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Study on pore-forming agents in processing of porous piezoceramics

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Porous piezoceramics have wide performance advantages over monolithic ceramic and polymer piezoelectric materials in underwater sensing and actuation applications. This paper describes the effect of various pore-forming agents during burnt plastic spheres (BURPS) processing of porous ceramics. Three kinds of polymeric materials were used as pore forming agents for BURPS processing of porous piezoceramics. Properties such as the piezoelectric charge coefficient, hydrostatic charge coefficient and hydrostatic voltage coefficient were studied. The effect of various pore forming agents on porous piezoceramics was also investigated. The microstructures of the porous piezoceramics were also recorded to study the effect of pore-forming agents on microstructure and properties. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Lead Zirconate titanate (PZT) is widely used as a transducer material because of its high piezoelectric coefficients [1]. However, for hydrophone applications, porous PZT is preferred for several reasons. Due to the lower dielectric constant, K, of porous piezoceramics they provide a hydrostatic voltage coefficient, g_h since, $g_h = d_h/\varepsilon \circ K$, where $\varepsilon\circ$, is permittivity of free space [2]. In addition, the hydrostatic charge coefficient, d_h, $(d_{33} + 2d_{31})$, is enhanced in porous piezoceramics [3]. Recently, researchers had given dedicated effort and huge attention in the field of porous piezoceramics due to the possibility of enhancing some parameters with respect to dense materials. These porous ceramics are represented by 2 digit numbers. The first represents the connectivity of the active phase of PZT, and second represents the connectivity of the passive phase of polymer or air. In the case of 3-3 porous piezoceramics, both ceramic phase and porosity are interconnected. It is found that 3-3 diphasic porous piezoceramics have vital role in the field of piezoelectric transducer applications.

Porous PZT ceramics are manufactured by lost wax replication of a coral skeleton [4], replamine foam [3, 5] and mixing of burnable plastic spheres (BURPS) processes [6, 7]. They offer lower acoustic impedance, higher hydrostatic coefficients, higher piezoelectric sensitivity, lower density and stiffness than monolithic piezoceramics. In addition, by varying the weight percentage of pore-forming agents, the material properties of a porous ceramic transducer can be altered to meet the necessities of various applications [8].

In the present work, a modified conventional sintering method was used to produce porous piezoceramics by the BURPS process [9]. An attempt was made in this method to create porosity in the sample using different pore forming agents such as polyvinyl chloride (PVC), polymethyl methacrylate (PMMA) and polyethylene oxide (PEO). These porous piezoceramics were investigated for hydrostatic and piezoelectric properties, and their corresponding microstructures were also recorded. The effects of different pore-forming agents during processing of porous piezoceramics were studied.

2. Experimental

To process the porous piezoceramics, commercial grade soft PZT 5A powder indigenously developed at our centre was used. These PZT 5A powder was mixed with polyvinyl chloride (PVC), polymethyl methacrylate (PMMA) and polyethylene oxide (PEO) pore-forming agents separately at the ratio of weight percentage of 50/50, 60/40 and 80/20. The initial average particle size of PVC, PMMA and PEO were 125 μm, 220 μm and 150 μm respectively. A desired quantity of polyvinyl alcohol, glycerol and fish oil was used as binders. Green specimens of 22 mm diameter were pressed at 150 MPa using uniaxial hydraulic press. To remove the pore forming agent, the specimens were slow heated at 550 °C and subsequently sintered at 1200 °C for 1hr. The specimens were poled by corona poling technique [10] and electroded using copper adhesive foils. Densities of sintered samples were measured from its mass and dimensions. An X-ray diffractometer (Philips PW-1710) with Cu K$\propto$ radiation was used to reveal the phases of sintered sample. The microstructure of the sintered sample

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was examined by a Quanta 200 scanning electron microscopy (FEI, Netherlands). Piezoelectric and hydrostatic properties were measured using PM 35 dual range piezometer system (Take Control, UK).

