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Piezoelectric and dielectric properties of piezoelectric ceramic–sulphoaluminate cement composites

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Abstract

0–3 piezoelectric composites with good performances were prepared using a sulphoaluminate cement and PMN ceramic particles. Piezoelectric and dielectric properties of the composites with different PMN contents were investigated. The influences of the cement hydration age on the piezoelectric constant of the composites were analyzed. The results indicate that the piezoelectric coefficients and dielectric constants of the composites rapidly increase as the PMN content increases. The piezoelectric characteristics of the sulphoaluminate cement-based piezoelectric composites are very different from those of the piezoelectric ceramics and polymer–ceramic piezoelectric composites. For the latter, the piezoelectric properties decrease with the prolonging of time, while the piezoelectric properties of the sulphoaluminate cement-based piezoelectric composite are improved with increasing the cement hydration age. When the cement hydration age exceeds 8 days, $\bar{d}_{33}$ tends to be constant.

Keywords: PMN; Cement-based piezoelectric composites; Cement hydration age; Piezoelectric properties; Dielectric properties

1. Introduction

With the development of smart or intelligent structures in civil engineering, the healthy monitoring and active vibration control of the structures are being introduced.[1] In a smart structure, sensors and actuators are essential components for sensing and controlling. The piezoelectricity has proved to be one of the most efficient mechanisms for the sensors and actuators in intelligent structures.[2,3] During the last few years, many piezoelectric materials have been fabricated and used. However, the traditional piezoelectric materials, such as piezoelectric ceramic, piezoelectric polymer and polymer based piezoelectric composite, have bad compatibility with concrete, the main structural material in civil engineering. It is known that in civil engineering, cement-based materials are the most commonly used structural material. In contrast to structural materials used in the other fields, such as metals and alloys, which are produced in factories and are stable in structure, concrete is cast in site. Besides, the hydration of cement is a long process and can last for decades.[4] In general, the changes of water status during hydration will cause shrinkage or expansion of the concrete. While the traditional piezoelectric materials do not contract synchronistically with concrete, therefore, they are not suitable for civil engineering applications. To meet the requirements, the cement-based piezoelectric composites that have good piezoelectric properties and compatibility with civil engineering structural materials are desirable.[5–7]

It has been proved that cement matrix piezoelectric composites can overcome the matching problem mentioned above. On the other hand, the 0–3 cement-based piezoelectric composites have a slightly higher piezoelectric factor and electromechanical coefficient than 0–3 PZT–polymer composites with a similar content of piezoelectric ceramic particles. This will benefit the sensor application. Although

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the study of cement-based piezoelectric composite has made great progress, a lot of problems remain to be solved. Cement-based piezoelectric composites with excellent sensorial effect and different connectivity need to be studied and developed further.[8,9]

The sulphoaluminate cement not only possesses the features of rapid hardening, early strength, high strength, and steadily strength, but also good corrosion and freezing resistance.[10] The PMN was employed instead of PZT or PT because of its excellent piezoelectric properties (e.g. $\bar{d}_{33} = 550\,\text{pC N}^{-1}$, $K_p = 66\%$, $K_t = 41\%$). In this article, the 0–3 cement-based piezoelectric composites with better piezoelectric properties were obtained from PMN and a sulphoaluminate cement. The influences of the content of PMN and the cement hydration age on the piezoelectric properties of composites are also discussed.

2. Experimental procedures

The 0–3 cement-based piezoelectric composites were fabricated from PMN and sulphoaluminate cement through the following procedure: initially, two raw materials were ball-milled for 30 min with ethyl alcohol in a resin mill. After drying, the mixed materials were pressed into disks of 15 mm diameter and 2 mm thickness under 80 MPa. The specimens were put in a curing room with a temperature of 20 °C and relative humidity of 100% for 3 days before measurements. After curing, the surfaces of the disks were polished and coated with a low temperature silver paint, then the poling was carried out at 130 °C in a stirred silicone oil bath. The optimum poling field was 4 kV/mm. In each kind of piezoelectric composite, the content of PMN is 60 wt.%, 70 wt.%, 80 wt.%, and 85 wt.%, respectively.

