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# Investigation of inorganic fillers on properties of 2–2 connectivity cement/polymer based piezoelectric composites

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## HIGHLIGHTS

- Cement/polymer based piezoelectric composite with inorganic filler was developed.
- Dielectric and electromechanical properties were studied.
- There exist potential applications of this composite in structural health monitoring.

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## ABSTRACT

The 2–2 cement/polymer based piezoelectric composites containing inorganic fillers were prepared. The influences of filler content and composite thickness on the composite properties were investigated. The results show that graphite powder shows larger effect on dielectric property of the composites than silicon powder and strontium ferrite (Sr-ferrite) powder, especially when graphite powder is larger than 10 wt.%. The Sr-ferrite can improve the thickness electromechanical coupling properties of the composites. When Sr-ferrite powder content is 15 wt.%, the composite has a $k_t$ value of 68.6% at a 2 mm thickness. The electromechanical quality factor ($Q_m$) of the composites shows fluctuation variation between 10 and 60 with increasing the composite thickness, which is far less than that of the pure ceramic. The coupling resonance effects between planar mode and thickness mode of the composites was reduced by decreasing the composite thickness, and the pure thickness mode resonance can be obtained at a small composite thickness.



## 1. Introduction

Piezoelectric ceramic is one of the most important intelligent materials and being widely used in many fields due to its direct and inverse piezoelectric effects [1–3]. However, there also exist some problems when they are used in civil engineering fields due to various compatibility problems between piezoelectric ceramic and concrete materials, such as acoustic impedance mismatching, long-term durability and reliability problems. Therefore, it is of great significance to develop novel piezoelectric smart materials to satisfy the online monitoring requirements of civil engineering structures. Recently, cement based piezoelectric composites has grown rapidly with the demands from new applications, such as structural vibration control, nondestructive evaluation and health monitoring [4]. The aim of this paper is to develop a novel cement/polymer based piezoelectric composite with additive of inorganic fillers for improving the dielectric and electromechanical coupling properties of cement based piezoelectric composites.

In 2002, Li et al. [5] first fabricated a 0–3 connectivity cement based piezoelectric composite by using cement as matrix phase and PZT piezoelectric ceramic powder as active phase. Their research showed that acoustic impedance of this composite could be compatible with that of concrete by adjusting the proportion of various components. In the following years, many scholars showed their great interest in this composite, and other novel cement based piezoelectric composites were also developed. It is known based on the connective characteristic of two-phase composite [6], piezoelectric composites can usually be divided into ten basic connectivity patterns. The 2–2 connectivity piezoelectric composites have received extensive attention due to the simple fabrication technique and superior sensing and actuating abilities, and many studies have also been reported referring to the fabricating technique, property and theoretical investigation of 2–2 connectivity piezoelectric composite [7–11]. In 2002, Zhang et al. [12,13] fabricated 2–2 connectivity cement based piezoelectric

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composites by casting cement-based mortar into a series of pre-arranged piezoelectric thin plates and investigated the sensing and actuating effects of this composite. In 2005, Dong et al. [14] fabricated 2–2 cement based piezoelectric composite and demonstrated its good sensing and actuation capabilities as self-sensing actuator for civil engineering structures. In 2009, Xu et al. [15] fabricated 2–2 cement based piezoelectric composite by using sulfoaluminate cement as matrix by employing dice and fill technique and studied the influences of piezoelectric ceramic volume fraction on properties of the composite. In 2014, Chaipainich et al. [16] fabricated 2–2 lead-free barium zirconate titanate-Portland cement composites and found that the composites show higher piezoelectric voltage coefficient and lower acoustic impedance than pure ceramic.

Although 2–2 connectivity cement based piezoelectric composites exhibit excellent piezoelectric and electromechanical coupling properties as well as the good acoustic impedance matching ability with concrete, there also exist some problems for this composite. Presently, cement was usually considered as matrix phase of the cement based piezoelectric composites due to its similar properties with concrete materials. However, it is known that cement paste will shrink during hydration process, which accordingly results in a poor interfacial bonding ability between cement matrix and piezoelectric ceramic. Furthermore, the acoustic impedance of cement based piezoelectric composites can only match with that of concrete material at a very low piezoelectric ceramic faction at the expense of piezoelectric properties. Therefore, it is important to improve the comprehensive properties of traditional cement based piezoelectric composites by modifying the matrix phase of the composites. It is well known that epoxy resin is widely used in civil engineering field to improve the mechanical and durability properties of cement mortar and concrete materials [17–21].

In this work, 2–2 connectivity cement/polymer based piezoelectric composites were fabricated by using PZT piezoelectric ceramic as active phase, mixture of cement powder and epoxy resin as matrix phase, and inorganic powders of graphite, silicon and strontium ferrite as modifying fillers of matrix phase. The effects of inorganic fillers content and thickness variation of the composite on dielectric and electromechanical coupling properties of the composites were mainly discussed.

## 2. Experimental method

The Lead Zirconium Titanate (PZT) ceramic was employed as piezoelectric phase, and mixture of cement powder (ordinary Portland 42.5R) and epoxy resin (bisphenol A diglycidyl ether) was used as matrix phase of the composite. Three types of inorganic powder were considered as the modified filler of cement/polymer matrix, that is, graphite powder (carbon content ⩾99.85%, particle size ⩽30 μm), silicon powder (silicon content ⩾99.0%, particle size 74 μm) and strontium ferrite (particle size 1.5 μm). The tensile strength, tension modulus and compressive strength of epoxy resin are 22.6 MPa, 2.165 GPa and 66.4 MPa, respectively. The main properties of PZT ceramic is listed in Table 1.

