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High piezoelectric and dielectric properties of 0–3 PZT/cement composites by temperature treatment

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ABSTRACT

Temperature treatment of 0–3 type PZT/cement composites before polarization yielded high dielectric and piezoelectric properties in materials with 50% PZT inclusions by volume and 50% cement matrix. Specimens were treated at seven temperatures from 23 °C to 150 °C and then applied by a 1.5 kV/mm poling field. The dielectric loss of the composites reduces at higher pretreatment temperatures, shorting the trigger time. Temperature treatment increased the piezoelectric strain factor d_{33}, the relative dielectric constant ε_r and the piezoelectric voltage factor g_{33} of PZT/cement composites, but did not affect significantly the electromechanical coupling coefficient K_t. Piezoelectric factors reach stable values after 70 days of aging, and samples that were not temperature pretreated reached stable values earlier. Specimens pretreated at 150 °C exhibit $d_{33} = 106.3$ pC/N and $\varepsilon_r = 477$ on the 70th aging day, almost two times greater than the composites without temperature treatment. The resonance frequency of the composites on the 70th day decreases with increasing temperature, with the exception of 150 °C. Temperature pretreatment can also improve the phase angle of the composites. In addition, the effect of curing time for PZT/cement composites is an important factor to dominate the feasibility of polarization.

1. Introduction

Cement-based piezoelectric composites are under development as "cement sensor" alternatives to conventional piezoelectric sensors or actuators for real-time monitoring of concrete structures such as bridges, tunnel lining, hillside structures, road pavement, material defects and smart buildings [1–12]. Cement sensors are an active topic of research, with work on piezoelectric ceramic/cement composites containing bar-like (1–3 type) and plate-like (2-2 type) piezoelectric inclusions exhibiting higher piezoelectric strain factors d_{33} of up to 200–350 pC/N [8,10,11] compared with 0–3 type composites (piezoelectric particles uniformly dispersed in a cement matrix). From the point of view of the overall piezoelectric properties, 1–3 type and 2-2 type cement piezoelectric composites can be selected as substitutes for conventional piezoelectric sensors used in concrete structures. It is far more difficult to fabricate 1–3 type and 2-2 type composites using embedding [1] and cutting [10,13] methods than it is to prepare 0-3 type composites. Moreover, the unavoidable mismatch of acoustic impedance and material density between the piezoelectric inclusions and the cement matrix degrades the sensitivity of the signal and the volume stability, similar to the disadvantages encountered using piezoelectric ceramic or polymer sensors for structural health monitoring.

The acoustic impedance of the piezoelectric ceramic lead zirconate titanate (PZT) is 21.2×10^{-6} kg m^{-2} s^{-1}, compared with 9.0×10^{-6} kg m^{-2} s^{-1} for concrete. This difference may make PZT sensors inaccurate when used in concrete structures. For PZT/cement composites, 40–50 vol% PZT in cement has been reported to provide an acoustic impedance matching that of concrete [3]. Researchers continue to investigate 0–3 type cement-based piezoelectric composites, as conventional sensors and actuators do not respond simultaneously with concrete structures [3,5,9,14–20], although the piezoelectric properties of these composites are not yet high enough to enable commercial use without a charge amplifier.

This work focuses on 0–3 type cement-based piezoelectric composites (PZT/cement composites) consisting of Type I Portland cement as the matrix and randomly oriented PZT particles as the functional inclusion. The dielectric and piezoelectric properties of PZT/cement composites are affected by many factors including fabrication methods, poling conditions, admixture, and the PZT size

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and content. The piezoelectric strain factor (d_{33}) of PZT/cement composites prepared by blending with water was found to be higher than that of composites fabricated by pressing without water [8,19]. Pan and Chen [19] suggested that PZT/cement composites should be manufactured by pressure forming with no water added due to the lower presence of variations and voids. Huang et al. [21] applied 32–128 MPa compression to sulfoaluminate cement piezoelectric composites and found that as the forming pressure increased, d_{33} and the relative dielectric constant ε_r increased, while the pore volume decreased. In addition, specimens cured at higher temperatures had a higher d_{33} and electromechanical coupling coefficient K_t [19,22–24].

Researchers have also investigated the effect of poling conditions on piezoelectric properties, finding that increasing poling temperature can increase the d_{33} [22] and K_t [23] values of PZT/cement composites. An electric voltage (poling field) is applied to evoke the piezoelectric properties of piezoelectric materials. The poling field is an important factor affecting d_{33} and K_t. Applying a higher poling field to piezoelectric materials results in higher d_{33} and K_t values [22,23]. Poling time is another factor that affects piezoelectric properties. The poling process induces alignment in the disordered ferroelectric domains of piezoelectric materials, but inadequate poling time will reverse ferroelectric domains back to a disordered state [25,26]. The values of d_{33} and K_t generally increase with increasing poling time, but decrease for poling times greater than 45 min [22,27] depending on the constituents of the composites.

A great deal of effort has been made over the last ten years to improve the dielectric and piezoelectric properties of 0–3 type cement-based piezoelectric composites. Huang et al. [22,28] discussed the effects of poling field, poling time, poling temperature, particle size and PZT content on d_{33}, obtaining a lower d_{33} value of 16 pC/N at the respective optimal poling field, poling time and poling temperature values of 4.0 kV/mm, 45 min and 120 °C. Li et al. [29] considered the effects of polarizing voltage, poling time and PZT volume fraction of PZT/cement composites, obtaining the maximum $d_{33} = 55$ pC/N and $\varepsilon_r = 300$ with a 4.3 kV/mm poling field. Chaipanich et al. [17,30] examined the composites poled at the poling field of 2 kV/mm in 130 °C silicone oil for 45 min, and obtained $d_{33} = 42$ pC/N and $\varepsilon_r = 290$ for 60% PZT and a median size of 620 μm. Meanwhile, Jaitanong et al. [9] continued to test the composites with 90% PZT, obtaining $d_{33} = 87$ pC/N and $\varepsilon_r = 536$. Hunpratub et al. [20] produced a new piezoelectric ceramic, BZT-BCT, mixed it with cement to form a composite, and obtained $d_{33} = 52$ pC/N and $\varepsilon_r = 107$ for 70% BCTZO particle content.

