High piezoelectric properties of cement piezoelectric composites containing kaolin

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ABSTRACT

To obtain high piezoelectric properties, PZT/cement composites with kaolin were fabricated and polarized by 1.5kV/mm electric field for 40 min, where lead zirconate titanate (PZT) inclusion with 50% by volume was used. After the polarization, piezoelectric properties of the composite were measured daily till 100 days. Results indicated that relative dielectric constant (ε_r) and piezoelectric strain constant (d_{33}) increase with aging day, and approach to asymptotic values after 70 days. Temperature treatment to the composite is a dominate factor to enhance piezoelectric properties. The d_{33} and ε_r values of PZT/cement composites treated at the ambient temperature (23℃) were 57pC/N and 275 at the 70th aging day respectively, and then reached 106pC/N and 455 in turn with 150℃ treatment. The composite contains 4% kaolin having the highest value of d_{33}=111pC/N and ε_r=500 at 90 days because the porosity is the less than the others. Cement piezoelectric composites containing kaolin own the higher d_{33} and ε_r value, compared with the other reported composites with 50% PZT. The porosity, the electromechanical coupling factor and impedance-frequency spectra of the cement piezoelectric composites were also discussed.

Keywords: cement, piezoelectric properties, kaolin, lead zirconate titanate, porosity, sensor

1. INTRODUCTION

Instead of conventional piezoelectric ceramics or polymers, cement-based piezoelectric composites as sensors for structural health monitoring in concrete structures were developed to overcome the matching problem with concrete. The manufactures of cement-based piezoelectric composites having high piezoelectric and dielectric constants are still ongoing. For 0-3 type cement-based piezoelectric composites (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 piezoelectric strain constant d_{33} and relative dielectric constant ε_r were near 60 pC/N and 300, respectively, with the exception of Wang et al.[1] who 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.

A great deal of effort has been made to improve the dielectric and piezoelectric properties of cement-based piezoelectric ways to enhance ferroelectric behavior. Some admixtures such as carbon[2], carbon black[3-4], carbon nanotubes[5] and pozzolanic materials[6-8] have been selected to use in cement piezoelectric composites, finding that adequate content of admixtures can slightly increase the d_{33} and ε_r values of PZT/cement composites. This work focuses on PZT/cement composites consisting of Type I Portland cement as the matrix and randomly oriented PZT particles as the functional inclusion, where kaolin addition was added to the composite.

2. EXPERIMENTAL PROGRAM

PZT particles are uniformly distributed to cement-based binders, so-called 0–3 cement piezoelectric composites. PP composite is a cement piezoelectric composite with 50% PZT and 50% cement by volume, where acoustic impedance (ρ_v) of PP is 10×10^{-6} kg-m^{-2}s^{-1} close to concrete with $\rho_v = 9.0\times10^{-6}$ kg-m^{-2}s^{-1}. Kaolin as a partial replacement of cement was added to the composite. There are six replacements of cement by kaolin, 1, 2, 4, 6, 8 and 10 vol.%, in PP composite. KPC materials represent the PP material containing kaolin. For instance, KPC1 represents 1 vol.% of cement replaced by kaolin in the PP composite.

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Cement is type I Portland cement with the fineness of 349m^2/kg and a specific gravity of 3.16. The specific gravity, particle diameter and the fineness of kaolin are 2.63, 1.5μm and 9000~11000m^2/kg, respectively. The main chemical components of kaolin and cement are listed in Table 1. PZT particles of 75–150μm were chosen, which have a specific gravity of 7.9, d_{33} = 470 pC/N, piezoelectric voltage constant $g_{33} = 24\times10^{-3}$ V-m/N, and ε_r = 2,100, as listed in Table 2.

