

# POROUS PIEZOELECTRIC CERAMICS WITH 0-3 CONNECTIVITY

B. Jadidian, and A. Winder  
J&W Medical LLC, 56 Partrick Road., Westport, CT 06880

## Abstract

*The processing-property relationship of porous piezoelectric ceramics with 3-0 connectivity is presented. It is recently shown that porous ceramics are potential candidates for the fabrication of low frequency ultrasonic transducers for hydrophone and medical imaging applications as well as therapeutic purposes. Porous ceramics have been commercially fabricated by mixing ceramic materials with the foaming agents and/or the organic beads. In this work, three different PZT's (TRS600, TRS100, APC841) powders were formed into porous ceramics utilizing fine starch powder. The PZT powders were mixed with the starch, pressed into solid disks, heat treated to remove the starch, and sintered. The volume fraction of the starch was varied between 0% to 40% in 10% increment. After sintering, the porosity volume fraction was in the range of 0 to 38%. The dielectric and piezoelectric properties of the samples were then measured according to the IEEE standard. In this paper we will report the effect of porosity volume fraction on the electromechanical properties of three different PZT materials.*

## Introduction

The low frequency ultrasonic transducers (1-200KHz) can be fabricated via the conventional bolted type Langevin structures and/or using very thick, dense piezoelectric ceramics. However, the design and manufacturing of such transducers are quite complicated and challenging. To ease the fabrication of low frequency UT's, the porous piezoelectric ceramics have become of interest because of their low acoustic impedance, good acoustic matching with water, high piezoelectric coefficients, and good transmitting and receiving sensitivities [1]. In addition, their low longitudinal acoustic velocity which makes possible use thinner piezoelectric elements for the fabrication of low frequency ultrasonic transducers.

At low porosity volume fraction (<40%), the porous structures are still mechanically strong and represent the 3-0 connectivity in which the pores are discretely distributed within the ceramic matrix. At high porosity volume fraction (>70%), the structures have a very low mechanical strength and demonstrate the 3-3 connectivity, in which both ceramic phase and pores are connected in three dimensions.

In the past, various methods have been used to introduce porosity into the piezoceramics. These include the ceramic powder compounding and sintering [2, 3], the coating of the polymeric sponge with ceramic slurry [4], the addition of the foaming agents to the ceramic slurry [5], the fugitive polymer beads to the ceramic powder [5-7], and the high volume content of polymer binder to the ceramic slurry [8]. At the same porosity fraction, the structures obtained with these methods present very different microstructures and consequently very different electromechanical properties.

Recently Lyckfeldt [9] showed that porous Al<sub>2</sub>O<sub>3</sub> with various complex shapes can be fabricated using starch as pore former. After burn-out of the starch and sintering of the ceramic matrix, the structures had porosities corresponding to the original amounts, shapes and sizes of the starch particles. Roncari [10] and Marselli [11] reported the fabrication of porous ceramic hydrophones with a total porosity of ≈40 vol.% by pressing a mixture of the PZT powder and rice starch into disks, removing the starch by heat treatment, and then sintering the samples.

In comparison with many fugitive polymeric materials, the starch is very inexpensive, easy to burn-out, and environmentally friendly. Thus the objectives of this work were to fabricate low frequency porous PZT ceramic ultrasonic transducers using starch powder; to determine the processing parameters on the morphology, pore volumes and pore size distributions; and to evaluate the electromechanical properties of the porous PZT ceramics.

### Experimental Procedure

Porous PZT ceramics were prepared by mixing potato starch with three different PZT's (TRS600, TRS100, APC841) powders obtained from TRS Ceramics (State College, PA) and American Piezo Ceramics Inc. (Mackeyville, PA), respectively. The volume fraction of the starch was varied between 0% to 40% in 10% increment. The mixtures were wet milled in a jar for 1 hour, vacuum filtered to form cakes, and dried at room temperature for 24 hours. The dried mixtures were then mixed with a PVA solution (20 wt.%), and pressed into disks of 25mm diameter and 10mm thickness. The samples were next heat treated at 680°C to slowly remove their starch content, bisque fired at 780°C, and sintered at 1285°C for 1 hour. After sintering the samples were polished to 5mm thickness, electroded with silver paint and fired at 550°C for 5 minutes, and poled in an oil bath for 10 minutes under a dc field of 25-30kV/cm.

