

Fabrication of PZT-polymer composite materials having 3–3 connectivity for hydrophone applications

N M GOKHALE, S C SHARMA and RAMJI LAL

Naval Chemical and Metallurgical Laboratory, Naval Dockyard, Bombay 400 023, India

MS received 19 March 1988; revised 24 June 1988

Abstract. Lanthanum-modified lead zirconate titanate (PZT) powder and volatilisable polymethylmethacrylate (PMM) polymer particles have been used for fabrication of porous sintered ceramics of interconnected porosity varying from 25% to 59%. Sintered ceramics are converted into piezoelectric PZT-polymer composites by incorporating silicone rubber elastomer followed by electroding and poling. Influence of the variation of PZT-PMM ratio and sintering temperatures on the open and closed porosity of the sintered ceramics as well as volume fraction PZT in the composites has been studied and correlated for the optimization of piezoelectric properties. The PZT-polymer composites possess low density, considerably high piezoelectric voltage coefficient and considerably lower ageing characteristics and are therefore considered suitable for designing highly sensitive hydrophone systems.

Keywords. PZT-polymer; composite; connectivity patterns; piezoelectric voltage coefficient.

1. Introduction

Ceramics having piezoelectric properties are being increasingly used in electronic devices. Among such materials lead zirconate titanate (PZT) solid solutions are widely used because of their superior properties and versatility over other materials. Piezoelectric voltage coefficient (g_{33}) is an important parameter of transducer materials for hydrophone applications. This parameter is related to piezoelectric strain coefficient (d_{33}) and dielectric constant (ϵ) as follows: $g_{33} = d_{33}/\epsilon_{33}^T$. Thus a problem arises during the use of single phase PZT in hydrophone because of its higher ϵ which results in a low piezoelectric voltage response to pressure change. Higher density of PZT does not allow efficient acoustic coupling with water in hydrophones. In addition, the d_{33} value of PZT being approximately equal to $-2d_{31}$ lowers its hydrostatic sensitivity. Considerable efforts have therefore been made towards reducing the value of ρ , ϵ , d_{31} and d_{32} of PZT by incorporating polymer as a low density and low permittivity phase in various connectivity patterns. Newnham *et al* (1978, 1980) used polymer as a second phase to laterally interconnect the ceramic phase. Safari's (1983) approach in this respect is based on the development of a structure embedded by elongated voids in solid PZT in a direction perpendicular to poling field. Another approach by Shrouf *et al* (1979) based on the development of PZT-polymer composite having 3–3 connectivity has also shown encouraging results. Recently Khan *et al* (1986) and Haun *et al* (1986) have produced materials with hydrostatic sensitivity nearly four orders of magnitude greater than the conventional PZT. These indicate that the piezoelectric properties of the composites are dependent on total porosity, pore structure and connectivity patterns of various phases which are considerably influenced with the variation in composition and processing parameters. However, the data available in this respect are limited. The objective of the present investigation is, therefore, to

study the influence of the variation of PZT/PMM ratio, open and closed porosity and sintering parameters on the piezoelectric properties of PZT-polymer composites having 3–3 connectivity.

2. Experimental

PZT powder of composition $\text{Pb}_{0.955} \text{La}_{0.030} (\text{Zr}_{0.55} \text{Ti}_{0.45}) \text{O}_3$ and particle size in the range of 1–2 μm was used in the present investigation. Volatilisable polymethylmethacrylate (PMM) particles varying between 50 and 150 μm in diameter were used for pore formation. Four batches of powders namely A, B, C and D having PZT and PMM ratio 60:40, 50:50, 40:60 and 30:70 respectively were prepared by thoroughly mixing in a homogenizer for 24 h. The mixed powders were compacted into circular discs of 24 mm diameter at 140 MPa using 6 wt% PVA as binder. Pores were formed by heating the compacted samples to 600°C at a slow heating rate of 40°C/h upto 300°C, 60°C/h from 300 to 450°C and thereafter 100°C/h to prevent cracking during PMM removal. The porous samples were then sintered for 2 h in SiC resistance heating furnace at temperatures varying from 1100°C to 1300°C under PbO atmosphere. For sintering samples were assembled as shown in figure 1 to suppress the lead volatility. Homogeneity of the mixed powders was verified by studying or variation in the weight loss in the samples after PMM removal. Open and closed porosity of the sintered ceramics was determined by the Archimedes principle using xylene. Porous sintered ceramics were impregnated with silicone rubber elastomer (SILPOT-10 of M/s Metroark Ltd.) by applying vacuum of 10^{-2} mm of Hg and cured for 24 h. Samples of PZT-polymer composites thus obtained were lapped and polished using SiC paper and diamond paste to make their surfaces flat and parallel which were electroded by applying air drying silver paste (epo-tek H2OE). Electroded samples were poled by applying a d.c. electric field of 30 kV/cm at 100°C for 15 minutes in a silicone oil bath. The density of the composite was determined by dimensional measurements after lapping and their piezoelectric properties were measured 24 h after poling.