Table 1. Main chemical components of kaolin and cement

Components	kaolin (%)	Cement (%)
SiO_2	52.87	21.24
AlO_3	44.53	4.44
K_2O	0.15	---
Fe_2O_3	0.52	3.44
CaO	---	64.51
MgO	---	2.35
TiO_2	1.24	---

Table 2. Properties of PZT

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

To prepare specimens, PZT particles, cement and kaolin were pre-mixed 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 15mm∯ cylindrical steel mold at 80 MPa compression to form a disk-like specimen. Afterwards, specimens were cured for 24 h at 90℃ and 100% relative humidity to produce suitable strength. After curing, the specimens sequentially were polished to a 2mm in thickness, and were monitored by optical microscopy (OM) at 350X magnification to visualize the constituents and the porosity of the composite.

Before the polarization, specimens were coated on both sides with silver paint and then baked in an oven at 150℃ for 30 minutes to form the electrode. After that, specimens were placed at ambient air temperature for one day. Finally, specimens were heated at 150℃ (pretreatment temperature) for 40 min. Here, PP material was treated at 23℃ (PP_{23} material) used as a reference.

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 (Model 6520A) at 1 kHz. Relative dielectric constant ε_r was calculated from $Ct/\varepsilon_0 A$ [9], where t is the thickness of specimen (here is 2mm), ε_0 is a vacuum dielectric constant (8.854pF/m), and A is the electrode area (15mm).

To create piezoelectric properties, voltage field applying to the composites is required. No piezoelectric properties are found without successful polarization. Poling voltage was applied to the specimen at 1.5kV/mm, in a 150□ silicone oil bath for 45 minutes. During the polarization, voltage increase should be carefully applied to prevent from current breakdown of the specimens. The piezoelectric properties were measured and calculated immediately when the specimen was successfully polarized, and then the data were recorded daily up to 100 days. Specimens were tested with an impedance phase analyzer 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 24℃ and 50% relative humidity, and the d_{33} value was measured at nine positions for each specimen.

3. RESULTS AND DISCUSSION

3.1 Porosity

Before the polarization, the specimens were monitored by optical microscopy (OM), and the OM image for PP material with 0% and 4% of kaolin were shown in Figure 1 and 2 respectively, where crimson spots represent the pores inside the specimen. Both figures indicate that no clustering of PZT particles was observed.

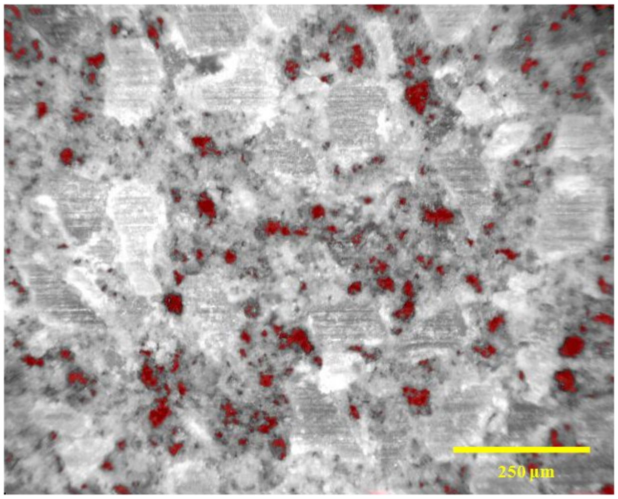

Figure 1. OM image of PP material (350X)

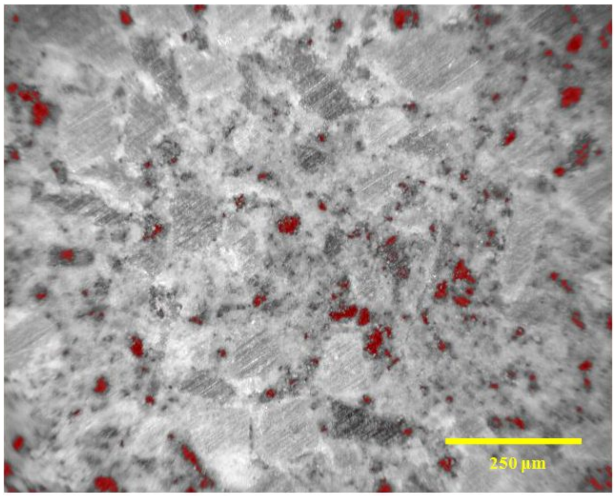

Figure 2. OM image of PKC4 material (350X)