In addition, cement-based piezoelectric composites with admixtures added as a conducting phase are an effective way to enhance ferroelectric behavior. Carbon addition was found to slightly increase the dielectric constant of PZT/cement composites at room temperature [31]. Carbon black addition was also studied by Huang et al. [32] and Gong et al. [33] for 70% P(LN)ZT and PZT, respectively, resulting in d_{33} and ε_r values of 28.5 pC/N and 202.6 for PZT/cement composites with 1.0 vol% carbon black [33]. For the composite with 80 vol% nano-PZT powder, the highest values of d_{33}, ε_r and K_t are 53.7 pC/N, 130.5 and 18.1%, respectively [18]. Furthermore, carbon nanotubes (CNTs) were also added to the composite with 70 vol% PZT, and the highest values were observed at a CNT content of 0.3% by volume: $d_{33} = 62$ pC/N, $\varepsilon_r = 145$ and piezoelectric voltage factor $g_{33} = 60 \times 10^{-3}$ V–m/N [34].

Many studies [11,17,18,20,22,30,32,34] have been performed studying the piezoelectric properties of 0–3 type cement-based piezoelectric composites cured for 1 or 3 days at 24 h after polarization. However, dielectric and piezoelectric constants continue to change with aging time (the age after polarization) [26,29,33,35–39]. Chen et al. [26] reported that d_{33} remained constant after 8 aging days. Li et al. [29] noted that d_{33} reached saturation after 40 days. For PZT/cement composites with carbon black [33] and silica fume, slag and fly ash [35], the d_{33} and ε_r values also increase with aging time and reach stable values after longer periods of time. Pan et al. [36–38] investigated PZT/cement composites with slag [36] and fly ash [37] under controlled conditions of 24 °C and 50% relative humidity, finding that the d_{33} and ε_r values reached a plateau after 60 aging days, while the values of K_t did not change significantly with aging time [38]. Chaipanich et al. [39] indicated that the saturation value of d_{33} for piezoelectric PZT ceramic-Portland cement composites was reached after 30 days. Hydration and moisture are presumed to cause enhancements in piezoelectric constants over aging time, but this presumption has not yet been fully confirmed.

For 0–3 type PZT/cement composites with adequate PZT content exhibiting good compatibility with concrete, the piezoelectric properties reported thus far are not high enough for application as cement sensors. The highest values of d_{33} and ε_r were near 60 pC/N and 300, respectively, with the exception of Wang et al. [24], who in 2012 fabricated 60%PZT/cement composites including a silica-based material, yielding $d_{33} = 70$ pC/N and 99 pC/N after 38 and 90 days, respectively. Therefore, the aim of this work is to fabricate PZT/cement composites with superior dielectric and piezoelectric properties.

The composite developed here consists of PZT as the inclusion and Type I Portland cement as the matrix, each 50% by volume, with no admixtures added. Specimens of PZT/cement composites were prepared and cured for 1 day to investigate the dielectric and piezoelectric properties. Prior to polarization, specimens were treated at 23–150 °C, with the results at 23 °C (room temperature) used as a reference.

2. Experiments

2.1. Materials and pretreatment temperature

PZT ceramic particles (inclusion) were uniformly distributed in a cement matrix at 50% PZT by volume to form a 0–3 type PZT/cement composite (named PP material). PZT particles of 75–150 μm were chosen, which have a density of 7.9×10^3 kg/m^3, $d_{33} = 470$ pC/N, $g_{33} = 24 \times 10^{-3}$ V–m/N, and $\varepsilon_r = 2{,}100$, as listed in Table 1. Fresh Type I Portland cement has a fineness of 349 m^2/kg and a specific gravity of 3.15. PZT particles and cement were premixed by a solar-planetary mill for 5 min without adding water. The resulting composite (mixture) was uniformly mixed. Then, the mixture was pressed in a cylindrical steel mold 15 mm in diameter at 80 MPa compression to form a disk-like specimen. Afterwards, specimens were cured for 24 h at 90 °C and 100% relative humidity to produce suitable strength.

After curing for 1 day, specimens were polished to a thickness of 2 mm, coated on both sides with silver paint (Type: SYP-4570) to

Table 1
Properties of PZT ceramic[a].

Parameter	Properties
Piezoelectric strain factor d_{33} ($\times 10^{-12}$ C/N)	470
Piezoelectric voltage factor g_{33} ($\times 10^{-3}$ V–m/N)	24
Planar electromechanical coupling coefficient K_p (%)	70
Thickness electromechanical coupling coefficient K_t (%)	72
Mechanical quality factor Q_m (%)	65
Elastic modulus E_{33} (N/m^2)	5.2×10^{10}
Density ρ ($\times 10^3$ kg/m^3)	7.9
Dielectric loss D (%)	1.5
Relative dielectric constant ε_r ($=\varepsilon_{33}^T/\varepsilon_0$)	2100

[a] Provided by Eleceram Technology Co., Ltd. (Taiwan).

form the electrodes, and then baked in an oven at 150 °C for 30 min. Then, specimens were placed at ambient air temperature for one day. Finally, prior to polarization, specimens were heated at 23 °C, 50 °C, 80 °C, 100 °C, 120 °C, 140 °C or 150 °C (pretreatment temperature) for 40 min.