The dielectric constant (ϵ) was measured at 1 kHz using an automated capacitance bridge and the piezoelectric strain coefficient (d_{33}) was determined by Berlincourt piezo $-d_{33}$ -meter. The piezoelectric voltage coefficient (g_{33}) was calculated using the formula.

$$g_{33} = d_{33}/\epsilon_{33}^T.$$

Polished specimens were examined by scanning electron microscopy (SEM) and their photomicrographs were obtained.

3. Results and discussion

The per cent weight loss of the compacted samples after PMM removal and sintering at 1200°C is given in table 1. The negligible variation in weight loss from sample to sample in a batch after PMM removal indicates homogeneous distribution of PMM particles in the mixed powders. There is no significant change in sample weight after sintering which indicates that volatility of PbO has been suppressed and the stoichiometry of the powder is maintained. Open porosity of the sintered ceramics increases with increase in PMM content of mixed powders

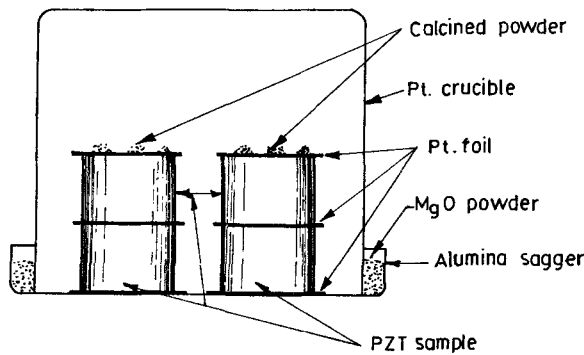


Figure 1. Schematic arrangement for sintering porous PZT ceramics.

Table 1. Density and porosity of porous ceramics sintered at 1200°C for 1 h.

Batch designation	PZT-PMM ratio	Wt. loss during PMM removal (%)	Wt. loss during sintering (%)	Density of porous PZT (g/cc)	Open porosity (%)	Closed porosity (%)
A	60:40	10.12	0.09	3.64	48.5	4.2
B	50:50	14.16	0.07	3.49	52.2	2.5
C	40:60	19.73	0.08	3.23	55.6	2.5
D	30:70	27.67	0.10	2.93	59.0	2.9

whereas no significant trend has been observed in the closed porosity. Open porosity of the sintered ceramics decreases and closed porosity increases with the rise in sintering temperature as shown in figure 2. Decrease in the values of open porosity can be explained due to the pore closure whereas increase in closed porosity is attributed to the entrapment of pores with the rise in sintering temperature. The curves plotted in figure 2 can also be extrapolated to determine the values of open and closed porosity for other intermediate compositions and sintering temperature with accuracy.

Variation of dielectric and piezoelectric properties of the composites with volume fraction PZT is shown in figure 3. The values of ϵ and d_{33} decrease with decrease in the volume fraction PZT in the composites thereby confirming the relationship proposed by Rittenmyer *et al* (1982). Variation of g_{33} with volume fraction PZT exhibits a very interesting trend. The values of g_{33} increase initially with increase in volume fraction PZT but decrease considerably when the volume fraction PZT exceeds 0.42 in the composites. Decrease in g_{33} values at high volume fraction PZT can be attributed to the sharp increase in ϵ values of composite at higher volume fraction PZT. The low values of g_{33} at lower volume fraction PZT is due to the faster decrease in d_{33} values compared to ϵ values and the lower degree of interconnectivity in PZT phase. Thus there is an optimum ratio of PZT and polymeric phase to obtain a maximum value of g_{33} in the composite. It has been concluded on the basis of microstructure property correlation that sintered porous PZT with 50% open porosity and minimum closed porosity give maximum degree of interconnectivity between PZT and polymer phases and optimum piezoelectric properties. SEM photomicrograph of the composites having 0.42 volume fraction PZT is

