

# Poling process and piezoelectric properties of lead zirconate titanate/sulphoaluminate cement composites

HUANG SHIFENG

*School of Materials Science and Engineering, Jinan University, Jinan 250022, People's Republic of China; School of Material Science and Engineering, Wuhan University of Technology, Wuhan 430070, People's Republic of China*  
E-mail: shifenghuang@163.com

CHANG JUN, LIU FUTIAN, LU LINGCHAO, YE ZHENGMAO, CHENG XIN

*School of Materials Science and Engineering, Jinan University, Jinan 250022, People's Republic of China*

The sulphoaluminate cement was, for the first time, used to fabricate 0-3 piezoelectric composites by compressing technique. The dependences of piezoelectric properties of composites on poling conditions, particle size and contents of Lead Zirconate Titanate (PZT) were discussed especially. The results show that the piezoelectric properties of composites are improved by increasing poling field  $E$ , poling time  $t$  and poling temperature  $T$ . The optimum  $E$ ,  $t$  and  $T$  are 4.0 kV/mm, 45 min and 120°C respectively in this work. The piezoelectric strain factor  $d_{33}$  is found to increase with increasing particle size of PZT. When the particle size of PZT is larger than about 130  $\mu\text{m}$ , the  $d_{33}$  is nearly independent of particle size. The  $d_{33}$ ,  $g_{33}$  and the electromechanical coupling coefficient  $K_p$ ,  $K_t$  of composites increase rapidly with increasing content of PZT. When the content of PZT reaches 85%,  $K_p$  and  $K_t$  are 28.54 and 28.19%, respectively. © 2004 Kluwer Academic Publishers

## 1. Introduction

To meet the requirements of development for smart or intelligent structures in civil engineering, a kind of new-type function composite, cement based piezoelectric composite, has been developed in recent years. This new composite can overcome the deficiency which the traditional piezoelectric materials (piezoelectric ceramic, piezoelectric polymer and polymer based piezoelectric composite) have bad compatibility with civil engineering main structural material—concrete. It will play a extremely important role in advancing all kinds of civil engineering structure to be intelligent. Today, the research and development of the cement based piezoelectric composite have attracted great attentions from researchers [1–3].

A 0-3 cement based piezoelectric composite consists of a three dimensionally connected cement matrix loaded with active piezoelectric ceramic particle connected in zero dimensions. At present, the researches of the cement based piezoelectric composite are being only carried out by Hong Kong University of Science and Technology and our laboratory in the world. Li *et al.* fabricated a 0-3 cement-based piezoelectric composite by using a normal mixing and spreading method with Portland cement for the first time [4]. It has showed that using cement as a matrix for piezoelectric composites can solve the mismatch problem. On the other hand, the 0-3 cement based piezoelectric composite have a

slightly higher piezoelectric factor and electromechanical coefficient than those of 0-3 PZT/polymer composites with a similar content of PZT particles. Thus, there is greatly potential for the application of cement based piezoelectric composite as sensors or actuators in civil engineering. Although the study of cement-based piezoelectric composite has been made some progress with positive significance, a lot of problems remain to be solved. Cement base piezoelectric composites with excellent performance and different connectivity need to be studied and developed further.

The sulphoaluminate cement has not only the characteristic of early and high strength, and steadily growing long-terms [5], but also good corrosion and freezing resistance. The purpose of this investigation is to prepare the 0-3 sulphoaluminate cement-based piezoelectric composites. The influences of poling conditions, particle size and contents of PZT on the piezoelectric properties of composites are discussed especially.

## 2. Experimental procedures

The main properties of PZT and sulphoaluminate cement used in this work are listed in Tables I and II. The composites were obtained through the following procedure: at first, two raw materials were ball-milled and mixed for 30 min with ethyl alcohol in a resin mill. After drying, the mixed materials were pressed into

TABLE I The main properties of PZT

$K_p$	$K_{31}$	$K_{33}$	$\bar{d}_{33}$ (pC·N <sup>-1</sup> )	$\tan \delta$ (%)	$\varepsilon$	$Q_m$	$T_c$ (°C)
0.65	0.39	0.70	400	2	2000	60–70	360

TABLE II The main properties of the sulphoaluminate cement

$\varepsilon$	$\tan \delta$ (%)	$\rho$ / g (cm <sup>3</sup> )	Median dia ( $\mu$ m)
8.55	26.1	2.078	17.70

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 3d 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 in a stirred silicone oil bath. In each kind of piezoelectric composite, the contents of PZT were 60, 70, 80 and 85 wt%, respectively.