Using a TG analyzer (Model 951 Dupont, Inc. Wilmington, DE), the Thermal Gravimetric Analysis (TGA) was performed to determine the pyrolysis behavior of the potato starch. The morphology of the starch powder was examined using electron microscopy (Model 1200 SEM, Amray Corporation, Bedford, MA). The bulk density of sintered samples were geometrically measured and their porosity volume fractions (P) were calculated by:

$$P = (1 - \rho/\rho_0) \times 100$$

where  $\rho_0$  is the density of the sintered ceramics without porosity. The dielectric and piezoelectric properties of the samples were measured in agreement with the IEEE standard using HP4194A Impedance/Gain-Phase analyzer (HP Inc., Palo Alto, CA). The dielectric constant (K), the piezoelectric voltage coefficient ( $g_{33}$ ), and the mechanical quality factor of the samples were calculated by:

$$\begin{aligned} K &= (C_p t)/(\epsilon_0 A) \\ g_{33} &= d_{33}/\epsilon_0 K \\ Q_m &= R^{-1} (L/C_a) \end{aligned}$$

where  $C_p$  is the capacitance,  $t$  is the thickness of the samples,  $A$  is the electrode area, and  $\epsilon_0$  is the permittivity of free space ( $8.854 \times 10^{-12}$  F/m). The piezoelectric charge coefficient ( $d_{33}$ ) of the

samples was measured at 100 Hz by a Berlincourt Piezometer (Channel Products, Inc., Chesterland, Ohio). The R, L, and  $C_a$  are, respectively, the resistance, the inductance, and the capacitance of the samples obtained from their equivalent circuit at their thickness series resonance frequencies. The acoustic impedance of the samples were then calculated from:

$$Z = \rho V = \rho (2tf_s)$$

where t and  $f_s$  are the thickness and the series resonance frequency of the samples, respectively.

## Results and Discussion

Fig. 1 shows that the potato starch burns out completely at 600°C. The first weight loss below 120°C is associated with the removal of the absorbed water. The major weight loss sharply occurs between 300 and 400°C followed by a slow dissociation until 600°C. Based upon the TGA plot, a heat treatment schedule was developed to successfully remove the starch of the green pressed samples without damaging them. The samples were heated to 280°C at 10°C/h, to 400°C at 5°C/h with a soak time of 3 hours, to 600°C at 10°C/h with a dwell time of 3 hours, and then followed by 210°C/h to 780°C with a hold time of 1 hour to finish the bisque firing.

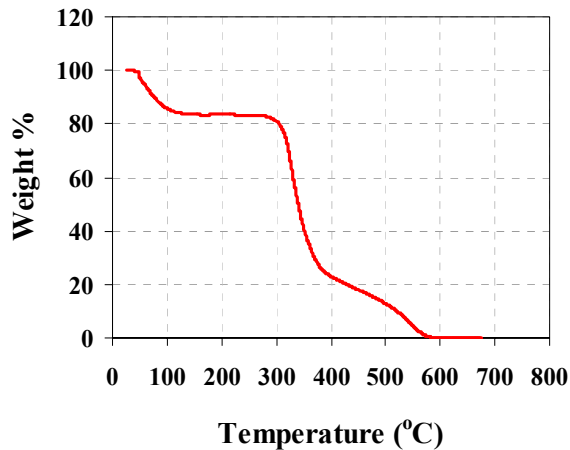


Fig.1- TGA plot of the potato starch.

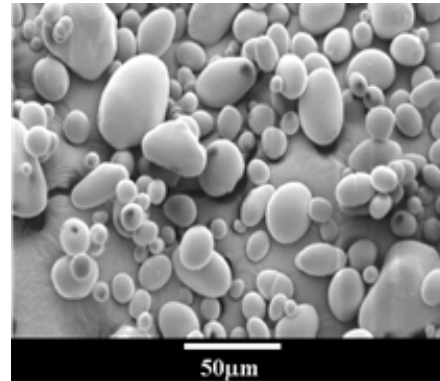


Fig. 2- SEM of potato starch after sifting through mesh 400.

Porous piezoceramics with a narrow pore size distribution demonstrate the highest electromechanical properties [8]. In general the particle size distribution of the potato starches is very wide and falls in the range of 5-75 $\mu$ m, as shown in Fig. 2. Thus before mixing with the PZT powders, the starch powder was sifted through a mesh 400 to narrow its particle size distribution and reduce it to below 38 $\mu$ m.