From the OM image, the porosity was calculated by image analysis software with pixel threshold criteria to obtain an average porosity for the PP material and KCP materials, as listed in Table3. Obviously, the porosity of the composite without kaolin (PP material) has a value of 2.33%, and the values with increasing kaolin (PKC materials) first decrease and then increase. PP material containing 4% kaolin (PKC4) has the lowest porosity, with 1.86%. Adding kaolin can reduce the pores in the composites because the particle of kaolin is smaller than that of cement.

Table 3. Porosity of PP material and PKC materials

Materials	PP	PKC1	PKC2	PKC4	PKC6	PKC8	PKC10
Porosity (%)	2.33	1.91	1.89	1.86	1.92	1.96	1.99

3.2 Dielectric loss and dielectric constant before the polarization

Cement-based composites do not have piezoelectric properties without a successful polarization. If a specimen has a higher dielectric losses D prior to the polarization, it will be difficult to polarize the specimen and easy to induce current breakdown during the polarization. We measured dielectric loss D and relative dielectric constant ε_r of the composites prior to the polarization. Thus, a lower D value is expected for PZT/cement composites to obtain efficient poling. As shown in Table 4, the higher pretreatment temperature of the specimen resulted in a lower dielectric loss D, indicating that temperature pretreatment facilitates polarization of the specimen. With 150℃ temperature pretreatment, PP materials have the lowest value D = 0.13 and PKC10 has the highest value D = 0.22 as reported in Table 4. Adding kaolin into PP material will increase the D value. The trend affected by temperature and kaolin for relative dielectric constant ε_r is similar to dielectric loss D.

Table 4. ε_r and D of PP and PKC materials before the polarization

Materials	ε_r		**D**	
	23℃	150℃	23℃	150℃
PP	111	41	0.29	0.13
PKC1	123	42	0.31	0.13
PKC2	152	45	0.36	0.14
PKC4	165	47	0.41	0.17
PKC6	182	48	0.49	0.18
PKC8	225	50	0.53	0.20
PKC10	252	53	0.58	0.22

3.3 Piezoelectric strain constants

The values of dielectric loss were pretty low listed in Table 4, indicating PKC materials can be poled in electric field. After the polarization, the piezoelectric strain constants d_{33} of cement piezoelectric composites cured for 24 h are shown in Figure 3, where solid lines represent PP_{150} and PKC materials subjected to a 150℃ temperature treatment and PP_{23} subjected to a 23℃. Piezoelectric strain constants in Figure 3 with dashed lines representing previous results[1,6,10]. Experiments indicated that the d_{33} values increase with aging time, and PP specimens pretreated at higher temperatures always exhibit higher d_{33} values. At the 70th day, the d_{33} values for PP_{23} and PP_{150} are 57 pC/N and 106.3 pC/N, respectively. Meanwhile, the d_{33} values of PP_{150} containing 1-6% kaolin are higher than that of PP_{150} after 90 days, indicating that proper kaolin content can increase the PP material. The d_{33} value of PP and PKC materials is shown in Table 5. PKC4 has the highest value of d_{33}, with the value of 111.1 pC/N. Compared with the results of Wang et al.[1], higher d_{33} values of cement piezoelectric composites has been manufactured.

