-fill technique [3] with different BZT contents at 40, 50, 60 and 70% by volume. A diamond saw (Buehler ISOMET Low speed saw) was used to cut the BZT ceramic in one direction (y axial). The grooves were then filled with cement paste (water:cement=0.5) and the samples were cured at a temperature of 60 °C for 5 days under a condition of 98% relatively humidity. Thereafter, the samples were cut and filled in second direction (x axial) and the samples were placed for curing for a further 5 days before measurements.

2.2. Testing methods

Microstructure and phase characterizations of composites were carried out by means of scanning electron microscopy (SEM; JEOL JSM-840A) and energy dispersive spectroscopy (EDS) analysis. The acoustic velocity of composites (V_c) was measured using an ultrasonic thickness meter (TM-8812). After that, silver paint was coated on both surfaces of composites. An impedance meter (Hewlett Packard 4194A) was used to obtain the capacitance and the dielectric loss of composites at room temperature. The piezoelectric coefficient (d_{33}) of the composites at poling field of 1.5 kV/mm was measured using a piezometer system model PM25. The dielectric constant (ε_r) and piezoelectric voltage factor (g_{33}) of the composites can be calculated using the following formulas:

$$\varepsilon_r = \frac{Ct}{\varepsilon_0 A} \tag{1}$$

$$g_{33} = \frac{d_{33}}{\varepsilon_r \varepsilon_0} \tag{2}$$

where C is the sample capacitance, t is the thickness, ε_0 is the permittivity of free space constant (8.854×10^{-12} Fm^{-1}), and A is the electrode area.

3. Results and discussion

Fig. 1(a) shows the SEM micrographs of 1–3 BZT–PC composite. The SEM micrographs of composites (60% BZT composite) shows a typical microstructure at the interfacial zone between the BZT ceramic and the cement matrix where BZT ceramic can be seen next to hydration products of Portland cement such as calcium sulfoaluminate hydrate (ettringite) and calcium silicate hydrates (CSH). Furthermore, the CSH gel (the main hydration products of Portland cement) acts as the binder which binds the composites together, suggesting good bonding between the BZT ceramic and the cement matrix. Energy dispersive spectroscopy (EDS) analysis of the composite can be seen in Fig. 1(b). EDS analysis of the composite shows the elements of BZT ceramic, CSH and ettringite where apart from gold which was used to coat the samples (hydrogen cannot be detected).

The dielectric constant (ε_r) and dielectric loss ($tan\ \delta$) on the BZT content are shown in Fig. 2. The ε_r values of the composites can be seen to increase linearly with increasing BZT volume fraction and the ε_r values are highest at 795 for 70% BZT composites at 1 kHz. The reason is probably that the higher the volume fraction of piezoelectric ceramic, higher is the contribution of the piezoelectric ceramic and interface polarization on the total polarization of the composite, which leads to an increase of the ε_r value of the composite [10,13]. In addition, the $tan\ \delta$ value is found to decrease with increasing BZT content and the $tan\ \delta$ value of 70% BZT composite is lowest at 0.08 (f=1 kHz). Furthermore, the parallel, series and cube models were compared to evaluate the experimental results for ε_r value of the 1–3 BZT-PC composites. The series and parallel mixing models represent the extreme cases where the model is alternating layers of each phase, perpendicular and parallel to the applied field, respectively [8]. For the cube model, Banno [9,10] proposed a "modified cube model," which took into account the anisotropic distribution of cubes in x, y, and z directions, which based on fundamental principal of the physical mixing. The mathematical equations of parallel (Eq. (3)), series (Eq. (4)), and cube (Eq. (5)) models for dielectric constant are described as follows:

$$\varepsilon = v_{BZT}\varepsilon_{BZT} + v_{PC}\varepsilon_{PC} \tag{3}$$

$$\frac{1}{\varepsilon} = \frac{v_{BZT}}{\varepsilon_{BZT}} + \frac{v_{PC}}{\varepsilon_{PC}} \tag{4}$$

$$\varepsilon = \frac{\varepsilon_{BZT}\ \varepsilon_{PC}}{(\varepsilon_{PC}-\varepsilon_{BZT})\ v_{BZT}^{1/3} + \varepsilon_{BZT}\ v_{BZT}^{-2/3}} + \varepsilon_{PC}\left(1-v_{BZT}^{2/3}\right) \tag{5}$$

where ε, ε_{BZT} and ε_{PC} are the dielectric constants of the composite, the ceramics phase and the cement phase, respectively. The v_{BZT} and v_{PC} are the volume fractions of the ceramics phase and the cement phase, respectively. Fig. 2 shows that the dielectric constant of the 1–3 non-lead composites is close to the prediction by the parallel models and the results are shown to be higher than 0–3 connectivity composites [11]. This is because the 1–3 connectivity essentially contains the piezoelectric ceramic fully aligned in one direction (1 connectivity prism) which allows the ceramic to possess greater dielectric constant and less loss that would otherwise occur in the 0–3 composites [12]. Moreover, the piezoelectric ceramic of 0–3 composites existed as random particles surrounded by