2.2. Electric properties prior to polarization

After temperature pretreatment, the specimen was cooled to room temperature, and we immediately measured capacitance (C) and dielectric loss (D) using an impedance phase analyzer and calculated the relative dielectric constant ε_r. Table 2 shows the electric properties of the PP (PZT/cement composite) and PC (100% cement) materials at 1 kHz. The C, D and ε_r of the PP and PC materials always decrease with increasing pretreatment temperature. The trend of these experimental results is similar to Chaipanich's report [40]. Apparently, a pretreatment temperature of 100 °C represents a threshold for capacitance C and relative dielectric constant ε_r. The values for PC are greater than those for PP (cement with PZT) below 105 °C, but the reverse is true above 105 °C.

Cement (PC material) is not a piezoelectric material, but the PP material is. Piezoelectric materials with higher D values make it difficult to apply the voltage required for poling PZT particles [33], often facilitating the induction of current breakdown in specimens during polarization. Thus, a lower D value is expected for PZT/cement composites to obtain efficient poling. As shown in Table 2, the higher pretreatment temperature of the specimen resulted in a lower dielectric loss D, indicating that temperature pretreatment facilitates polarization of the specimen. PP materials have the lowest value D = 0.129 at 150 °C.

2.3. Experimental parameters

To elicit the dielectric and piezoelectric properties of PZT/cement composites, specimens were poled with a 1.5 kV/mm electric field in 150 °C silicone oil for 40 min. Here, poling time of 40 min was adopted due to having a better poling efficiency, based on previous reports [22,27,38].

For the effect of temperature treatment, specimens were cured for 1 day at 90 °C and 100% relative humidity, and then were pretreated prior to polarization at 23 °C, 50 °C, 80 °C, 100 °C, 120 °C, 140 °C or 150 °C, with a heating time of 40 min. The reason for choosing the temperature treatment period of 40 min is that 40 min being the optimum time has been found to expel most of free water within specimens because increases rate of d_{33} reduces tremendously after 40 min. After temperature pretreatment, specimens were cooled down to room temperature and prepared for the polarization. In addition, specimens were also cured for 1, 3, 7, 14, 28 and 56 days at 90 °C, with the samples placed at 100% relative humidity on the first curing day and then immersed in 90 °C water starting on the second day, to explore the effect of the curing time on PZT/cement composites.

Table 2
Electric properties of PP and PC materials before the polarization.

Pretreatment	C (pF)		ε_r		D	
	PP	PC	PP	PC	PP	PC
23 °C	87.0	120.2	111.2	153.7	0.288	1.13
50 °C	80.1	112.3	102.4	143.6	0.279	1.08
80 °C	76.2	101.8	97.4	130.1	0.221	1.02
100 °C	71.4	79.1	91.3	101.2	0.194	0.81
120 °C	62.2	53.8	79.5	68.7	0.143	0.74
140 °C	46.4	40.1	59.3	51.3	0.131	0.52
150 °C	32.5	24.7	41.5	31.6	0.129	0.49

The piezoelectric properties were measured and calculated immediately when the specimen was successfully polarized, and then the data were recorded daily up to 150 days. Specimens were tested with an impedance phase analyzer (Model 6520A) at 1 kHz and a d_{33} piezometer (Model P/N 90-2030) with a frequency of dynamic force at 110 Hz. Each experimental value shown here represents an average of three specimens tested at 23 °C ± 1 °C and 50% ± 2% relative humidity, and the d_{33} value was measured at nine positions for each specimen.

3. Results and discussion

3.1. Porosity

After a 1 day curing period, specimens were monitored by optical microscopy (OM) at 350 × magnification as shown in Fig. 1 to visualize the constituents of the PP material. The OM image consists of three parts: PZT particles, cement binder and pores, where crimson spots represent the pores inside the specimen. No clustering of PZT particles was observed. The porosity was then calculated by using image analysis software (Power Image Analysis System, PIA) with pixel threshold criteria (pixel: 1280 × 1024 and the dividing value of black and white: 70), by counting the area ratio of crimson spots and the entire OM image shown in Fig. 1, to obtain an average porosity of 2.24% for the PP material. Compared with normal concrete and mortar, this porosity value is fairly small because the specimen was dry formed at 80 MPa. The specimen was compacted, and the resulting isolation of pores resists water transport during curing, as seen in the image.

3.2. Dielectric loss

The poling duration from 0 to the designated final poling field (here is 1.5 kV/mm) is referred to as the trigger time. If a specimen has a longer trigger time, it is difficult to polarize the specimen and easy to induce current breakdown during polarization. The D values of the PP material cured for 1 day, as reported in Table 2, decrease from 0.288 to 0.129 as the pretreatment temperature increases from 23 °C to 150 °C. The trigger time for the PP material pretreated at 23 °C and 150 °C was approximately 9–10 min and 3–4 min, respectively. PZT/cement composites with higher dielectric losses D always have longer trigger times.