After poling, the composites were aged for 24 h prior to the measurement. The piezoelectric strain factor  $\bar{d}_{33}$  was directly measured using a Model ZJ-3A  $d_{33}$  meter. Capacitance factors  $C$  were measured at 1 kHz with a Agilent 4294A Impedance Phase Analyzer. The dielectric constant  $\varepsilon$  and piezoelectric voltage factor  $g_{33}$  of each specimen were calculated as:

$$\varepsilon = Ct/A, \quad g_{33} = \bar{d}_{33}/\varepsilon\varepsilon_0$$

where  $t$  and  $A$  are the specimen thickness and electrode area, respectively. The thickness electromechanical coupling coefficient  $K_t$  were calculated from a plot of electric impedance against frequency the following formula [6]:

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

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

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

where  $f_m$  and  $f_n$  are frequency at minimum and maximum electric impedance, respectively. The planar electromechanical coupling coefficient  $K_p$  can approximately be evaluated by using the curve of  $K_p$  versus  $\Delta f/f_n$ . The distribution and combination status of the PZT particles in the composites were observed on a Hitach S-2500 Scanning Electro Microscope (SEM).

### 3. Result and discussion

#### 3.1. Effect of the poling field $E$ on $\bar{d}_{33}$

Fig. 1 shows the piezoelectric strain factor  $\bar{d}_{33}$  as a function of the poling field  $E$  at the poling time  $t = 20$  min and the poling temperature  $T = 120^\circ\text{C}$ .

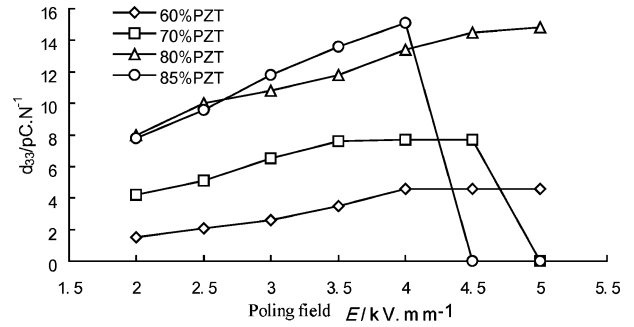


Figure 1 The piezoelectric strain factor  $\bar{d}_{33}$  of the composites as a function of the poling field  $E$ .

It can be seen that the  $\bar{d}_{33}$  increases with increasing of poling field  $E$ . However, when the poling field  $E$  exceeds 4.0 kV/mm, the  $\bar{d}_{33}$  changes very small. Since the poling field is the driving force which make the ferroelectrics domain reversal in the course of the poling, the greater the intensity of poling field, the greater the driving force which make the ferroelectrics domain align directionally. At the same time, it is easy that ferroelectrics domain reorientation takes place at high poling field. So the  $\bar{d}_{33}$  is first remarkably enhanced with increasing the poling field. When the polarization intensity excesses a certain value, the composites reach saturation poling and the  $\bar{d}_{33}$  tends to be constant.

It can also be observed from Fig. 1 that if the poling field  $E$  continually increases, some samples will be broken down. This is due to the presence of some matrix pores, particle pores, and interface pore in the bulk. In addition, there are many conducting ions (such as  $\text{Ca}^{2+}$ ,  $\text{OH}^-$  and  $\text{SO}_4^{2-}$  and so on) in the sulphoaluminate cement matrix. As the poling field increases, conducting ions migration takes place, leading to a rise of conductivity.

#### 3.2. Effect of the poling time on $\bar{d}_{33}$

Fig. 2 shows the relationship between the  $\bar{d}_{33}$  and the poling time  $t$ . Under the condition of the same the poling field and the poling temperature, the values of the  $\bar{d}_{33}$  increase remarkably with increasing the poling time in the initial period of poling and saturates beyond 45 min. This is because that the reversal of the 180° ferroelectrics domain takes place mainly at the initial

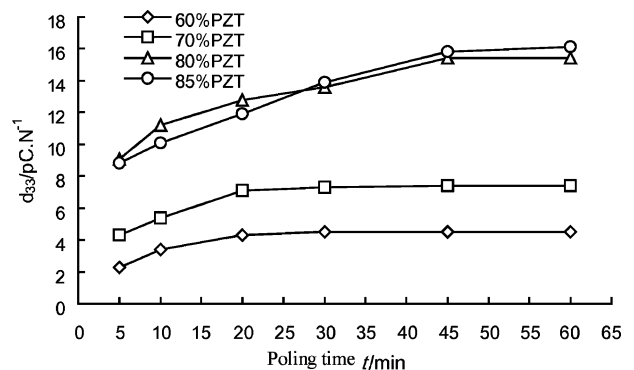


Figure 2 The piezoelectric strain factor  $\bar{d}_{33}$  of the composites as a function of the poling time  $t$ .