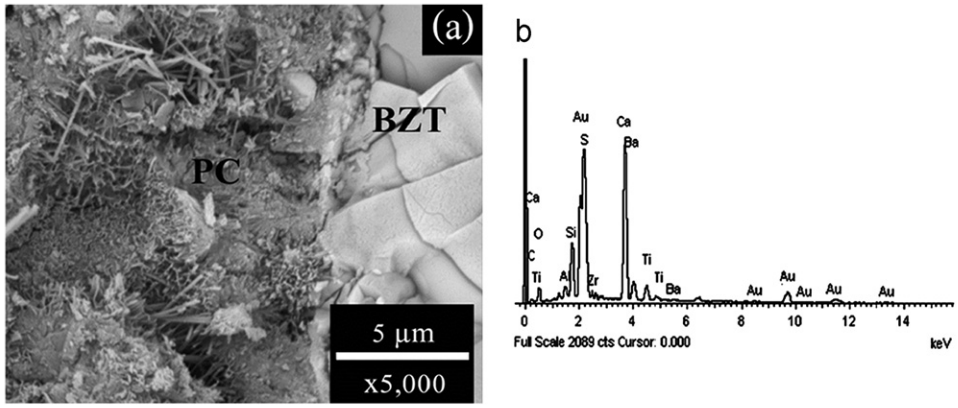

Fig. 1. Microstructure of 1–3 BZT–PC composite: (a) SEM micrograph and (b) EDS analysis.

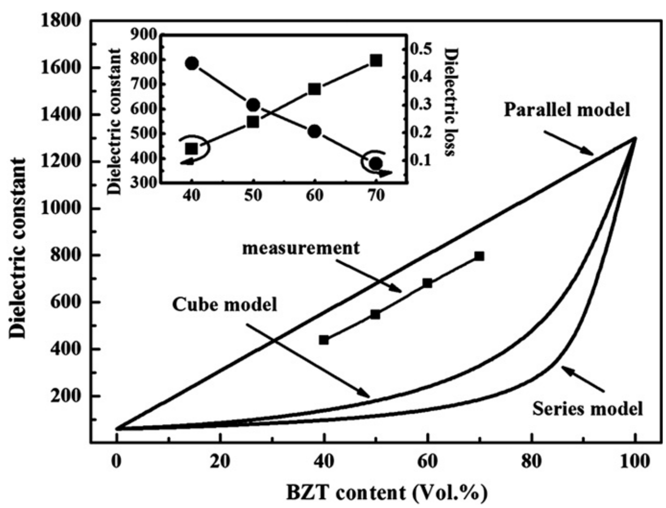

Fig. 2. The dielectric properties and comparison of models with dielectric constant of 1—3 BZT–PC composites.

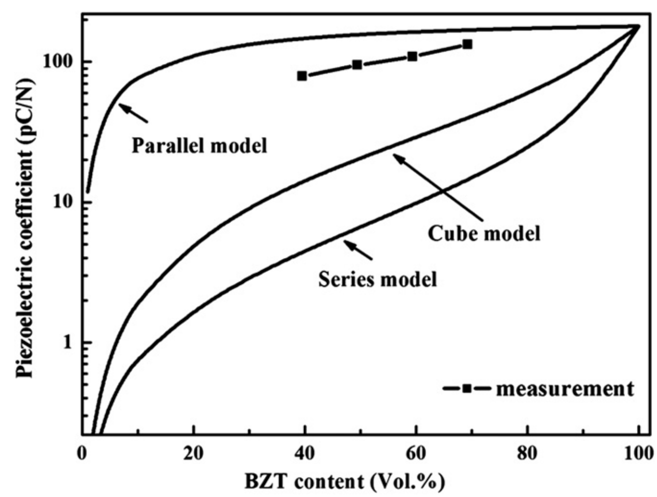

Fig. 3. Comparison of models with the piezoelectric coefficient results of 1–3 BZT–PC composites.

cement matrix and thus the 0–3 composites are more closely related to the series or cube models [13].

The effect of BZT on piezoelectric coefficient (d_{33}) can be seen in Fig. 3. The d_{33} value was higher at 133 pC/N for composite with 70% BZT composite as compared to that of 40% BZT composite (79 pC/N). Moreover, the test results of d_{33} values of the composites are plotted against BZT content with prediction curves for different models. The theoretical equations [2, 14] of parallel (Eq. (6)), series (Eq. (7)), and cube (Eq. (8)) model for the d_{33} values can be denoted as follows:

$$d_{33}=\frac{v_{BZT}d_{33(BZT)}S_{33(PC)}+v_{PC}d_{33(PC)}S_{33(BZT)}}{v_{BZT}S_{33(PC)}+v_{PC}S_{33(BZT)}} \quad (6)$$

$$d_{33}=\frac{v_{BZT}d_{33(BZT)}\varepsilon_{PC}+v_{PC}d_{33(PC)}\varepsilon_{BZT}}{v_{BZT}\varepsilon_{PC}+v_{PC}\varepsilon_{BZT}} \quad (7)$$