The relationship between curing time and D is plotted in Fig. 2, where PP_{23} and PC_{23} represent PP and PC materials treated at 23 °C, respectively. The dielectric losses of PC_{23} materials (100% cement

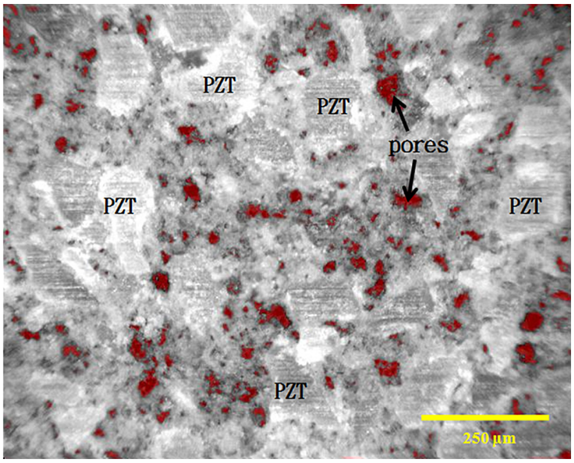

Fig. 1. OM image of the PP material after a 1 day curing period.

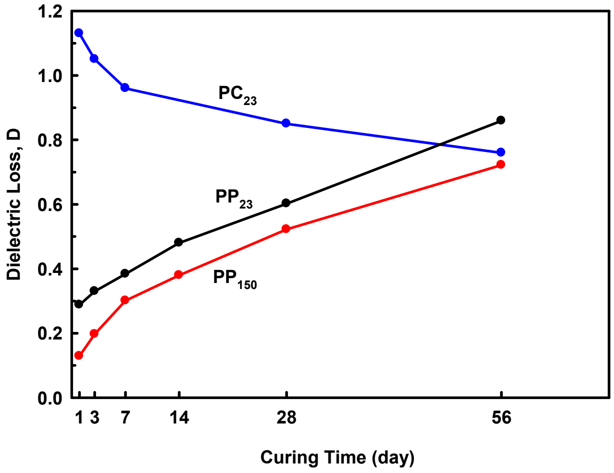

Fig. 2. Curing time effect on dielectric loss D before the polarization.

with 23 °C pretreatment) decrease with increasing curing time, but the development of D with curing time for PP materials is reversed. The trigger time of PP materials rapidly increase as the dielectric loss develops with the curing time. It is noted that specimens for both PP_{23} and PP_{150} (PP with 150 °C pretreatment) cured for 56 days have the occurrence of current breakdown, that is, the polarization fails due to the D value greater than 0.73 [38]. Curing time has a significant effect on dielectric losses for both PC and PP materials. The trend of lower dielectric losses at higher pretreatment temperatures still holds.

3.3. *Piezoelectric strain factor*

The piezoelectric strain factor d_{33} of PZT/cement composites cured for 1 day are shown in Fig. 3, where solid lines represent PP materials subjected to pretreatment temperature from 23 °C to 150 °C and aging time is the day counted after specimens were successfully polarized. In Fig. 3, the d_{33} values and some previous results with 50% PZT [18,20,24,29,30,36,41] are marked with triangles or redrawn as dashed lines despite the fact that some experimental conditions were not quite the same. Comparisons with experimental data and previous results indicate an acceptable range of accuracy in these experiments, although the d_{33} values of the PP_{23} material were low on the first 4 aging days.

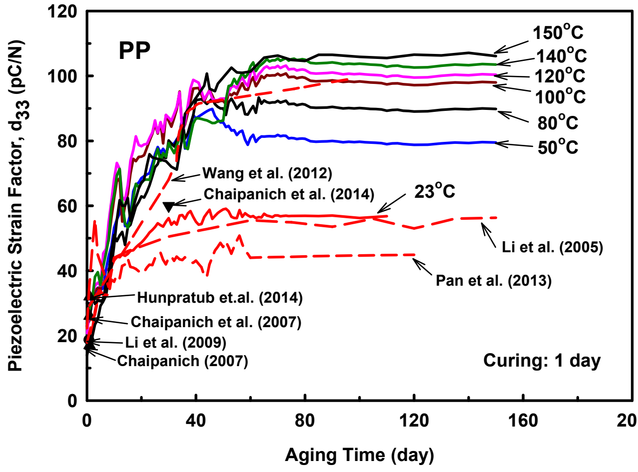

Fig. 3. Comparisons of piezoelectric strain factor d_{33} at 1 curing day.

The d_{33} values for PZT/cement composites increased with age and pretreatment temperature. For the PP_{23} material, the rate of increase gradually decreases with age, and is only 1.44% at the age of 28 days after polarization. That is, the d_{33} reaches a saturation value after 28 days. The d_{33} values for the PP_{23} material are 53.6 pC/N and 57 pC/N at 28 days and 70 days, respectively. However, the d_{33} values continue to develop for materials pretreated at temperatures greater than 23 °C until ages of more than 60 days, when the rate of increase is less than 1%. At early specimen ages (1–6 days), the rate of increase in d_{33} for PP material at room temperature (23 °C) is similar to the rate of increase for specimens pretreated at higher temperatures.

At longer aging times (after 60 days), all d_{33} values approach constants, with dashed lines representing previous results [24,29,36] such as those of Li et al. [29], who applied a 4.3 kV/mm electric field to the composite and Wang et al. [24], who examined the composite containing silica-based materials. Experiments indicated that PP specimens pretreated at higher temperatures always exhibit higher d_{33} values, and the PP_{150} material has the highest d_{33} value. The d_{33} values of PP materials pretreated at temperatures greater than 100 °C are even higher than that of the composite containing 60% PZT and 20 wt% silica-based material as determined by Wang et al. [24]. The d_{33} values for PP_{23} and PP_{150} respectively are 57 pC/N and 106.3 pC/N, almost double for the materials containing 50% PZT and no admixtures. Higher temperature pretreatment likely expels more water from the specimen, leading to more effective poling. Therefore, temperature pretreatment of PZT/cement composites before polarization is an effective way to increase d_{33}.