3. Results and discussion

Fig. 1 shows the XRD patterns of the porous piezoceramics PZT-50PVC, PZT-50PMMA and PZT-50PEO sintered at 1200 °C for 1hr. It is prominent that porous PZT 5A materials with perovskite structure were exhibited for all the sintered porous piezoceramics. The recorded XRD results clearly indicate that no other phase was detected and the process of synthesis and sintering of PZT employed in the present work are appropriate. However, insignificant splitting of peaks were observed in case of PZT-50PVC specimens that may be likely leading to the low symmetry tetragonal distortions in the composition.

Fig. 2 gives the relation of density with amount of various pore-forming agents mixed in the PZT powder, when polymers were burned out at 550 °C and sintered at 1200 °C for 1 hr. It shows that, density is high for PZT-PEO porous piezoceramic followed by PMMA and PVC. As the amount of polymer increases, the density of all porous ceramics decreases linearly and subsequently porosity increases at fixed sintering temperature. The density of the material has a direct relationship with its acoustic impedance (z), since it is a product of material density and the velocity of sound in the material ($z = \rho v$). Therefore, a decrease in density of porous ceramics, leads in decreasing the acoustic impedance, and it matches with water when the porous piezoceramics is used for underwater applications.

It was reported in our earlier studies [9] that the hydrostatic charge (d_h) and voltage coefficient (g_h) increases with increase in amount of pore-forming agent and piezoelectric coefficient (d_{33}) decreases with increase in amount of pore-forming agents. The effect

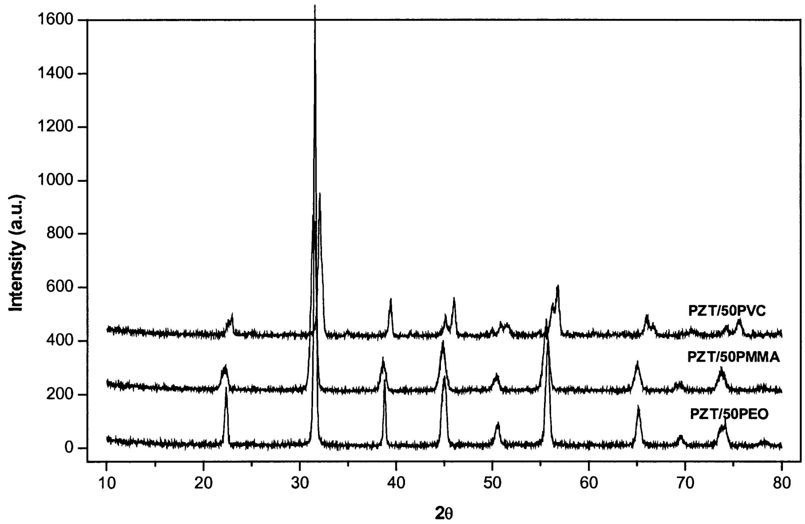


Figure 1 XRD of porous piezoceramics made of PVC, PMMA, PEO sintered at 1200 °C.

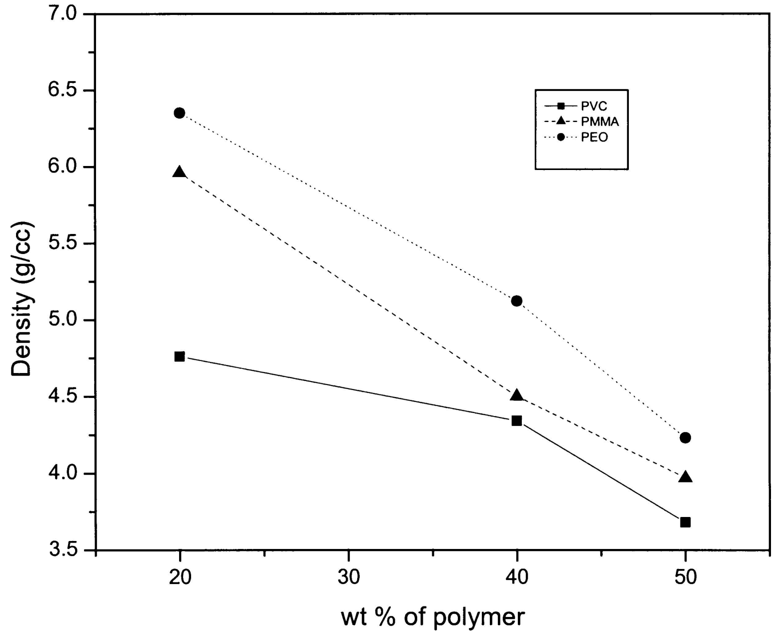


Figure 2 Variation of density with polymers. Density of dense PZT 5A = 7.8 g/cc.