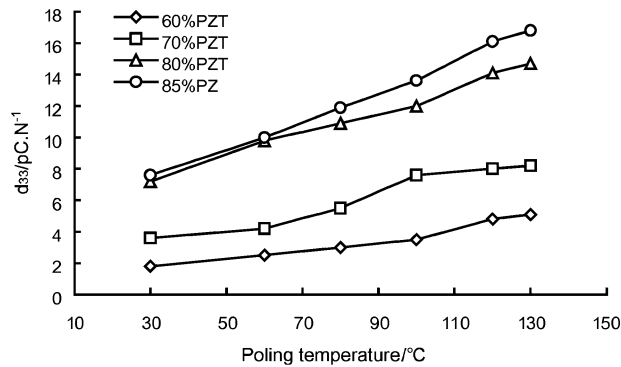


Figure 3 The piezoelectric strain factor  $\bar{d}_{33}$  of the composites as a function of the poling temperature  $T$ .

stage of poling, which can not give rise to local stress and is performed in short time. However, at anaphase, the reversal of  $90^\circ$  ferroelectrics domain plays an important role, which is accompanied by producing of the local stress and strain. This means that it is not easy to make the  $90^\circ$  ferroelectrics domain reversal. Therefore, the degree of poling can be improved by extending the poling time, but when the poling time exceeds 45 min, the  $\bar{d}_{33}$  tends to be constant because the orientation of the ferroelectrics domains is completed directionally.

### 3.3. Effect of the poling temperature on $\bar{d}_{33}$

In order to investigate the influence of the poling temperature on the  $\bar{d}_{33}$ , all composite samples were polarized under the conditions which  $E$  was 4.0 kV/mm and  $t$  was 45 min. The dependence of the  $\bar{d}_{33}$  on poling temperature is shown in Fig. 3. It is evident that the  $\bar{d}_{33}$  increases remarkably as the poling temperature increases under  $120^\circ\text{C}$  and tends to level off subsequently. It is well known that The higher the poling temperature is, the better the piezoelectric property of the composites. But, for sulphoaluminate cement based piezoelectric composite, if the poling temperature is higher than  $130^\circ\text{C}$ , the main hydrated products of the sulphoaluminate cement, such as  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$ ,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$ ,  $\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ , would lose a large amount of crystal water [5], which would change crystal structure of sulphoaluminate cement matrix and finally result in deterioration of the composites properties. Therefore,  $120^\circ\text{C}$  is chosen as the optimum poling temperature in this work.

### 3.4. Effect of the particle size on $\bar{d}_{33}$

In order to investigate the effect of the particle size of PZT on the  $\bar{d}_{33}$ , the study was performed under the same poling condition, and the content of PZT in all composite samples was kept constant at 80%. The piezoelectric constant the  $\bar{d}_{33}$  of composites having different particle sizes is shown in Fig. 4. For the range of particle sizes under  $130\ \mu\text{m}$ , the  $\bar{d}_{33}$  increases at a faster rate with increasing particle size of PZT. When the particle size is larger than about  $130\ \mu\text{m}$ , the  $\bar{d}_{33}$  is nearly independent of particle size. On the one hand, this is because that the size and shape of large particles permits greater connectivity of the ceramic phase than composites prepared with smaller particles, which leads to a larger electric

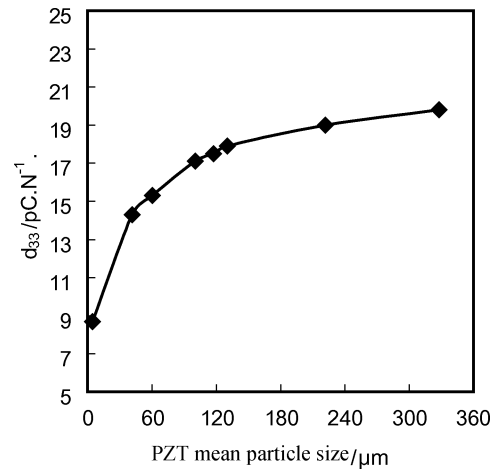


Figure 4 Dependence of the piezoelectric constants  $\bar{d}_{33}$  on PZT mean particle size.

field acting on the ceramic giving a greater remanent polarization. The composites with greater connectivity (3-3) of the ceramic phase pole more efficiently than composites of lower connectivity (0-3) and consequently have a higher piezoelectric constant. On the other hand, it is suggested that the surface layer possesses lower piezoelectric constant or perhaps is no piezoelectric than the bulk because the surface area-to-volume ratio increases with decreasing particle size.