3.4. *Relative dielectric constant*

Table 3 reports the capacitance C of PZT/cement composites measured after polarization. The C values of PP_{23} increase with age and reach a plateau after 28 days. As the composites are pretreated at higher temperatures, the capacitance increases significantly with aging time up to 56 days, and reaches an approximately constant value after 70 days. Meanwhile, increasing pretreatment temperature can enhance the capacitance of cement piezoelectric composites. For instance, the capacitance values of the PP_{23} and PP_{100} materials are 216.3 pF and 341 pF at 70 days, respectively, approximately a 62% increase for the high temperature treated specimen. This higher value probably results from the loss of water from the cement. Comparisons between Tables 2 and 3 show that the C values of the PZT/cement composites measured after polarization (0 days) were lower than those before polarization pretreated at temperatures below 100 °C. All C values continue to increase with age after polarization, rising far above the values before polarization.

The relative dielectric constant ε_r depending on the capacitance, the specimen thickness, the permittivity of the free space constant ε_0 and the electrode area can be calculated by Ref. [29].

Table 3
Capacitance of PZT/cement composites after the polarization (pF).

Materials	Aging time				
	0 day	7 days	28 days	56 days	70 days
PP_{23}	60.8	147.5	200.7	214.8	216.3
PP_{50}	75.9	124.5	228.1	287.7	296.0
PP_{80}	72.1	124.8	235.3	316.1	320.7
PP_{100}	78.3	145.2	259.7	332.9	341.0
PP_{120}	66.5	148.7	252.7	337.6	348.9
PP_{140}	77.8	145.9	228.2	340.6	354.3
PP_{150}	35.5	119.3	251.5	356.0	373.0

$$\varepsilon_r = \frac{C\,t}{A\,\varepsilon_0} \tag{1}$$

where $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m and the capacitance C was measured at 1 kHz. t and A are specimen thickness and electrode area, respectively. The value of ε_r is proportional to the capacitance C. In Fig. 4, the ε_r value of the composites continues to develop with age, gradually approaching a steady value after 28 days for 23 °C pretreatment and after 56 days for specimens pretreated above 50 °C. The ε_r value for PP_{150} at the age of 56 days was 455, 1.66 times the value for the sample treated at 23 °C ($\varepsilon_r = 274.6$). Similar to the piezoelectric strain factor d_{33}, the composites subjected to temperature pretreatment at temperatures higher than room temperature can exhibit an enhanced ε_r value. The rate of increase decreases to zero at an age of 70 days, leading to a stable value of ε_r. At this stage, ε_r is 477 for the composites subjected to 150 °C pretreatment.

3.5. Piezoelectric voltage factor

The piezoelectric voltage factor g_{33}, another important factor for piezoelectric materials used as sensors, is calculated from d_{33} and ε_r as Ref. [21].

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

In Table 1, the g_{33} value of PZT piezoelectric ceramic is 24×10^{-3} V–m/N. Fig. 5 shows the development of g_{33} for the composite with 50% PZT. The fluctuations of g_{33} with aging time varied dramatically at early ages, gradually becoming stable after 60 days, except for the PP_{23} material, which became stable on about the 7th day. The g_{33} of specimens pretreated at higher temperatures tended to increase after 56 days (or after 130 days as shown in Fig. 5). The rate of increase in the g_{33} values of PZT/cement composites was less than 1% after 28 days, and approached zero after 56 days, leading to stable g_{33} values. The g_{33} values for the composites pretreated at temperatures from 23 °C to 150 °C were $24–26 \times 10^{-3}$ V–m/N at day 70, and those values were even higher than that of the PZT ceramic in Table 1. These results show that the sensitivity of PZT/cement composite sensors is better than that of PZT sensors.

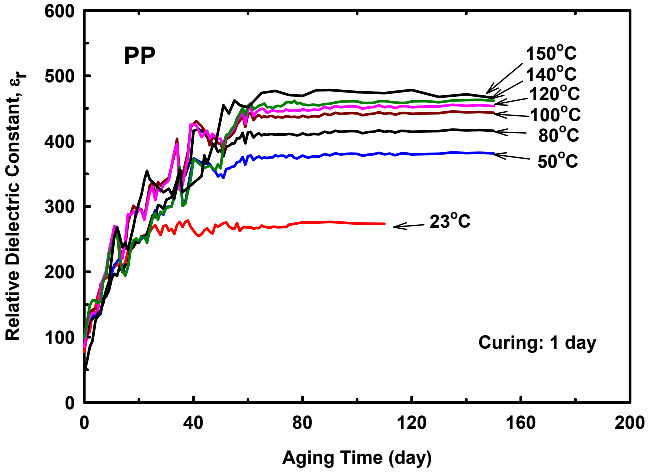

Fig. 4. Relative dielectric constant ε_r and aging time.

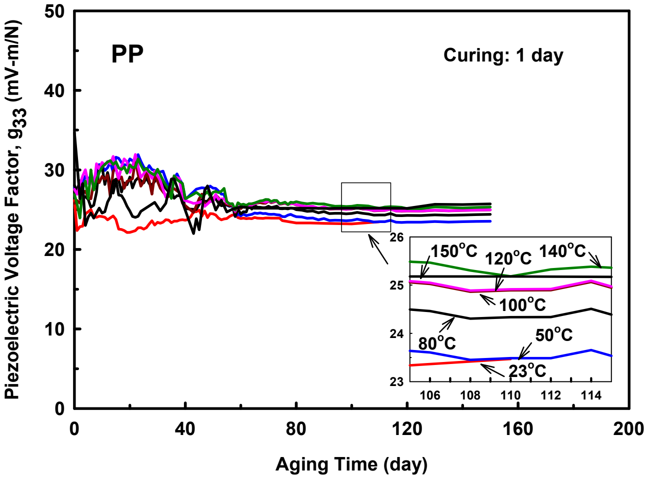

Fig. 5. Piezoelectric voltage factor g_{33} and aging time.