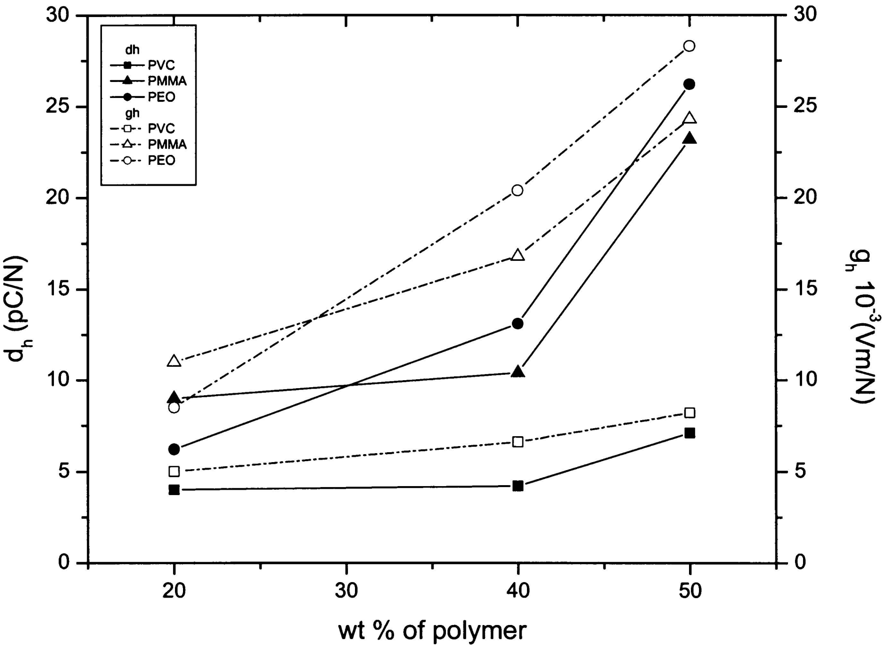


Figure 3 Variation of d_h and g_h with polymers. PZT 5A, $d_h = 8$ pC/N and $gh = 1.5 \times 10^{-3}$ m/N.

of pore-forming agents on d_h and g_h has been shown in Fig. 3. It is seen that, d_h and g_h values are relatively low in the case of the porous specimen made from PVC where is high in the case of PMMA and PEO. This clearly shows that, order of porosity and 3-3 connectivity in case of PVC specimens was low as compared to PMMA and PEO. Fig. 3 also shows that, both d_h and g_h increases linearly with increase in the amount of polymer, since d_h and g_h values directly depend on the amount of porosity and connectivity. Fig. 4. indicates the effect of pore-forming agents on d_{33} of the porous piezoceramics and shows that, porous specimens made with PVC exhibit a low value of d_{33} compared to specimens made with PMMA and PEO.

Scanning electron micrographs (SEM) of the fracture surfaces of unpoled porous piezoceramics (both high and low porosities i.e. 50/50 and 80/20) processed using PVC, PMMA and PEO are shown in Fig. 5. It indicates that, as the amount of polymer increases, the inter connectivities between the pores and pore size increases in all the porous samples. Irregular distributions of pores (0–3 connectivity) were noticed in Fig. 5(b), (d) and (f) respectively. This was relating to the low porosity present in the porous piezoceramic. However, Fig. 5(c) indicates dominating (prominent) 3–3 connectivity structure of PMMA as compared to PVC and PEO porous piezoceramic. While Fig. 5(a) and (e) shows increased connectivity in the porous piezoceramic made from PEO than PVC, while the interior microstructure