### 3.5. Effect of the content of PZT on $\bar{d}_{33}$

The variation of piezoelectric constant as a function of content of PZT has been studied and the results were depicted in Fig. 5. From Fig. 5, we can see a roughly nonlinear increase of the  $\bar{d}_{33}$  values of the composites as a function of the PZT content. When the content of PZT exceeds 70%, the  $\bar{d}_{33}$  values increase much more sharply. When PZT content is up to 80%, the  $\bar{d}_{33}$  is  $16\ \text{pC}\cdot\text{N}^{-1}$ .

This variation of piezoelectric constant  $\bar{d}_{33}$  for a composite system can be explained by the following relation given by Furukawa *et al.* [7]:

$$\bar{d}_{33} = 15\varphi\varepsilon_1d_{33}/(1 - \varphi)(2 + 3\varphi)\varepsilon_2$$

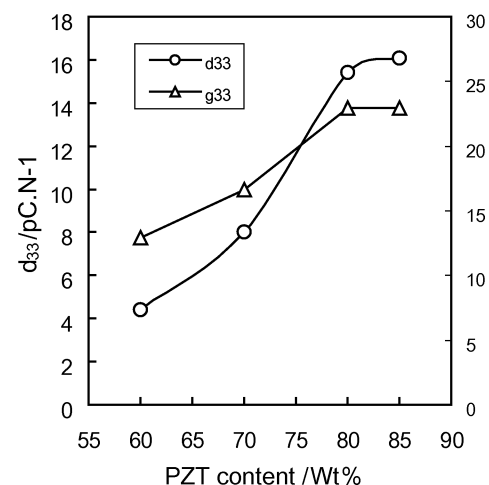


Figure 5 Dependence of the piezoelectric constants on the content of PZT.

where  $\bar{d}_{33}$  and  $d_{33}$  are the piezoelectric strain factors of the composite and PZT,  $\varphi$  the volume fraction of PZT,  $\varepsilon_1$  and  $\varepsilon_2$  the dielectric constants of the matrix and PZT, respectively. It can be seen that The  $\bar{d}_{33}$  is dependent on  $d_{33}$ ,  $\varphi$ ,  $\varepsilon_1$  and  $\varepsilon_2$ . Since  $d_{33}$ ,  $\varepsilon_1$  and  $\varepsilon_2$  remains constant, the  $\bar{d}_{33}$  is only influenced by the volume fraction  $\varphi$ . Consequently, the  $\bar{d}_{33}$  increases rapidly with increasing content of PZT.

Dependence of the piezoelectric voltage factor on the PZT content is also showed in Fig. 5. Compared with the  $\bar{d}_{33}$ , the  $g_{33}$  increases relatively slower with the increase of PZT content. When PZT content is up to 80%, the  $g_{33}$  is  $22.94 \times 10^{-3} \text{ Vm}\cdot\text{N}^{-1}$ .

### 3.6. Effect of the content of PZT on $K_p$ and $K_t$

Fig. 6 shows the impedance magnitude and the phase spectra of the composites containing 60, 70, 80 and 85 wt% PZT. Some peaks appear in all phase curves. It means the addition of PZT brings the electromechanical coupling behavior to the composites, which is caused by the piezoelectric effect and reverse piezoelectric effect. Moreover, the larger the PZT content, the higher the peaks in the spectra, which means that a larger PZT content brings a higher piezoelectric effect to the composites.