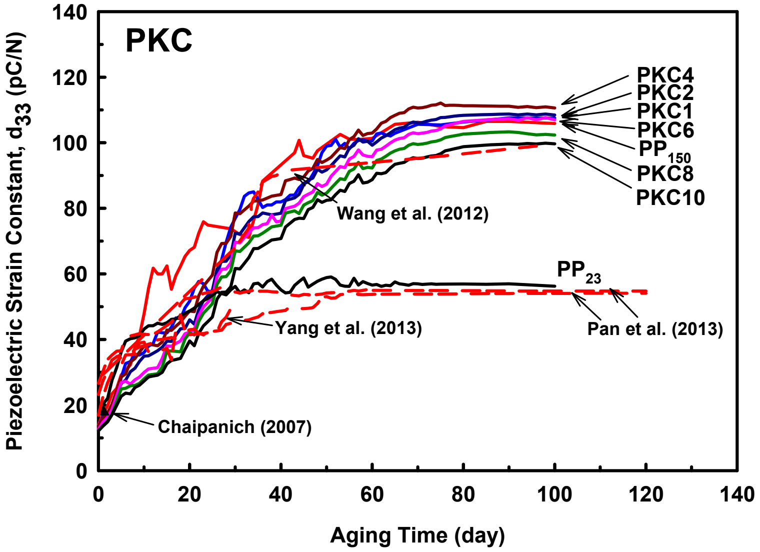

Figure 3. Piezoelectric strain constant of cement piezoelectric composites

Table 5. The d_{33} value of PP and PKC materials (pC/N)

Materials	**Age after the polarization (day)**						
	0	7	28	56	60	70	90
PP	13.9	32.3	73.8	101.0	101.3	106.3	106.5
PKC1	13.3	33.3	69.6	99.8	100.5	105.6	107.6
PKC2	13.6	30.2	63.9	99.2	99.2	106.0	108.7
PKC4	13.3	33.1	69.4	101.9	102.9	110.6	111.1
PKC6	12.6	26.4	61.5	95.8	95.7	102.8	107.4
PKC8	12.2	25.9	59.2	92.0	92.3	99.5	103.3
PKC10	12.2	23.4	54.4	88.3	88.7	95.2	99.6

3.4 Relative dielectric constant

The relative dielectric constant ε_r depends on the capacitance, the specimen thickness, the permittivity of the free space constant ε_0 · and the electrode area[11]. In Figure 4, the ε_r value of the composites continues to develop with age, gradually approaching a steady value after 28 days for 23℃ pretreatment and after 60 days for 150℃. The ε_r value for PP_{150} at the age of 56 days was 455, 1.66 times the value for PP_{23} (ε_r =274.6). At the 90th day, the ε_r values for PKC materials (treated by 150℃) were higher than that for PP_{150} with 478.2, where the value of PKC1, PKC2, PKC4 and PKC6 were 486.3, 489.3, 500 and 483.9 (PKC6) respectively. Similarly to the piezoelectric strain constant d_{33}, the composites subjected to 150℃ temperature pretreatment and proper kaolin content can exhibit an enhanced ε_r value.

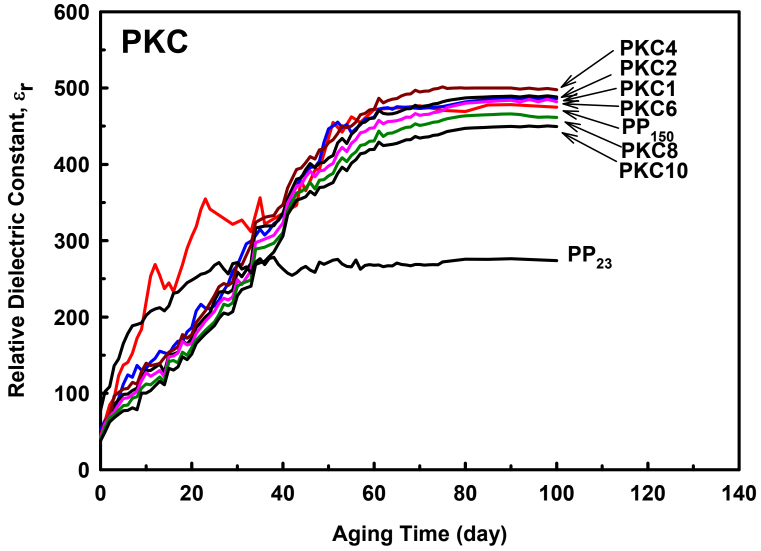

Figure 4. Relative dielectric constant of cement piezoelectric composites

3.5 Electromechanical coupling factor

The thickness electromechanical coupling factor 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 spectrum[12]. After pretreatment at