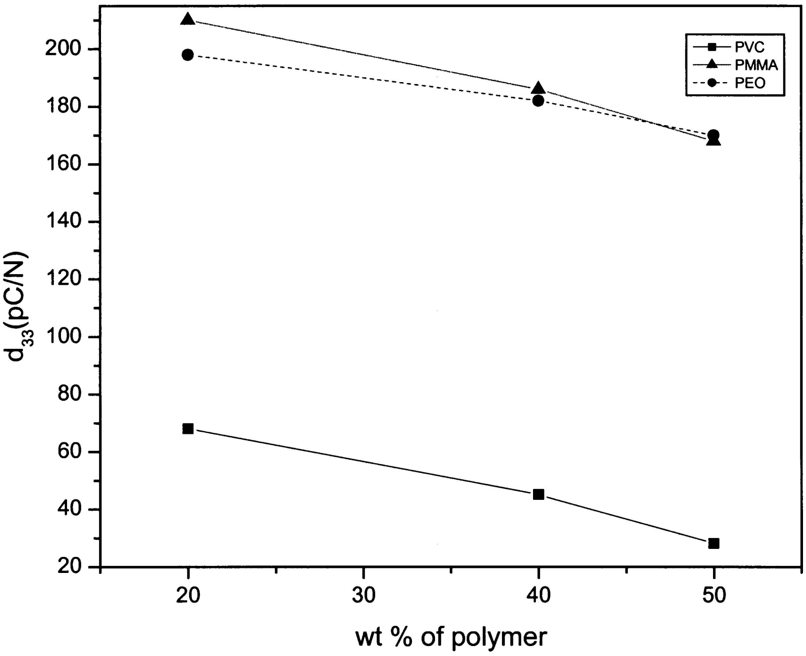


Figure 4 Variation of d_{33} with polymers. PZT 5A, $d_{33} = 390$ pC/N.