After poling, the composites were aged for 24 h prior to the measurements. The piezoelectric strain factor $\bar{d}_{33}$ was directly measured using a Model ZJ-3A d_{33} piezometer. The frequency of dynamic force is fixed at 110 Hz. At least six measurements were made over the surface of the sample in order to obtain an acceptable average $\bar{d}_{33}$ value. Capacitance (C_p) was measured at 1 kHz with a Agilent 4294A Impedance Phase Analyzer. The dielectric permittivity ε_{33}^T and piezoelectric voltage factor g_{33} of each specimen were calculated as:

$$\varepsilon_{33}^T = \frac{C_p t}{A\varepsilon_0}, \quad g_{33} = \frac{\bar{d}_{33}}{\varepsilon_{33}^T \varepsilon_0}$$

where t and A are the specimen thickness and electrode area, respectively. The thickness electromechanical coupling coefficient K_t and Q_m were calculated from a plot of electric impedance against frequency using the following formula:[11]

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

$$Q_m = \frac{1}{2}\pi f_s\, RC \frac{f_p^2 - f_s^2}{f_p^2}$$

where f_s and f_p are the series frequency and the parallel resonance frequency, respectively, and are approximated by:

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

$$Q_m = \frac{1}{2}\pi f_m\, R_m C \frac{f_n^2 - f_m^2}{f_n^2}$$

where f_m and f_n are frequency at minimum and maximum electric impedance, respectively. R_m is the magnitude of the electrical impedance at f_m. The planar electromechanical coupling coefficient K_p can approximately be evaluated using the curve of K_p versus $\Delta f/f_n$. The combination status of the PMN particles in the composites were observed on a Hitachi S-2500 scanning electro microscope (SEM).

3. Results and discussion

3.1. Piezoelectric properties

The variation of piezoelectric coefficient as a function of the content of PMN has been studied. The results are depicted in Fig. 1. From Fig. 1a, we can see a roughly nonlinear increase of the $\bar{d}_{33}$ values of the composites as a function of the PMN content. Initially there is slowly increase, but when the content of PMN exceeds 70%, the $\bar{d}_{33}$ values increase much more sharply. With 80% PMN addition, $\bar{d}_{33}$ is up to $25.4\,\text{pC N}^{-1}$.

This variation of piezoelectric coefficient $\bar{d}_{33}$ for a composite system can be explained by the following relation given by Furukawa et al.:[12]

$$\bar{d}_{33} = \frac{15 v \varepsilon_1 d_{33}}{(1 - v)(2 + 3v)\varepsilon_2}$$

where $\bar{d}_{33}$ and d_{33} are the piezoelectric strain factors of the composite and PMN, v the volume fraction of PMN, ε_1 and ε_2 the dielectric permittivity of the matrix and PMN, respectively. It can be seen that $\bar{d}_{33}$ is dependent on d_{33}, v, ε_1 and ε_2. Since d_{33}, ε_1 and ε_2 remain constant, $\bar{d}_{33}$ is only influenced by the volume fraction v. Consequently, $\bar{d}_{33}$ increase rapidly with the increasing the content of PMN.

Dependence of the piezoelectric voltage factor, g_{33}, on the PMN content is showed in Fig. 1b. It can be seen that in the range where the PMN content is less than 80%, g_{33} increases with the increase of PMN content. On the contrary, when the PMN content is over 80%, g_{33} decreases rapidly. The main reason is that upon increasing the PMN content, the increase of the dielectric permittivity of the composites is much faster than that of $\bar{d}_{33}$, while g_{33} is calculated as $g_{33} = \bar{d}_{33}/\varepsilon\varepsilon_0$.