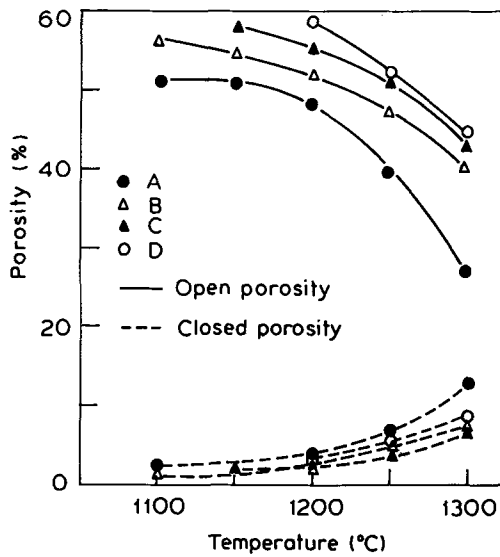


Figure 2. Variation of open and closed porosity with temperature of sintered porous ceramics.

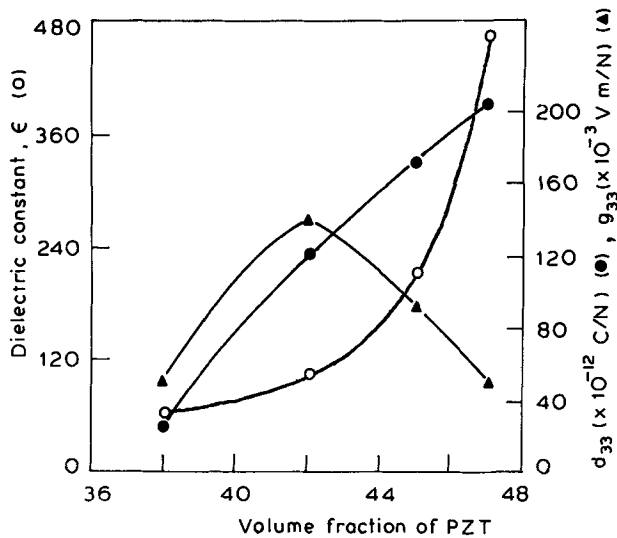


Figure 3. Variation of piezoelectric properties with volume fraction PZT in composite material.

shown in figure 4 which exhibits interconnectivity between PZT and polymeric phases and the size of the polymeric phase varies between $20 \mu\text{m}$ and $120 \mu\text{m}$. It is also apparent that the vacuum impregnation of polymer is nearly complete. The higher breakdown voltage of the composite ($> 30 \text{ kV/cm}$) also indicates that there is not much noticeable voids. Physical, dielectric and piezoelectric properties of 12 samples of a particular batch of PZT-polymer composite having volume fraction PZT between 0.42 and 0.44 are reported in table 2. Since there is no significant

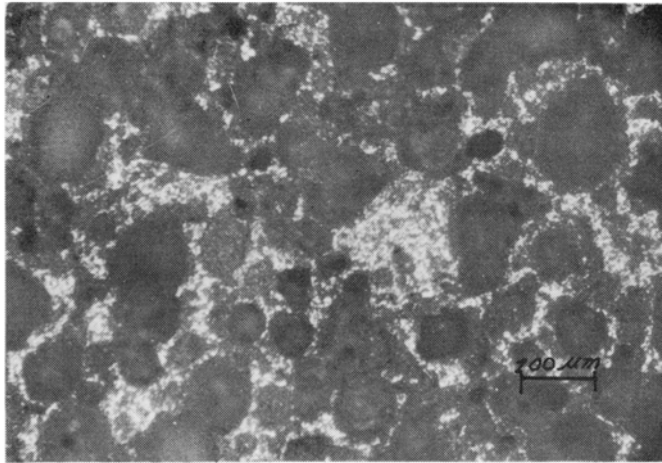


Figure 4. SEM photomicrograph of PZT-polymer composite.