3.6. Electromechanical coupling coefficient

The thickness electromechanical coupling coefficient K_t is calculated from the resonance frequency at the minimum impedance f_m and at the maximum impedance f_n captured in impedance-frequency spectra as follows [26].

$$K_t^2 = \frac{\pi}{2}\frac{f_m}{f_n}\tan\left(\frac{\pi}{2}\frac{f_n - f_m}{f_n}\right) \tag{3}$$

Higher K_t values represent more efficient conversion between electrical and mechanical energy. The K_t values exhibit only a 1% reduction as the specimen ages as plotted in Fig. 6, indicating the negligible influence of aging time. The values vary from 13.16 to 13.52 among all pretreatment temperatures after 70 days. Although increasing temperature can slightly increase the K_t value except for specimens treated at 150 °C, this effect was minor.

3.7. Impedance-frequency spectra

After pretreatment at 150 °C and successful polarization, impedance-frequency spectra of PZT ceramic (PZT_{150}) subjected to a 1.5 kV/mm electric field were measured relative to aging time as shown in Fig. 7, indicating that aging time had no effect on the

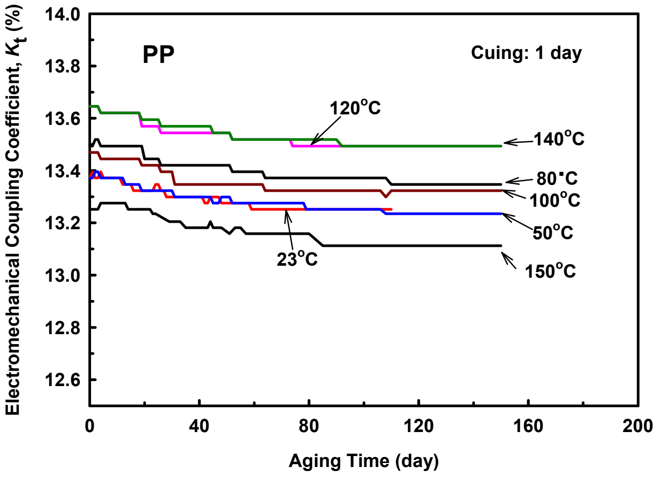

Fig. 6. Electromechanical coupling coefficient K_t and aging time.

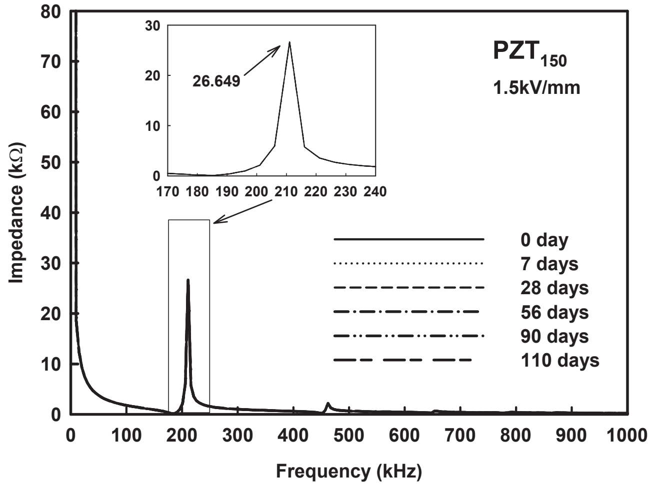

Fig. 7. Aging time effect on impedance-frequency spectra for the PZT_{150} ceramic.

resonance frequency at minimum and maximum impedance. The f_m and f_n values of PZT_{150} remained approximately constant at 184.17 and 210.30 kHz, respectively, during the 110 day aging period. The effect of pretreatment temperature on PZT is also presented in Fig. 8, with f_m values lying between 180.65 kHz and 184.67 kHz and f_n values between 209.29 kHz and 211.31 kHz for all pretreatment temperatures after a 70 day aging period. These results suggest that pretreatment temperature does not have a major influence on the resonance frequency of PZT.

Fig. 9 presents impedance-frequency spectra for the PP_{150} material over 70 aging days. The impedance of the resonance frequency decreases with aging time, especially in the first 7 days. This is when because PZT/cement composites are subjected to a poling voltage, residual charge likely remains inside the specimen, and then the electric properties gradually become more stable with age. For example, the impedance only exhibits a slight change after 7 days in Fig. 9. The resonance frequencies of PP materials pretreated at temperatures from 23 °C to 150 °C is plotted in Fig. 10 versus aging time, demonstrating that both the f_m and f_n values increase with age after 7 days and lie between 131 kHz and 143 kHz. Fig. 11 shows that the resonance frequency on the 70th day decreases with increasing temperature except for 150 °C. Meanwhile, the differences between f_m and f_n were all equal to 1.01 approximately.

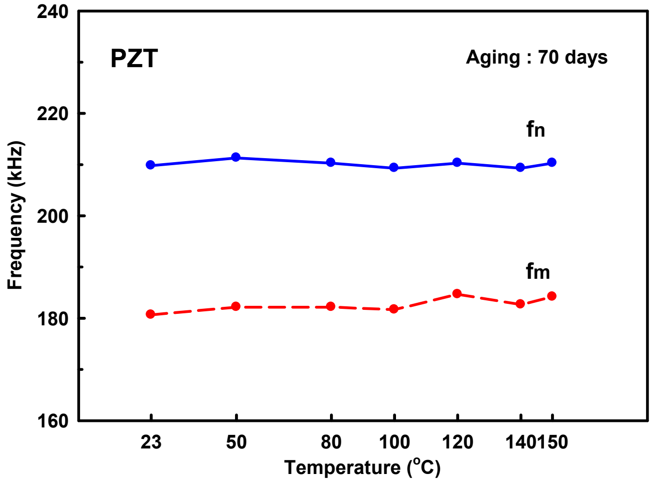

Fig. 8. Pretreatment temperature effect on resonance frequency at minimum and maximum impedance for PZT ceramics.