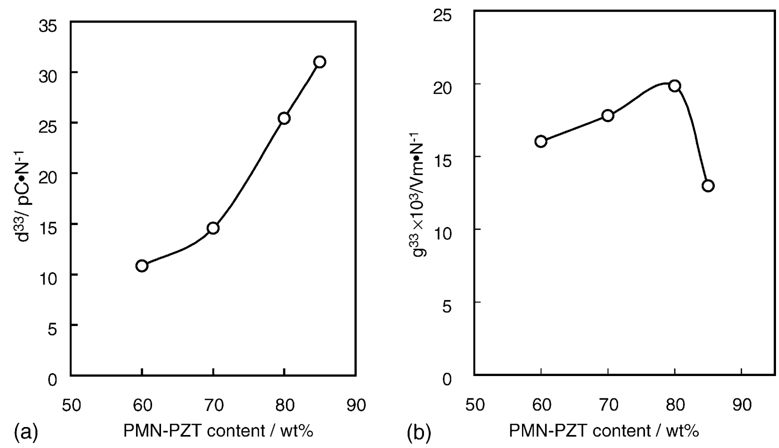

Fig. 1. Dependence of the piezoelectric constant on PMN content.

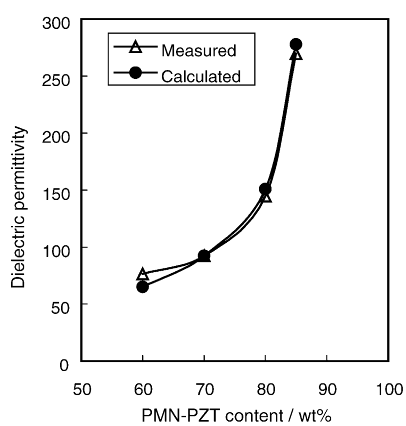

Fig. 2. The influence of PMN content on the dielectric constant of the composites.

3.2. Dielectric properties

As shown in Fig. 2, the dielectric permittivity of the composites increases with increasing the contents of PMN. In addition, the dielectric permittivity of the composites is much smaller than that of the pure PMN. It is evidenced that when the contents of PMN-PMN is 60%, the dielectric permittivity decreases from 3350 for pure PMN to 76.41 for the composites. When PMN content is up to 80%, the dielectric permittivity is 144.79. The variation of dielectric permittivity with different PMN contents are evaluated by the following relation, which was introduced by Yamada et al.[13] for polymer-based piezoelectric composite system:

$$\varepsilon = \varepsilon_1 \left[1 + \frac{nq(\varepsilon_2 - \varepsilon_1)}{n\varepsilon_1 + (\varepsilon_2 - \varepsilon_1)(1-q)} \right]$$

where n is the parameter attributed to the shape of the ellipsoidal particle and q is the volume fraction of PMN; ε_1 and ε_2 are the dielectric dielectric permittivity of the matrix and PMN, respectively. In our case, the experimentally measured values of dielectric dielectric permittivity at 1 kHz for the sulphoaluminate cement ($\varepsilon_1 = 8.55$) and PMN ($\varepsilon_2 = 3350$) and a value of $n = 8.8$ have been used to evaluate ε. It can be seen from Fig. 2 that there exists a remarkable good agreement between the calculated values and the experimental values.

3.3. Thickness mode electromechanical coupling constant K_t and planar coupling constant K_p

Fig. 3a–e are the impedance magnitude and the phase spectra of the pure cement and the composites containing 60 wt.%, 70 wt.%, 80 wt.%, and 85 wt.% PMN, respectively. It can be seen that the impedance of the pure cement is quite high and the phase changes smoothly with the frequency. Compared with the pure cement, the impedance of the composites with different content of PMN significantly decreases. At the same time, some peaks appear in all phase curves. This means that the addition of PMN brings an electromechanical coupling behavior to the composites, which is caused by the direct and inverse piezo-

Table 1
The electromechanical coupling properties of the composites

PMN content (wt.%)	f_m (kHz)	f_n (kHz)	R_m (kΩ)	Δf (kHz)	K_p (%)	K_t (%)	Q_m
60	150.03	151.28	25.76	1.25	14.4	14.21	36.48
70	142.54	143.78	15.25	1.24	14.7	14.57	40.41
80	136.28	137.53	10.18	1.25	15.2	14.90	38.79
85	127.53	139.03	5.80	1.50	16.0	21.56	19.84