Table 1 represents the physical and electromechanical properties of the porous PZT's (TRS600, TRS100, and APC841). The variation of the dielectric constant and the mechanical quality factor ( $Q_m$ ) of the samples with porosity volume fraction are shown in Figures 3 and 4, respectively.

Table 1- The physical and electromechanical properties of the porous PZT ceramics.

Porosity (%)		$d_{33}$	K	$\tan\delta$	$Q_m$	$g_{33}$	$d_{33}g_{33}$	$f_s$	V	Z
Designed	Actual	pC/N		%		$10^{-3}Vm/N$	$10^{-15}m^2/N$	kHz	m/s	MRayls
<b>TRS600-Starch</b>										
0	0.00	550	3366	2.100	57	18.5	10154.7	417	4122	32.8
10	8.30	440	2830	2.633	52	17.6	7728.6	350	3381	24.5
20	15.35	420	2393	2.067	51	19.8	8329.3	314	2981	19.8
30	22.16	400	2000	2.200	43	22.6	9039.5	270	2961	17.0
40	38.34	390	923	1.780	32	47.7	18611.4	167	1650	8.0
<b>TRS200-Starch</b>										
0	0.00	380	1513	0.325	607	28.4	10781.2	420	4131	29.9
10	8.83	380	1306	0.293	460	32.9	12523.1	352	3442	23.4
20	16.06	370	1018	0.450	266	41.1	15198.8	302	2813	17.6
30	23.00	345	756	0.430	115	51.6	17800.8	250	2300	14.0
40	30.81	310	577	0.470	79	60.7	18809.9	210	2115	10.5
<b>APC841-Starch</b>										
0	0.00	290	1223	0.375	1573	26.8	7772.4	419	4190	33.2
10	9.47	290	1000	0.360	976	32.8	9502.7	358	3585	25.6
20	14.38	280	874	0.365	618	36.2	10132.9	330	3377	21.9
30	20.55	275	670	0.390	349	46.4	12754.0	287	2867	17.8
40	31.02	265	500	0.400	132	59.9	15882.2	220	2198	11.2

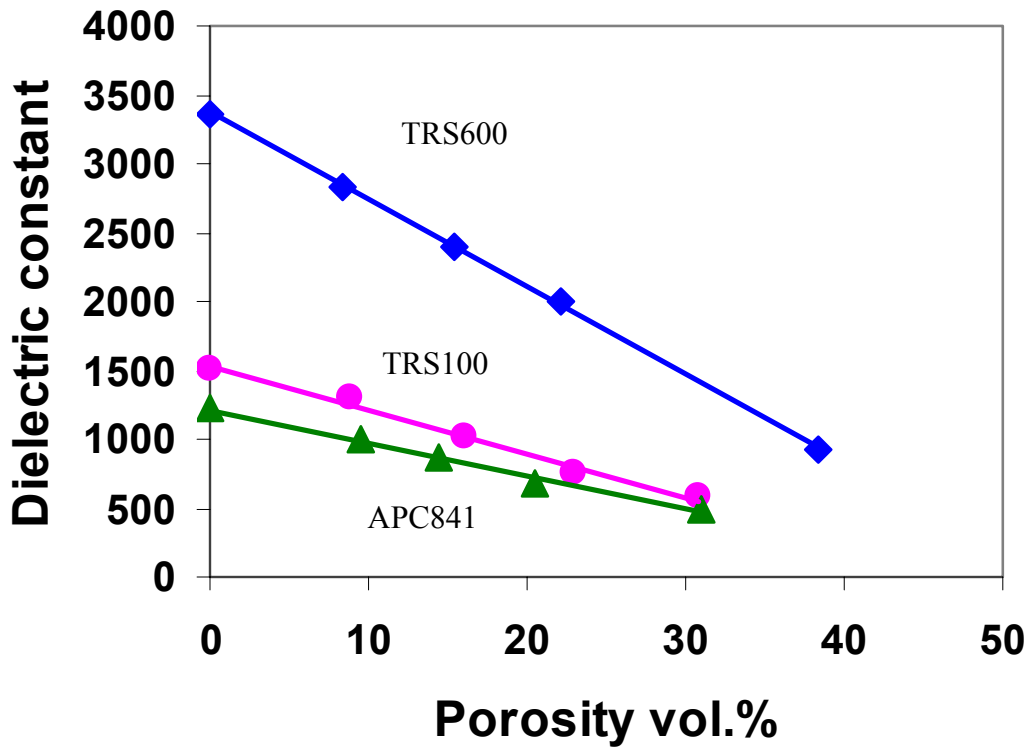


Fig. 3- The dielectric constant of porous ceramics as a function of porosity volume fraction.