The 2–2 connectivity cement/polymer based piezoelectric composites were fabricated by dicing-and-filling method through the following procedures. First, series of piezoelectric ceramic slices were cut accurately by using diamond cutter parallel to the polarization axis (Z-direction) of bulk piezoelectric ceramic, and a common ceramic base with a thickness of 0.5 mm was remained to maintain the above ceramic slices. The piezoelectric ceramic body was then put into the ultrasonic cleaner for 10 min to eliminate the ceramic residue. After drying in the air, the ceramic body was fixed into the mould for casting. Cement, epoxy resin and hardener were weighed according to a mass proportion of 4:4:1 and mixed together, and the inorganic powder of graphite powder, silicon powder and strontium ferrite were also weighed with mass percentages of 1 wt.%, 5 wt.%, 10 wt.%, 15 wt.% of above mixture. The inorganic fillers were mixed into the cement/polymer matrix, respectively, and the mixture were then put into a vacuum pumping system for about 10 min to eliminate the internal pores. The cement/polymer matrix containing inorganic fillers was finally poured into the piezoelectric ceramic body. After solidifying for 48 h in the air, the 2–2 connectivity cement/polymer based piezoelectric composites were successfully prepared after cutting off the ceramic base. Fig. 1 shows the illustration of 2–2 cement/polymer based piezoelectric composite containing inorganic fillers.

**Table 1**
Properties of the piezoelectric ceramic.

| Ceramic | $k_p$/% | $k_t$/% | $d_{33}$/pC N$^{-1}$ | $\varepsilon_{33}^T$ | $\tan\delta$ | $Q_m$ | $\rho/10^3$ kg m$^{-3}$ |
|---|---|---|---|---|---|---|---|
| PZT | 58 | 48 | 260 | 1050 | <0.3% | 1000 | 7.5 |

$k_p$, $k_t$-planar and thickness electromechanical coupling coefficient; $d_{33}$-piezoelectric strain constant; $\varepsilon_{33}^T$-relative dielectric constant at constant stress; $\tan\delta$-dielectric loss; $Q_m$-mechanical quality factor; $\rho$-density.

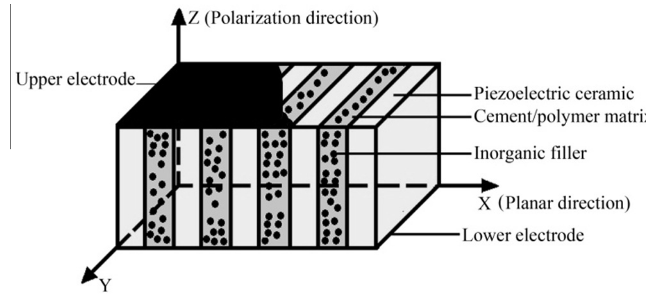


**Fig. 1.** Schematic illustration of 2–2 cement/polymer based piezoelectric composite containing inorganic fillers.

For testing purpose, both surfaces of the piezoelectric composites perpendicular to polarization direction were polished by using $Al_2O_3$ grinding medium, and a thin layer of silver paint was coated on the surfaces as electrodes. The piezoelectric ceramic volume fraction of all composites was 47.5 vol.%, and the dimensions were 10 ± 0.2 mm in length, 7.5 ± 0.2 mm in width. The $Al_2O_3$ grinding medium was used to polish the composite to different thicknesses. The specimens with different inorganic fillers are grinded step by step to 10 ± 0.2 mm, 8 ± 0.2 mm, 6 ± 0.2 mm, 4 ± 0.2 mm and 2 ± 0.2 mm, respectively. The specimens of different thicknesses were fixed on the testing fixture with point contact, and an Agilent 4294A Impedance Phase Analyzer was used to measure the impedance spectra of the composite under different frequency, as well as the capacitance $C^T$ and dielectric loss $\tan\delta$ at 1 kHz.

## 3. Results and discussion

### 3.1. Effects of filler content on composite properties

#### 3.1.1. Dielectric property

The relative dielectric constant of 2–2 connectivity cement/polymer based piezoelectric composite ($\varepsilon_{33}^T$) can be calculated in terms of the following equation:

$$\varepsilon_{33}^T = Ct/(A\varepsilon_0) \quad (1)$$

where $C$ is capacitance; $t$ and $A$ are the thickness and electrode area of the composites, respectively; $\varepsilon_0$ is vacuum permittivity with a value of $8.85 \times 10^{-12}$ Fm$^{-1}$.

Fig. 2 shows the relative dielectric constant ($\varepsilon_{33}^T$) and dielectric tangent loss ($\tan\delta$) of the piezoelectric composites as a function of inorganic filler content at a frequency of 1 kHz. It can be seen that when piezoelectric ceramic volume fraction is 47.5 vol.%, the relative dielectric constant value of all composites without inorganic fillers is almost the same under different thicknesses whose value is about 700. With increasing the inorganic filler content, $\varepsilon_{33}^T$ value of the piezoelectric composite takes on fluctuation variation. By contrast, the influence of graphite powder on dielectric constant of the composites is more obvious than that of silicon powder and Sr-ferrite powder. In addition, it also can be observed that when composite thickness is 2 mm, the fluctuation variation of $\varepsilon_{33}^T$ value of the composites is particularly obvious with increasing the inorganic fillers content. It is known that dielectric properties of piezoelectric composite mainly depend on piezoelectric ceramic, cement/polymer matrix and inorganic fillers. Because the relative dielectric constant of both the inorganic fillers is orders of