150℃ and subjected to a 1.5 kV/mm electric field, Figure 5 was impedance-frequency spectra of PKC4 material relative to the age after the polarization, indicating that aging time had no effect on the resonance frequency at minimum and maximum impedance. The resonance frequency of f_m and f_n for PKC materials was within the range of 120 kHz–136 kHz, shown in Figure 6. Compared with the PP material with the resonance frequency between 142.2 kHz and 143.2 kHz, adding kaolin into PP material will have the lower resonance frequency.

Higher K_t values represent more efficient conversion between electrical and mechanical energy. Table 6 is the results of electromechanical coupling factor for cement piezoelectric composites calculated from f_m and f_n. The K_t values exhibit only a 1% reduction as the specimen ages as listed in Table 6, indicating the negligible influence of aging time. Although the K_t value continues to increase with kaolin content, this effect was minor due to only 8% increase for PKC10.

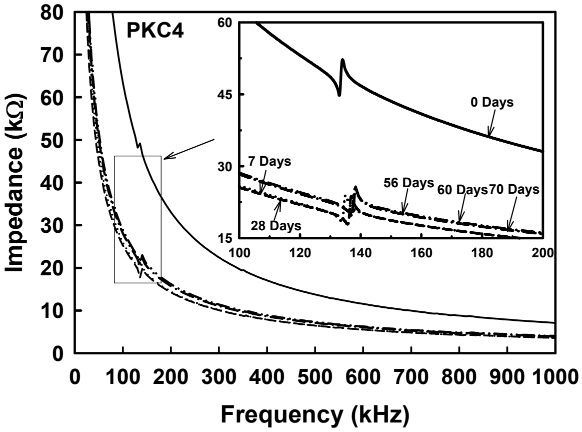

Figure 5. Impedance-frequency spectra of PKC4 material

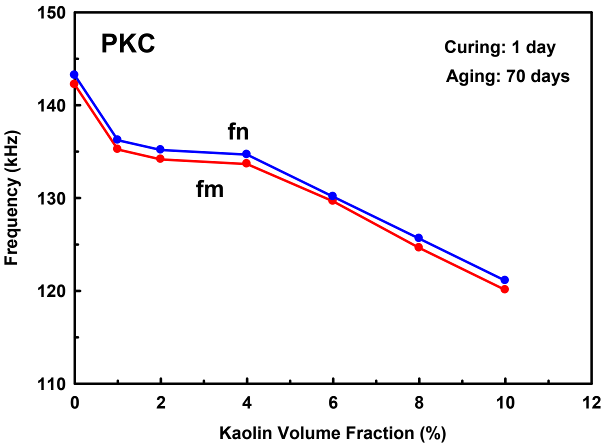

Figure 6. Resonance frequency of PKC materials

Table 6. Electromechanical coupling factor of cement piezoelectric composites (%)

Materials	Age after the polarization (day)						
	0	7	28	56	60	70	90
PP	13.3	13.3	13.2	13.2	13.2	13.2	13.1
PKC1	13.4	13.3	13.3	13.2	13.2	13.2	13.2
PKC2	13.5	13.5	13.4	13.2	13.2	13.2	13.4
PKC4	13.5	13.5	13.4	13.4	13.4	13.4	13.4
PKC6	13.7	13.7	13.7	13.6	13.6	13.6	13.6
PKC8	14.0	14.0	13.9	13.9	13.9	13.9	13.9
PKC10	14.3	14.3	14.3	14.2	14.2	14.2	14.2

3.6 Phase angle

To manufacture sensors or actuators made by cement piezoelectric composites, we also need to know the information of phase angle. Phase angle continues to develop with the age, plotted in Figure 7. Figure 8 shows the phase angle at the age of 90 days for PKC materials. The value of phase angle for PP and PKC10 is -62.1° and -72.1°, respectively. Phase angle will increase with kaolin content, except for PKC1 and PKC2. It seems that to establish the connection between the porosity and the phase angle for PKC materials is still difficult at this stage.