Table 2. Piezoelectric properties of PZT-polymer composite material.

Sample no.	Volume fraction PZT	Density (g/cc)	ϵ	d_{33} C/N ($\times 10^{-12}$)	g_{33} VM/N ($\times 10^{-3}$)
1	0.42	3.74	121	152	142
2	0.42	3.71	117	143	138
3	0.42	3.72	124	156	142
4	0.43	3.76	129	149	130
5	0.43	3.74	118	142	136
6	0.42	3.68	110	128	131
7	0.42	3.70	120	148	139
8	0.42	3.72	116	157	153
9	0.43	3.73	113	144	144
10	0.43	3.75	120	147	138
11	0.44	3.73	132	158	135
12	0.42	3.70	123	153	140

variation in the properties from sample to sample, the process is considered reproducible.

Ageing characteristics of PZT-polymer composite material shown in figure 5 indicate that the values of dielectric constant and d_{33} constant decrease exponentially with ageing time at a very low rate. The slow ageing characteristics can be attributed to the presence of compliant polymer phase surrounding each PZT grain in the material. However, the g_{33} values remain almost unchanged with time as it is the ratio of d_{33} and the dielectric constant.

4. Conclusions

Piezoelectric voltage coefficient (g_{33}) of the PZT-polymer composites can be improved by optimising the PZT/PMM ratio in the mixed powder and sintering

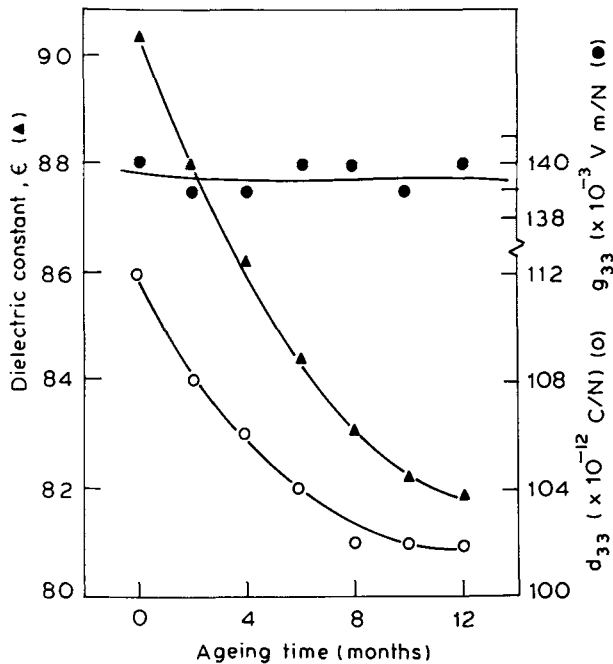


Figure 5. Ageing characteristics of PZT polymer composite materials.

parameters. Composites having 0.42 volume fraction PZT have shown a maximum value of g_{33} in the entire compositional range. Using a homogeneous mixture of PZT and PMM powders and optimizing the sintering temperatures, it is possible to develop PZT-polymer composite in a reproducible manner having 3-3 connectivity and g_{33} values in the range 130-150. The materials developed possess considerably low ageing characteristics in respect of piezoelectric voltage coefficient. Thus the process is considered industrially feasible for production.

Acknowledgement

The authors are grateful to Dr R Krishnan for his encouragement and interest.

References

- Haun M J, Newnham R E and Schulze W A 1986 *Adv. Ceram. Mater.* **1** 361
- Khan M, Rice R W and Shadwell D 1986 *Adv. Ceram. Mater.* **1** 55
- Newnham R E, Skinner D P and Cross L E 1978 *Mater. Res. Bull.* **13** 525
- Newnham R E, Bowen L O, Klicker K A and Cross L E 1980 *Mater. Eng.* **2** 93
- Rittenmyer K, Shrout T, Schulze W A and Newnham R E 1982 *Ferroelectrics* **41** 181
- Safari A 1983 *Perforated PZT polymer composites with 3-1 and 3-2 connectivity for hydrophone applications*, Ph.D. Thesis, The Pennsylvania State University
- Shrout T R, Schulze W A and Biggers J V 1979 *Mater. Res. Bull.* **14** 1553