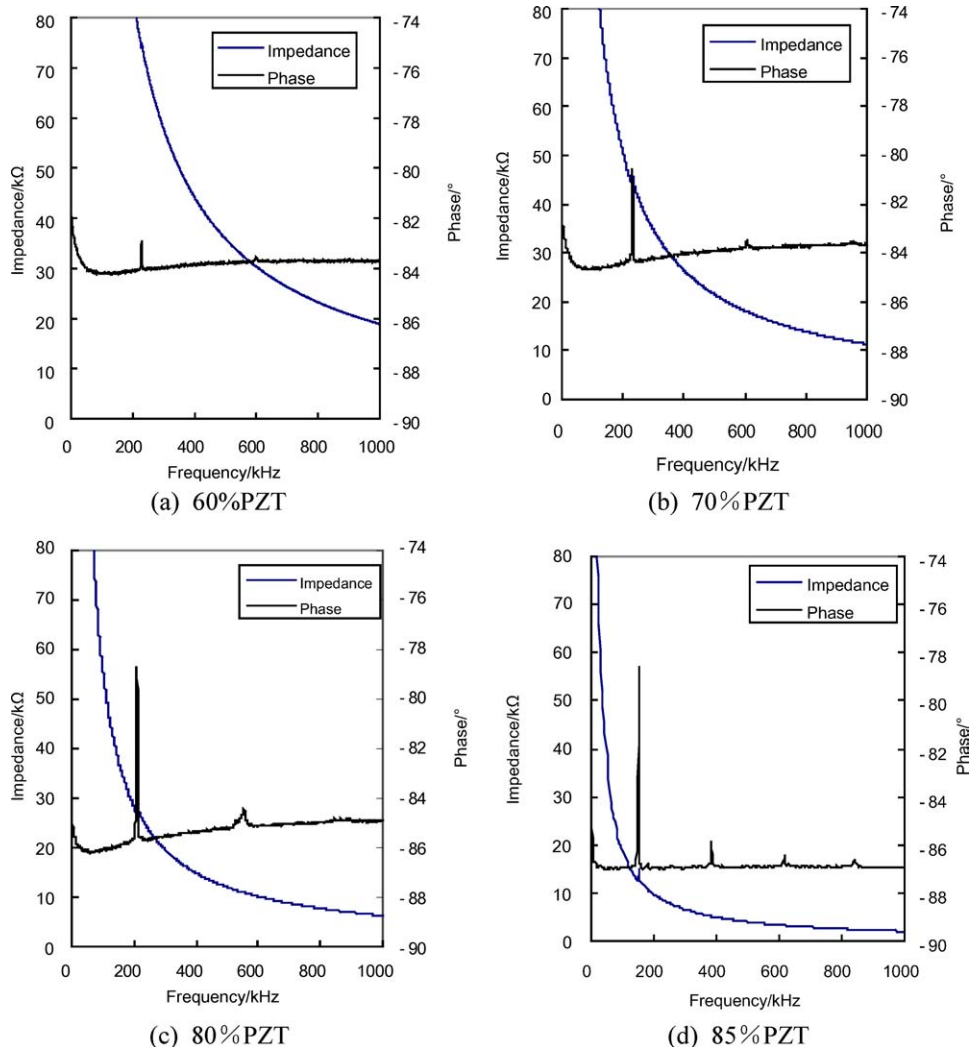


Figure 6 The impedance magnitude and the phase spectra of the composites containing 60, 70, 80 and 85 wt% PZT.

TABLE III The electromechanical coupling properties of the composites

PZT content wt (%)	$f_m$ (kHz)	$f_n$ (kHz)	$\Delta f$ (Hz)	$K_p$ (%)	$K_t$ (%)
60	227.53	228.78	1250	11.79	11.57
70	230.03	232.53	2500	15.76	16.19
80	208.78	211.28	2500	17.20	16.97
85	145.03	150.03	5000	28.54	28.19

The calculated results of the electromechanical coupling coefficients of the composites are listed in Table III. It can be seen that the  $K_t$  values for all the composites range from 17.57 to 28.19%, the  $K_p$  values from 11.79 to 28.54%. Further, the values of  $K_t$  and  $K_p$  are found to be increasing rapidly with increasing content of PZT, which means that an efficient conversion between electrical and mechanical energy is remarkably influenced by content of PZT.