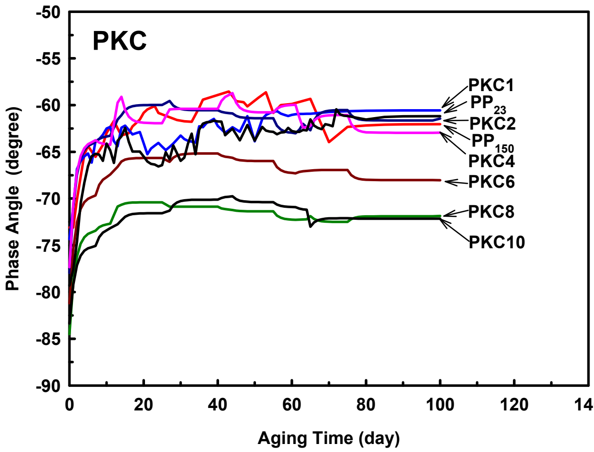

Figure 7. Age effect on phase angle.

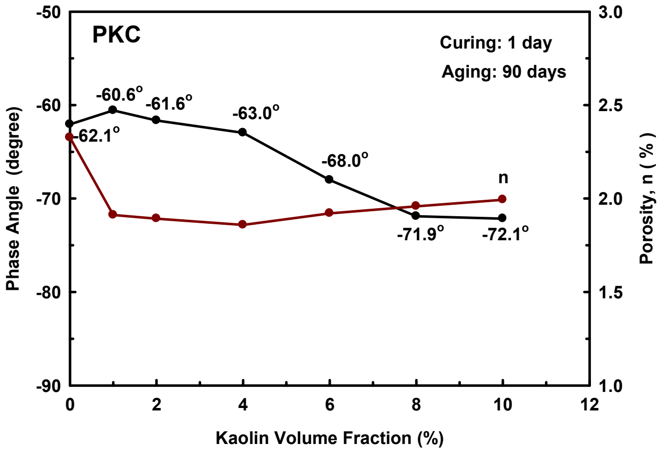

Figure 8. Phase angle at the age of 90 days for PKC materials

3.7 Kaolin effect

With 150℃ pretreatment, piezoelectric properties at the age of 90 days are listed in Table 7 or shown in Figure 9 and 10 for cement piezoelectric composites subjected to 1.5kV/mm poling voltage. In Table 7, experiment data of the d_{33} values lie in 99.6 –111.1 pC/N which is greater than d_{33} = 90 pC/N reported by Wang et al.[1]. To manufacture higher d_{33} value of cement piezoelectric composites has achieved.

Figure 9 indicates that the composite containing 4% kaolin has the highest value of d_{33} and ε_r, with d_{33} = 111.1 pC/N and ε_r = 500. Adding kaolin can increase d_{33} and ε_r, but its volume content should not be greater than 6%. The electromechanical coupling factor will continue to increase as kaolin increases, shown in Figure 10. The electromechanical coupling factor for PKC10 is 14.2%. The K_t value has 8% increasing if kaolin content increases from 0 to 10%. For the piezoelectric voltage constant g_{33}, however, kaolin has a less effective to the composite. Meanwhile, comparisons between the porosity and piezoelectric properties imply that reducing pores in the composites can increase d_{33} and ε_r.