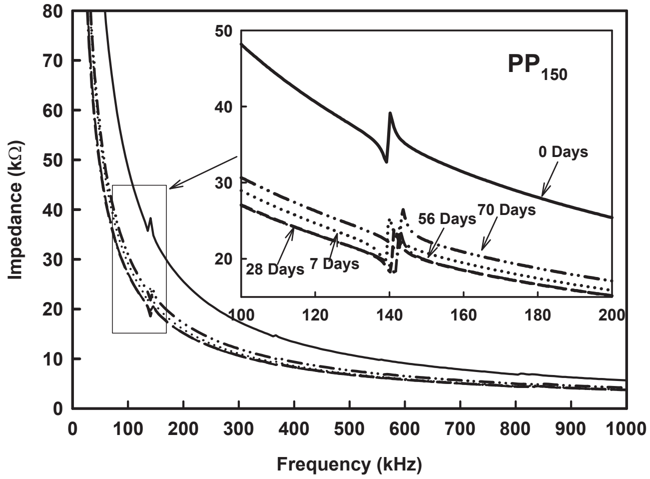

Fig. 9. Aging time effect on impedance-frequency spectra for the PP_{150} material.

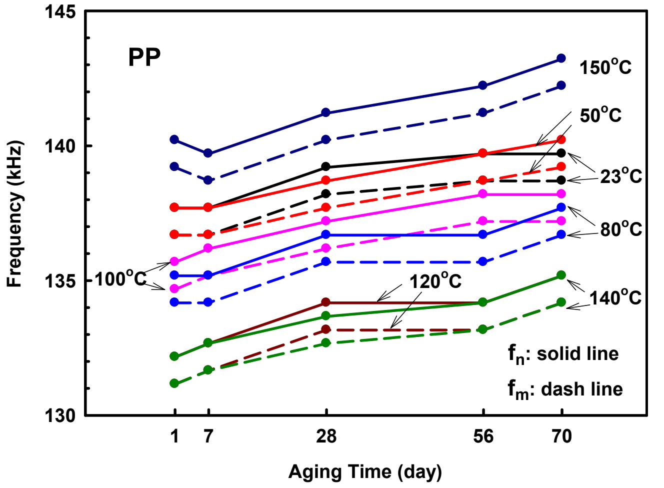

Fig. 10. Resonance frequency of PP materials related to aging time and pretreatment temperature.

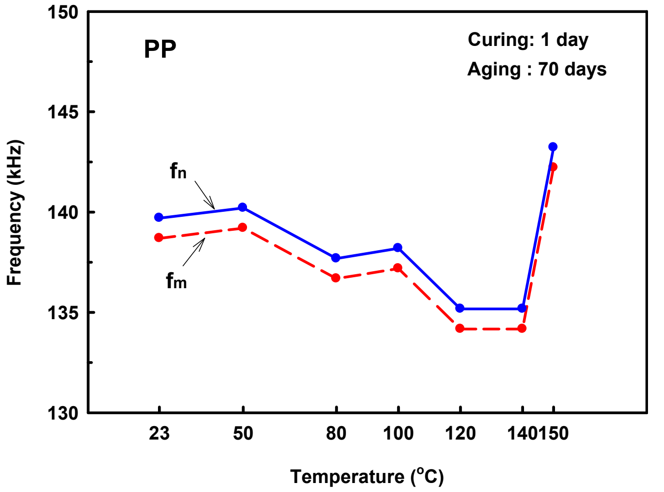

Fig. 11. Pretreatment temperature effect on resonance frequency of PP materials.

For example, the f_m and f_n values for samples pretreated at 120 °C were 134.17 kHz and 135.18 kHz, respectively, and the corresponding values for 150 °C were 142.21 kHz and 143.22 kHz. Nevertheless, the electromechanical coupling coefficient K_t for samples pretreated at 120 °C is slightly higher than that for samples pretreated at 150 °C as shown in Fig. 6, due to the smaller f_n value.

3.8. Pretreatment temperature effect

To demonstrate the benefits of piezoelectric factors affected by pretreatment temperature, first, PZT specimens were subjected to the same temperatures ranging as PP materials before polarization, and then a 1.5 kV/mm poling field was applied at 150 °C for 40 min. The piezoelectric strain factors of PZT ceramics were measured from the beginning of the aging time to 150 days. All experimental data lie in between 396 and 400 pC/N and the differences in the d_{33} values of PZT ceramics are approximately 1% or less, regardless of the effects of pretreatment temperature and aging time. These results indicate that pretreatment temperature and aging time do not exert a significant influence on the d_{33} values of PZT ceramics. This relationship to aging time is different from the report by Chaipanich et al. [39] that the d_{33} values of PZT first decreased at an early age, with the reduction in d_{33} values becoming less significant at longer aging times. The constituents of PZT ceramic and poling conditions (poling field, poling time and poling temperature) are believed to be the keys resulting in the difference, compared with the result of Chaipanich et al. (with a poling field of 2 kV/mm for 45 min at a poling temperature of 130 °C) [39].