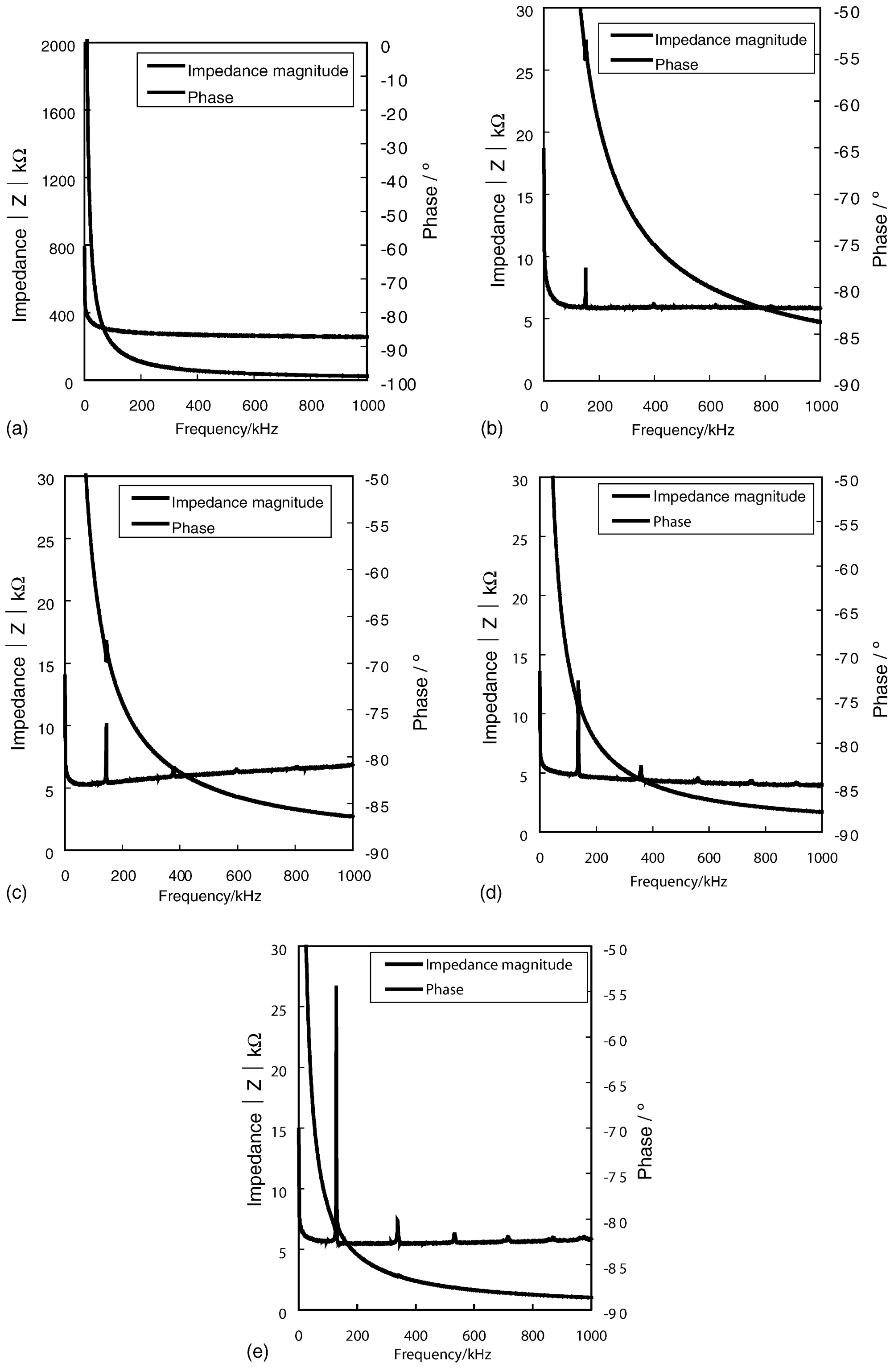

Fig. 3. The impedance magnitude and the phase spectra of the hardened cement paste and the composites: (a) the hardened cement paste; (b) 60 wt.% PMN; (c) 70 wt.% PMN; (d) 80 wt.% PMN; and (e) 85 wt.% PMN.

electric effect. Moreover, the larger the PMN content, the higher the peaks in the spectra, which means a larger PMN content brings a higher piezoelectric effect to the composites.