### 3.7. Morphology of the composites

Fig. 7 shows the SME microphotographs of composite containing 70 wt% PZT, in which the white phase are PZT particles and the black are the sulphoaluminate cement matrix. From Fig. 7a, it can be seen that the PZT particles distribution in the sulphoaluminate

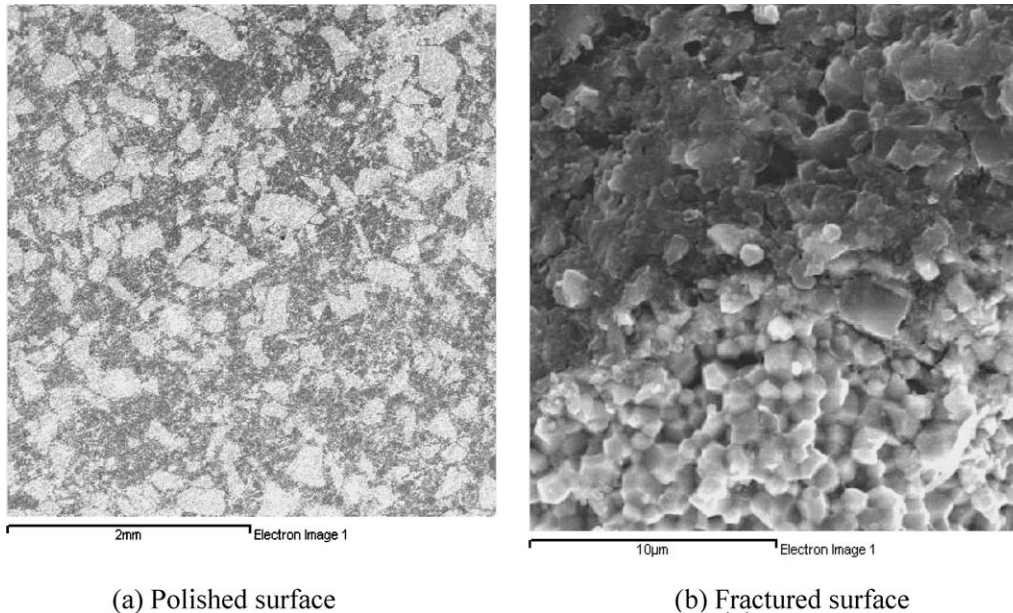


Figure 7 Scanning electron micrographs of the composites: Containing 70 wt% PZT.

cement matrix is homogeneous. The adhesion of interface between the PZT and the cement is good (Fig. 7b). Moreover, no big pores are observed in the microstructure.

#### 4. Summary

The following conclusions can be drawn from the current studies:

(1) For the 0-3 sulphoaluminate cement-based piezoelectric composites, the optimum poling conditions are that the poling field  $E$  is 4.0 kV/mm, the poling time  $t$  is 45 min and the poling temperature is 120°C.

(2) With the increase of the content of PZT, the  $\bar{d}_{33}$  and  $g_{33}$  increase nonlinearly. When the content of PZT is up to 80%, the  $\bar{d}_{33}$  and  $g_{33}$  are 16 pC·N<sup>-1</sup> and 22.94 × 10<sup>-3</sup> Vm·N<sup>-1</sup>, respectively.

(3) For the range of particle sizes under 130 µm, the  $\bar{d}_{33}$  increases at a faster rate with increasing particle size of PZT. When the particle size of PZT is larger than about 130 µm, the  $\bar{d}_{33}$  is nearly independent of the particle size.

(4) The electromechanical coupling coefficient  $K_p$  and  $K_t$  of composites increase rapidly with increasing

contents of PZT. When the content of PZT reach 85%,  $K_p$  and  $K_t$  are 28.54 and 28.19%, respectively.

#### Acknowledgment

This work is Supported by National Natural Science Foundation of China (50272024) and Natural Science Foundation of Shandong Province (03BS060).

#### References

1. DONG ZHANG, KERU WU and ZONGJIN LI, *J. Build. Mater.* **5**(2) (2002) 141.
2. ZONGJIN LI, DONG ZHANG and KERU WU, *Mater. Struct.* **34** (2001) 506.
3. SHIFENG HUANG, RONGHUA XU and XIN CHENG, *Bull. China Ceram. Soc.* (4) (2003) 58.
4. ZONGJIN LI, DONG ZHANG and KERU WU, *J. Amer. Ceram. Soc.* **85**(2) (2002) 305.
5. YANMOU WANG, MUZHEN SU and LIANG ZHANG, "Sulphoaluminate Cement" (Beijing University of Technology Press, Beijing, 1999) p. 12.
6. IEEE Standard on Piezoelectricity, ANSI/IEEE Std.176—1987, IEEE, New York, 1987.
7. T. FURUKAWA, K. ISHIDA and E FUKADA, *J. Appl. Phys.* **50**(7) (1979) 4904.

Received 4 November 2003

and accepted 27 July 2004