Table 7. Piezoelectric properties at the age of 90 days

materials	**d_{33} (pC/N)**	**ε_r**	**g_{33} (mV-m/N)**	**K_t (%)**	**Porosity (%)**
PP	106.5	478.2	25.2	13.1	2.32
PKC1	107.6	486.3	25.0	13.2	1.91
PKC2	108.7	489.3	25.1	13.4	1.89
PKC4	111.1	500.0	25.1	13.4	1.86
PKC6	107.4	483.9	25.1	13.6	1.92
PKC8	103.3	466.1	25.0	13.9	1.96
PKC10	99.6	449.8	25.0	14.2	1.99

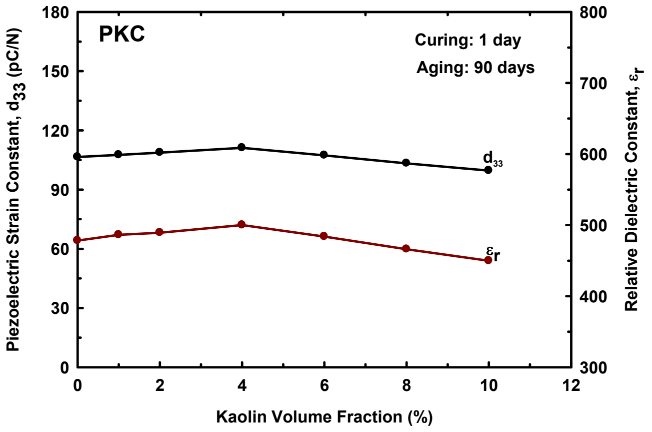

Figure 9. Piezoelectric strain constant and relative dielectric constant at the age of 90 days

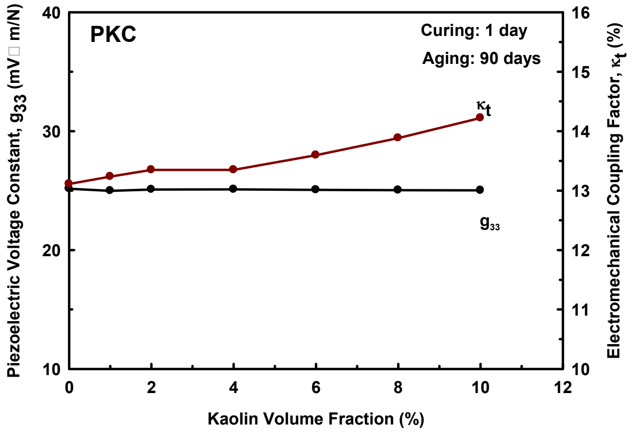

Figure 10. Electromechanical coupling factor and piezoelectric voltage constant Phase angle at the age of 90 days

4. CONCLUSIONS

Cement piezoelectric composites containing kaolin have been manufactured and can be successfully poled by 1.5 kV/mm. The main findings from the experiments on piezoelectric properties related to the pore and the temperature are as follows:

- Adding kaolin into PP material can reduce the pores in the composites. The composite contains 4% kaolin (PKC4) has the lowest porosity, with 1.86%.

- Before the polarization, the composites pretreated at 150℃ exhibited a lower dielectric loss D and relative dielectric constant ε_r. However, PKC materials containing higher kaolin result in a higher value of D and ε_r.

- Relative dielectric constant and piezoelectric strain constant increase with aging day, and approach to asymptotic values after the age of 70 days.

- The d_{33} value of PP composites pretreated at 150℃ reaches 106.3 pC/N at aging day 70, while the sample pretreated at 23℃ has a value of 57 pC/N. The d_{33} values of PP material containing kaolin lie in 99.6 –111.1 pC/N that is higher than d_{33} = 90 pC/N reported by Wang et al.[1].

- PKC materials exhibit a higher piezoelectric strain constant d_{33} and the composite with 4% kaolin has the highest d_{33} (111.1 pC/N). However, kaolin content should not be greater than 6% by volume due to the increase of the porosity.

- Adding kaolin can increase d_{33} and ε_r, but its volume content should not be greater than 6%.

- The resonance frequency of the composite continues to decrease with increasing kaolin. For the electromechanical coupling factor K_t, there is 8% increasing if 10% kaolin is added.

- Phase angle continues to develop with the age, and also with kaolin content except for the composite containing 1% and 2% kaolin.

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