The results of the electromechanical coupling coefficients of the composites are summarized in Table 1. It can be seen that the K_t values for all the composites range from 14.21% to 21.56%, K_p values from 14.4% to 16.0%. Moreover, both

K_t and K_p increase with increasing the PMN-PMN content, which means an efficient conversion between the electrical and mechanical energy is mainly influenced by the PMN content. It can be also seen that mechanical quality factor Q_m varies from 19.84 to 40.41.

3.4. Effect the hydration ages of the sulphoaluminate cement on piezoelectric properties

The phenomenon that the piezoelectric performances of piezoelectric ceramics or piezoelectric composites change with the time going after the poling is usually called the aging phenomenon. As to piezoelectric ceramics, during the poling process, the poling field forces the 90° ferroelectrics domain, which are disordered in the unit cell, to orient in parallel with the field. In addition, the axis *C* changes its direction, accompanying with great stress, which causes great internal strain. After removing the poling field, this kind of internal strain will cause disequilibrium force inside the grains, ferroelectrics domain walls. So under the internal strain, parts of the diverted 90° ferroelectrics domains recover to a disorder state and release the strain. The disordered ferroelectrics domains increase as the time goes on. Hence the remanent polarization reduces continuously which causes decrease of the piezoelectric performances of the composites. For the polymer matrix piezoelectric composites, the piezoelectric properties decrease with the time going on because the polymer matrix age easily, resulting in looseness of the combination between the polymer matrix and piezoelectric ceramic particle. However, as it will be illustrated in the following section, the piezoelectric characteristics of sulphoaluminate cement-based piezoelectric composite are very different from those of piezoelectric ceramic and polymer–ceramic piezoelectric composites.

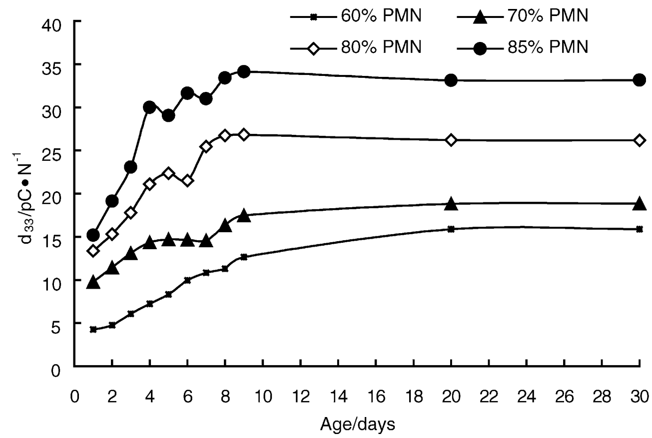

Fig. 4. The influence of ages on the piezoelectric strain factor $\bar{d}_{33}$ constant of the composites.

The effect of hydration age of the sulphoaluminate cement on the piezoelectric strain factor $\bar{d}_{33}$ is shown in Fig. 4. It can be seen that before 4 days, the $\bar{d}_{33}$ value of piezoelectric composites increase at a faster rate as the hydration age increases; between 4 days and 8 days, the $\bar{d}_{33}$ value presents certain waves, but the amplitude is not significant. After 8 days, the $\bar{d}_{33}$ value tends to be constant.

For a two-phase composite:[14]

$$\bar{d}_{33} = \phi L_T L_E d_1$$

where ϕ and d_1 are the volume fraction and the piezoelectric constant of the PMN, respectively, and L_T and L_E, the local stress and field. It is clear that ϕ and d_1 are constant and L_E is unchangeable after the poling. Therefore, $\bar{d}_{33}$ is only dependent on L_T. L_T is the ratio of the effective strain exerted on the PMN ceramic particles to the external strain.