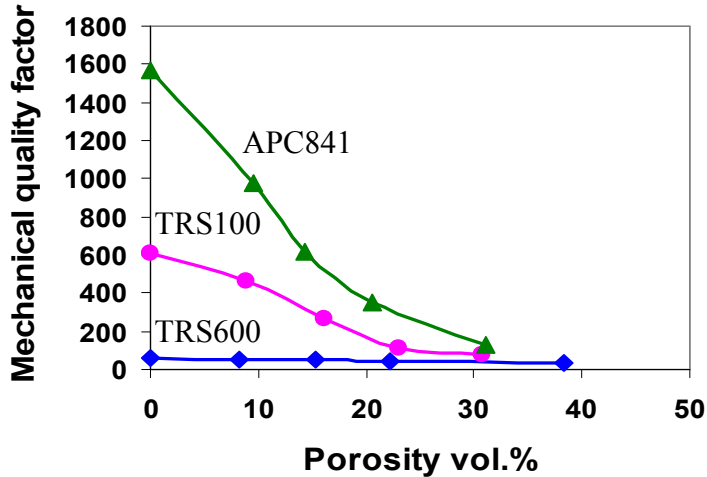


Fig. 4- The mechanical quality factor of porous ceramics as a function of porosity content.

It is clear that the dielectric constant and mechanical quality factor of three PZT decreases as the porosity volume fraction increases. The dielectric constant of the soft PZT-TRS600 varies more significantly with the increase of porosity. On the other hand, the variation of the mechanical quality factor of the hardest PZT-APC841 with the increase of porosity volume fraction is more pronounced.

Figures 5 and 6a depict the acoustic impedance and resonance frequency of the PZT porous ceramics as a function of porosity content. As shown, the increase of porosity linearly and quite similarly decreases the acoustic impedance and resonance frequency of PZT ceramics. From Figures 5 and 6a, one can deduce that the variation of the acoustic impedance and resonance frequency as a function of the porosity are solely dependent upon the porosity content and are independent of the type of PZT material. Figure 6b shows the normalized resonance frequency of the samples versus porosity volume fraction. As shown, the resonance frequencies of the PZT ceramics with  $\approx 40$  vol.% porosity are significantly reduced to almost 40% of the resonance frequencies of their solid counterparts.

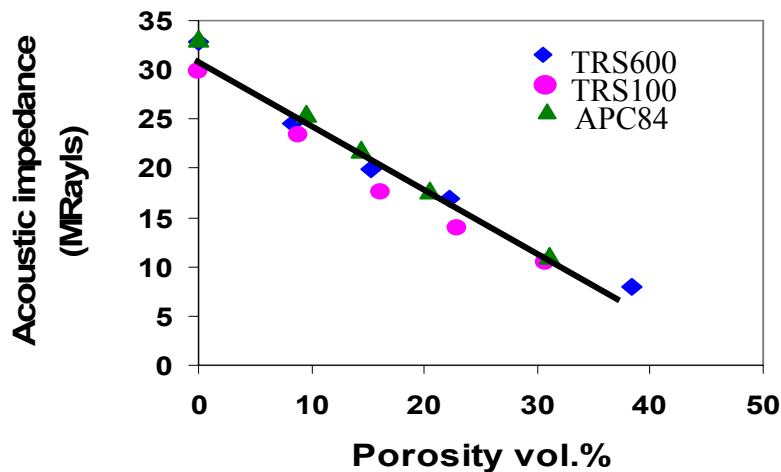


Fig. 5- The acoustic impedance of porous ceramics as a function of porosity content.