Properties approaching stable values were selected to compare the piezoelectric factors of PZT/cement composites subjected to pretreatment temperature prior to polarization. Figs. 12 and 13 show piezoelectric factors on aging day 70 with respect to the pretreatment temperature. Increasing pretreatment temperature brings higher values of the piezoelectric factors. For the PP_{23} material, the d_{33} and ε_r values shown in Fig. 12 were 57 pC/N and 269, respectively, close to previous reports studying 50% PZT [29,36,37,39]. When the composites were pretreated at 150 °C, the d_{33} and ε_r values increased to 106.3 pC/N and 477, respectively, almost 186% and 177% enhancements. In Fig. 13, the g_{33} and K_t values of the composites treated at 23 °C are 23.95×10^3 V−m/N and 13.25%, respectively, and the highest values for both factors occur at 140 °C, with 26.27×10^3 V−m/N and 13.52%.

The phase angle of the PZT/cement composite also depends on aging time and approaches a constant value after 80 days, while that of the PZT ceramic does not. The phase angle for PZT ceramic and PP materials was measured on aging day 90 and is shown in Fig. 14 with respect to pretreatment temperature. For PZT ceramic, the phase angles for PZT_{23} and PZT_{150} were 84.5° and 85.3°, respectively. Pretreatment temperature does not exert a significant influence on the PZT phase angle. However, subjecting PP materials to higher temperatures before polarization can benefit the phase angle. For example, the phase angle of PP_{23} is −61.2°, and that of PP_{140} is −67.6°. This trend of increasing phase angle with temperature is not suitable for the PP_{150} material, which has a phase angle of −62.1°.

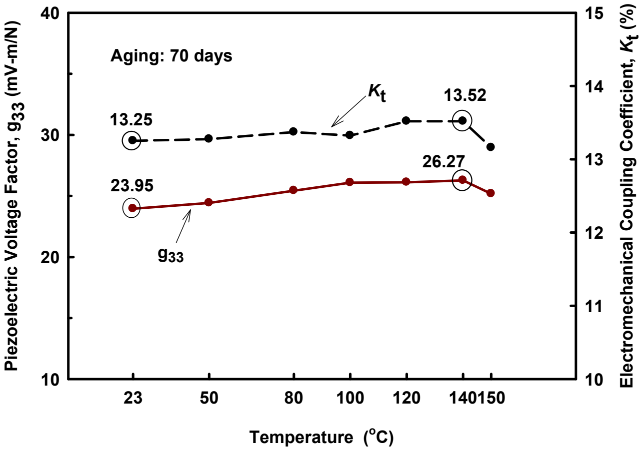

Fig. 13. Pretreatment temperature effect on g_{33} and K_t of PP materials.

4. Conclusions

High temperature pretreatment of cement-based piezoelectric composites containing 50% PZT prior to polarization produced high piezoelectric factors. The composites pretreated at higher temperatures exhibited a lower dielectric loss, shortening trigger time of the polarization. As pretreatment temperature increases, the d_{33} and ε_r values of PZT/cement composites increase significantly, and g_{33} increases moderately. The d_{33} value of the composites pretreated at 150 °C reaches 106.3 pC/N at aging day 70, while the sample pretreated at 23 °C has a value of 57 pC/N. The ε_r value of the composite subjected to 150 °C pretreatment, 477, is 177% greater than that for the sample pretreated at 23 °C. The g_{33} and K_t values of the composite pretreated at 140 °C are relatively high, and the resonance frequency continues to decrease with increasing pretreatment temperature until 140 °C. The effect of curing time on

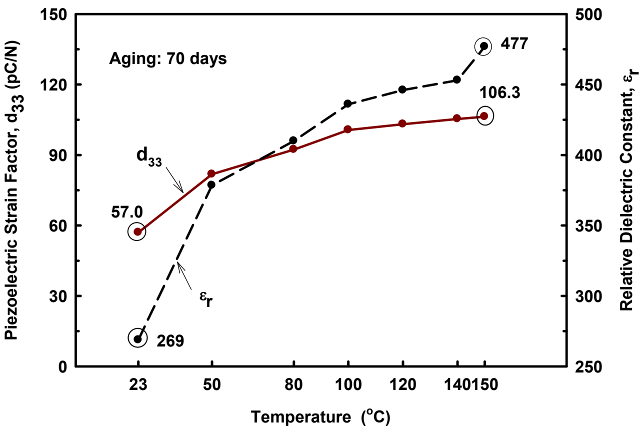

Fig. 12. Pretreatment temperature effect on d_{33} and ε_r of PP materials.

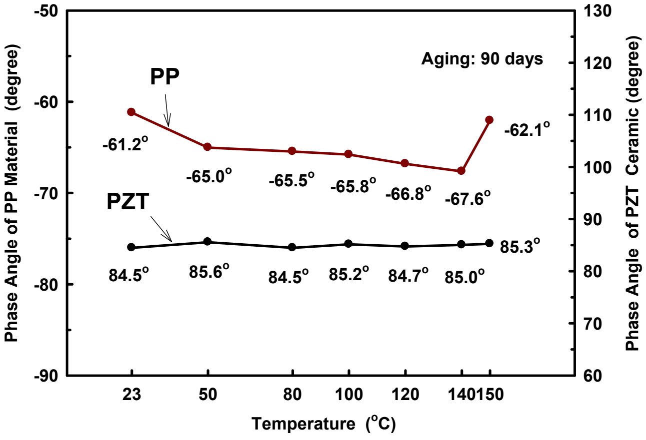

Fig. 14. Pretreatment temperature effect on phase angle of PP and PZT materials.

dielectric losses is significant, affecting the feasibility of polarization.

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