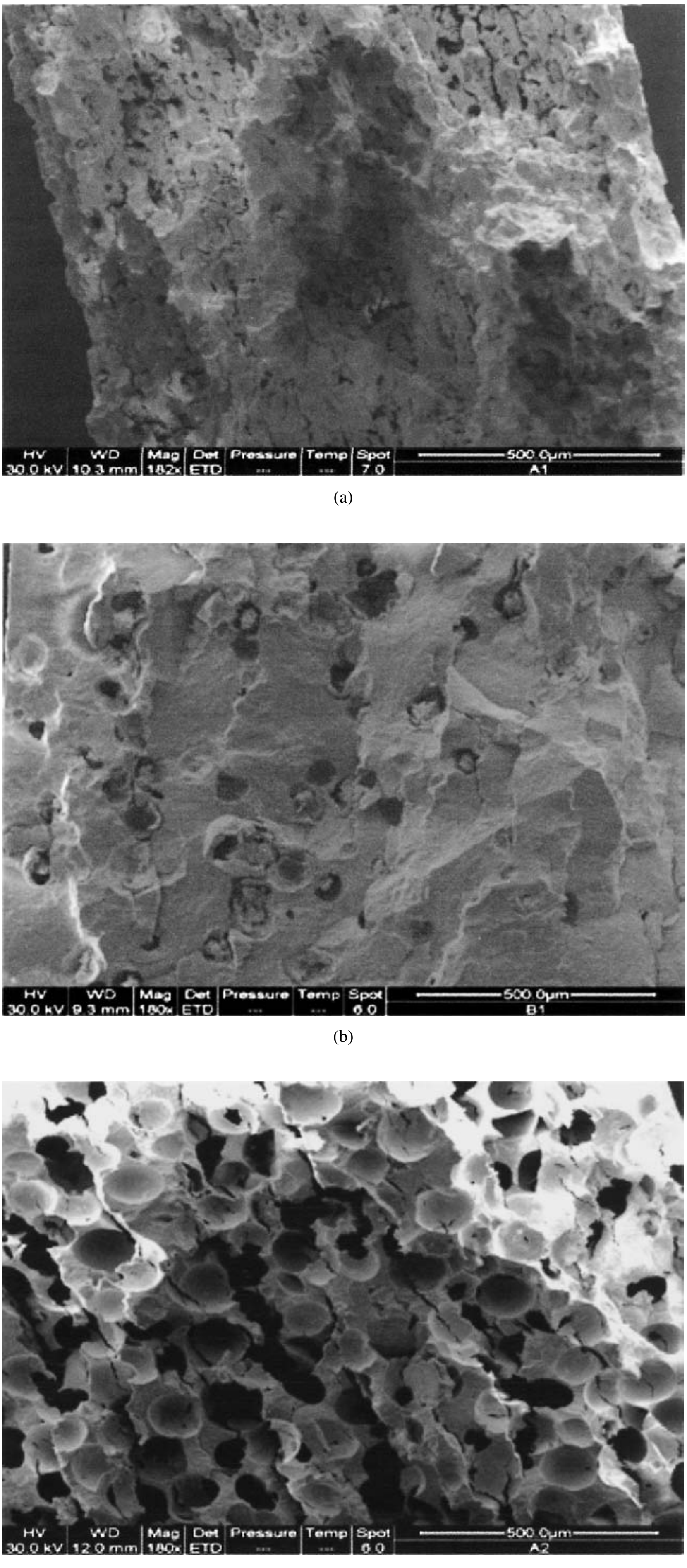
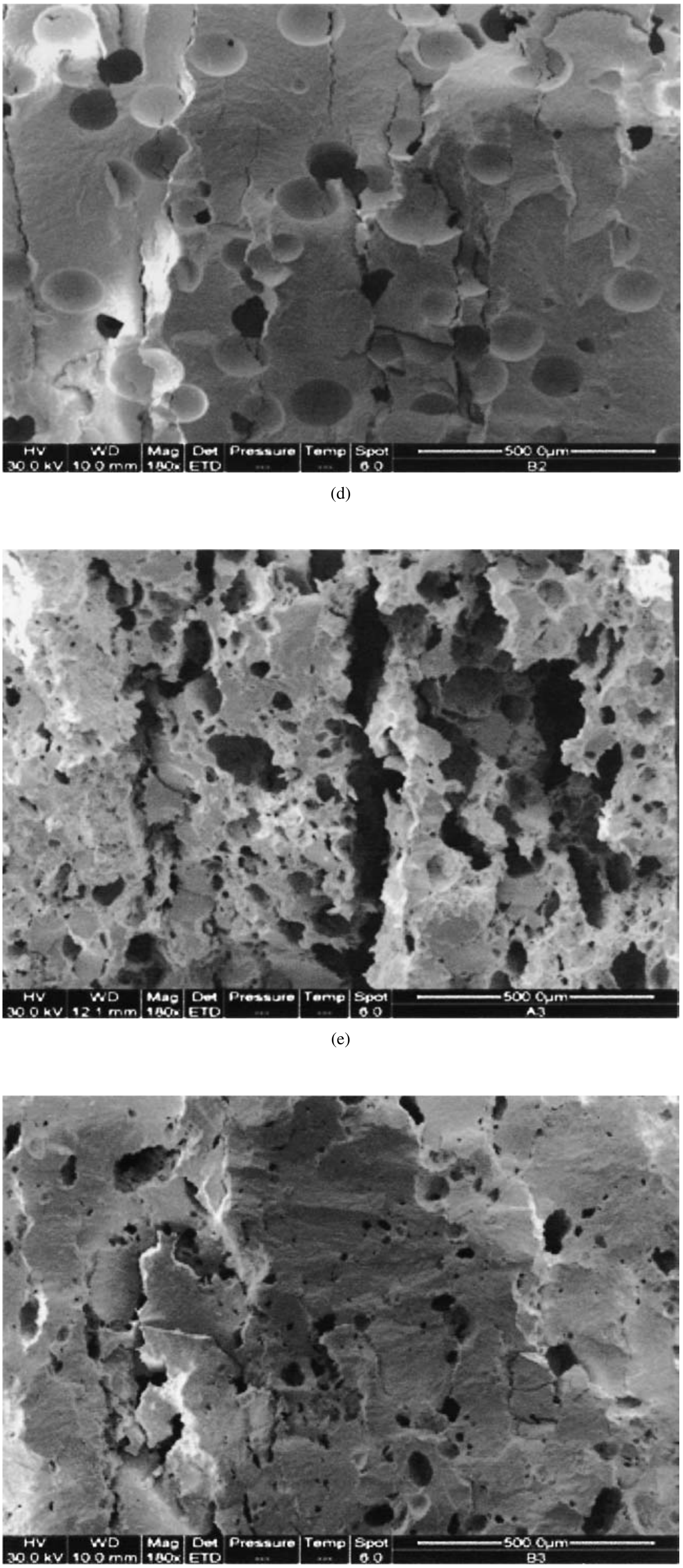