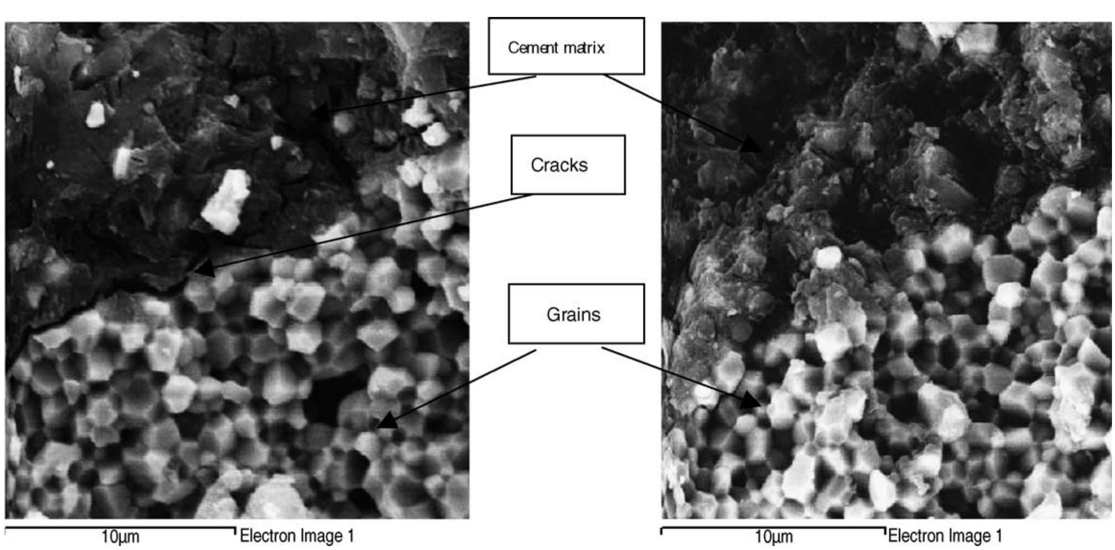

Fig. 5. SEM micrographs of the fracture surface of the composites: (a) early hydration and (b) last hydration.

At the early stage of the hydration process, there are usually some big pores in the cement matrix. Moreover, the interfaces between the cement matrix and the piezoelectric ceramic particles are not perfect, some interfacial cracks have been observed (see Fig. 5a). These pores and interfacial cracks play a role as a stress buffer and remarkably diminish the local stress L_T applied on PMN particle, resulting in a smaller $\bar{d}_{33}$ value.

With the increase of cement hydration ages, the porosity in the cement matrix remarkably decreases, accompanying with some volume expansion at the same time, leading to a better combination between the piezoelectric ceramic particles and the cement matrix (see Fig. 5b). In this case, the external strain can be transferred to the piezoelectric ceramic particles effectively. Therefore, L_T increases continuously and $\bar{d}_{33}$ increases finally. This phenomenon is in contrast to that in the case of traditional piezoelectric ceramics and polymer–ceramic piezoelectric composites, in which $\bar{d}_{33}$ decreases with the prolonging of time. When the hydration of cement becomes more and more smooth, namely the hydration age reaches 8 days, L_T changes no longer and $\bar{d}_{33}$ tends to be stable as well.

4. Summary

The following conclusions can be drawn from the current studies:

(1) The 0–3 piezoelectric composites with good performances have been prepared using a sulphoaluminate cement and PMN ceramic particles.

(2) The $\bar{d}_{33}$ and ε_{33}^T values of the 0–3 cement-based piezoelectric composites show a roughly nonlinear increase as a function of the PMN content. When PMN content was up to 80%, $\bar{d}_{33}$ and ε_{33}^T are 25.4 pC N^{-1} and 144.79, respectively. The ε_{33}^T experimental values of the composites have a remarkable good agreement with the calculated values.

(3) The addition of PMN particles brings the electromechanical coupling behavior to the composites. The electromechanical coupling coefficient K_p and K_t of composites increases with increasing the content of PMN. When the contents reaches 85%, K_p and K_t are 16.0% and 21.56%, respectively. The mechanical quality factor Q_m is in the range from 19.84 to 40.41.

(4) In contrast to piezoelectric ceramic and polymer–ceramic piezoelectric composites, the piezoelectric properties of the sulphoaluminate cement-based piezoelectric composite are improved with increasing the cement hydration age. When the cement hydration age exceeds 8 days, $\bar{d}_{33}$ tends to be constant.

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