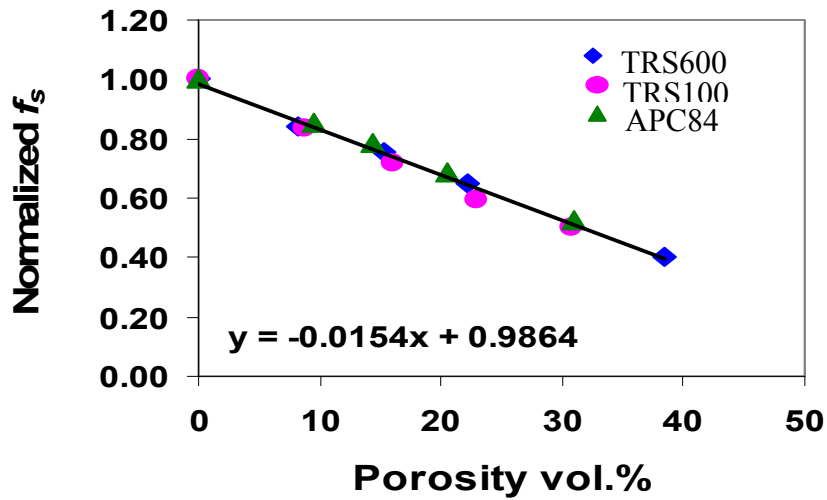


Fig. 6- The resonance frequency of the porous ceramics as a function of porosity content.

For transducers with high receiving and transmitting sensitivities, very high values of piezoelectric Figure of Merit (FOM) are desirable. The FOM's of the hard PZT samples (TRS100 and APC841) linearly and notably improve by increasing the porosity volume fraction, as shown in Fig. 7. However, the soft PZT-TRS600 behaves differently. This indicates that the transducers made of porous soft PZT ceramics with less than 25vol.% porosity have weak receiving sensitivities.

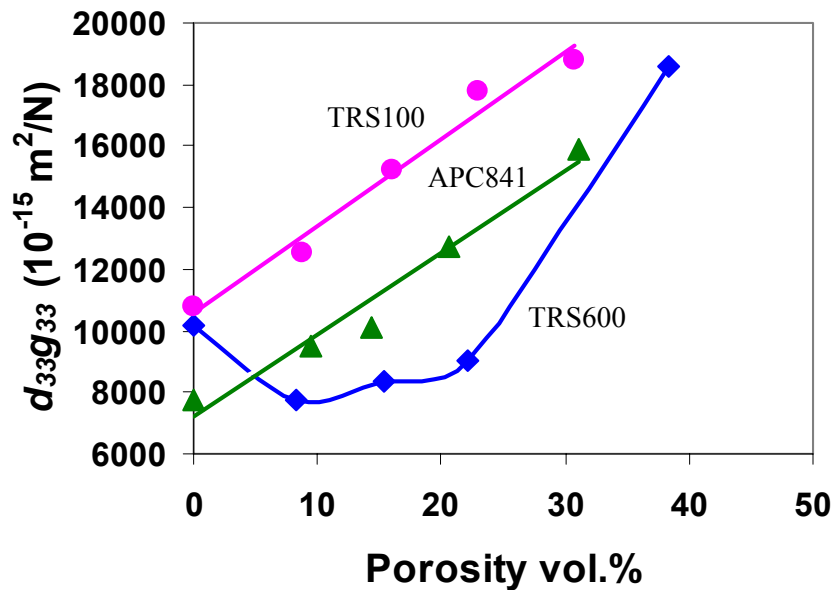


Fig. 7- The piezoelectric Figure of Merit of porous PZT ceramics as a function of porosity content.

## Conclusion

Porous ceramics of three different PZT's (TRS600, TRS100, and APC841) were successfully prepared using environmentally friendly and inexpensive potato starch as the fugitive material. The PZT and starch powders were mixed and pressed into disks. The green ceramics were carefully heat treated under a controlled heating schedule to remove their starch content. After sintering, the physical and electromechanical properties of the porous ceramics were evaluated as a function of porosity volume fraction. It was realized that the physical properties, the dielectric constant, the mechanical quality factor, and the piezoelectric charge coefficient ( $d_{33}$ ) of the samples decreased by increasing the porosity volume fraction. The reduction of the dielectric constant and the mechanical quality factor as a function of porosity were very significant for PZT-TRS600 and PZT-APC841, respectively. In addition, the resonance frequency of the porous ceramics had a linear relationship with the volume fraction of porosity. The reduction of the resonance frequency was independent of the type of PZT material.

## References

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