$$d_{33} = \frac{d_{33(BZT)}v_{BZT}}{\left(v_{BZT}^{1/3}+\frac{\varepsilon_{BZT}}{\varepsilon_{PC}}\left(1-v_{BZT}^{1/3}\right)\right)\left(1-v_{BZT}^{1/3}+v_{BZT}\right)} \quad (8)$$

where d_{33}, d_{33}($_{BZT}$) and $d_{33(PC)}$ are the d_{33} values of the composite, the ceramics phase and the cement phase, respectively. $S_{33(BZT)}$ and $S_{33(PC)}$ are the elastic compliance of the ceramics phase and the cement phase, respectively. The d_{33} values of the 1–3 non-lead composites are close to the parallel models and this is in good agreement with the results of the dielectric constant measurement. The experimental results are far from the series model throughout the entire range and it is clear that the cube model gives the lower limit compared to the measured results for d_{33} values of 1–3 non-lead composites. This is because the 1–3 connectivity is more closely related to the 2—2 parallel models with the complete phase of BZT ceramic in the Y direction.

The piezoelectric voltage constant (g_{33}) means the sensitivity of a receiving voltage, which was calculated from Eq. (2). The results of g_{33} values of the composites are plotted against BZT content with parallel models and the experimental results can be seen to be most closely related to the theoretical value of the parallel model in Fig. 4(a). The theoretical equations of parallel, model for the g_{33} values can be denoted as follows [14]:

$$g_{33}=\frac{v_{BZT}d_{33(BZT)}S_{33(PC)}+v_{PC}d_{33(PC)}S_{33(BZT)}}{\left(v_{BZT}S_{33(PC)}+v_{PC}S_{33(BZT)}\right)\left(v_{BZT}\varepsilon_{(BZT)}+v_{PC}\varepsilon_{(PC)}\right)} \quad (9)$$

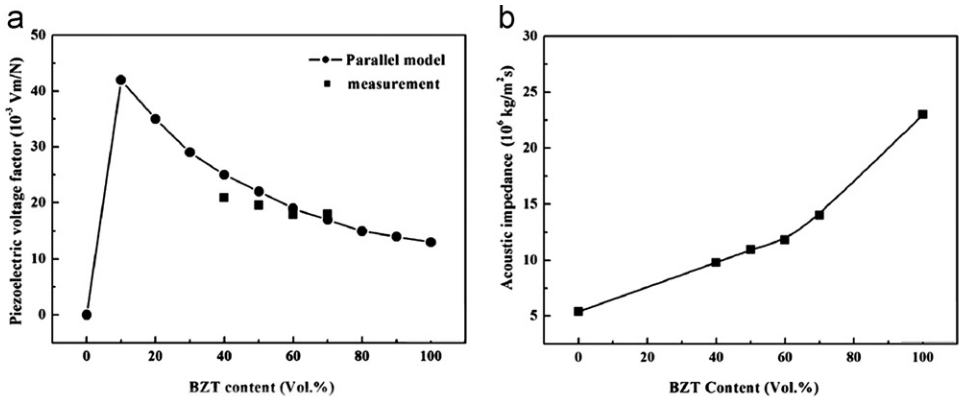

Fig. 4. The effect of BZT content of 1–3 BZT–PC composites on (a) piezoelectric voltage constant results and (b) acoustic impedance results.

Furthermore, the results show that g_{33} values of 1–3 non-lead piezoelectric cement composites in this work at 50% BZT by volume ($g_{33} \approx 19$ pC/N) were found to be close to the previous work of 1–3 lead-based piezoelectric cement composites at 54.9% PZT by volume ($g_{33} = 24.5$ pC/N) by Xu et al. [15]. However, these results were more likely to be affected by the technique used and cannot be compared directly.

The acoustic impedance (Z_c) of the composite can be obtained by the following equations

$$Z_c = V_c \rho_c \quad (10)$$

where V_c was acoustic velocity of composites and ρ_c are the density of the composites. Fig. 4(b) shows the acoustic impedance (Z_c) of the composites with the different BZT content. This further demonstrated that, by adjusting volume fraction of piezoelectric ceramic ($\approx$ 30–50% BZT composites), the Z_c value of composite can be seen to be close to that of concrete and match that of concrete structure.

4. Conclusions

The 1–3 non-lead barium zirconate titanate-Portland cement composites were successfully fabricated and have good potential for use in concrete structural applications. From SEM micrographs, calcium silicate hydrates acts as the binder which binds the composites together, suggesting good bonding between the BZT and PC materials. The dielectric constant and loss were 795 and 0.08, respectively for 70% BZT composite. The dielectric constant, piezoelectric coefficient and piezoelectric voltage constant of 1–3 composites were found to fit closest to that of the parallel model. The piezoelectric coefficient was highest at 133 pC/N for 70% BZT composites. Moreover, the new 1–3 non-lead composites at 30–50% BZT composites have good compatibility with concrete structure and good potential for use in smart concrete structures.

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