Figure 5 SEM of fracture surfaces of unpoled porous piezoceramics sintered at 1200°C prepared using (a) 50% PVC, (b) 20% PVC, (c) 50% PMMA, (d) 20% PMMA, (e) 50% PEO, and (f) 20% PEO. (Continued)



(d)

(e)

(f)

Figure 5 (Continued)

is collapsed in the case of PEO specimens. In addition, Fig. 5(c) and (d) shows cracks perpendicular to the pressing direction in PMMA specimens. This has been reported earlier [6, 11] and is more probably due to the pressing force that compresses the PZT powder more than the PMMA polymer. These varied microstructures obtained during the processing of porous piezoceramics were mainly due to (i) different percentage of pore forming agents used, (ii) presence of organic binders and; (iii) diffusion of organic binders and various pore forming agents during burnout stage.

4. Conclusions

Porous piezoceramics consisting of PZT 5A powder with different weight ratios (50/50, 60/40, 80/20) of PVC, PMMA and PEO were processed using BURPS process. Relatively low values of d_{33}, d_h, and g_h were noticed in case of porous specimen made with PVC as against PMMA and PEO. This was related to low 3–3 connectivity present in the microstructure. However, PMMA porous specimen exhibited a greater 3–3 connectivity as compared to PEO. The pore size of PMMA and PEO microstructure varies, but final properties were more or less remains same. Results also indicate that, both PMMA and PEO porous specimens are equally good in all respects except the microstructure and connectivity. The above study reveals that both PMMA and PEO is suitable pore forming agents for the processing of porous piezoceramics by BURPS process.

References

1. A. SAFARI, G. SA-GONG, J. GINIEWICZ and R. E. NEWNHAM, in Proceedings of the 21st University Conference on Ceramic Science (1986) vol. 20, p. 445.
2. C. R. BOWEN and V. YU. TOPOLOV, *Acta Mater.* **50** (2003) 4965.
3. M. J. CREEDON and W. A.SCHULZE, *Ferroelectrics* **153** (1994) 333.
4. D. P. SKINNER, R. E. NEWNHAM and L. E. CROSS, *Mater. Res. Bull.* **13** (1978) 599.
5. F. F. LANGE and K. T. MILLER, *Adv. Ceram. Mater.* **2** (1987) 827.
6. K. RITTENMYER, T. SHROUT, W. A. SCHULZE and R. E. NEWNHAM, *Ferroelectrics* **41** (1982) 189.
7. H. KARA, R. RAMESH, R. STEVENS and C. R. BOWEN, *IEEE Trans. Ultra. Ferro. Freq. Cntrl.* **50** (2003) 289.
8. W. A. SMITH, in Proceedings of the 1985 IEEE Ultrasonics Symposium (1985) p. 642.
9. B. PRAVEENKUMAR, H. H. KUMAR and D. K. KHARAT, in Proceedings of the International symposium on Advanced Materials & Processing, IIT Kharagpur, (2004) vol. 2, p. 1151.
10. D. WALLER and A. SAFARI, *Ferroelectrics* **87** (1988) 189.
11. C. R. BOWEN, A. PERRY, A. C. F. LEWIS and H. KARA, *J. Eur. Ceram. Soc.* **24** (2004) 541.

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