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Large area 0-3 and 1-3 piezoelectric composites based on single crystal PMN-PT for transducer applications

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Abstract

0-3 and 1-3 composites have been fabricated using piezoelectric single crystals (PSCs). These two connectivities were specifically chosen for large area fabrication. In particular, a lamination technique was used for 1-3 piezocomposites instead of the standard "dice and fill" method. For 0-3 connectivity, the thickness coupling factor of fabricated materials using PSC phase is twice the value obtained using standard PZT powder for the same volume fraction (60%). But the efficiency of the poling stays low. For the 1-3 piezocomposites, the properties (such as the thickness coupling factor) of the samples fabricated by the lamination technique are comparable to those obtained with standard methods. Finally, three ultrasonic transducers with center frequency between 600 and 850 kHz were fabricated to evaluate the performance of these new piezoelectric composites.

Keywords: Piezoelectric single crystals; piezocomposites; ultrasonic transducers

1. Introduction

For SONAR applications, large area piezoelectric elements with high piezoelectric properties are often required. Piezoelectric single crystals (PSCs) deliver high electromechanical coupling factor but it is difficult to obtain these materials in large size while keeping homogeneous properties. Piezoelectric composites obtained by mixing a PSC phase with an inert phase (typically a polymer) can be fabricated in large pieces when connectivity [1], describing

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the spatial arrangement between the two phases, and the fabrication process are judiciously chosen. In this study, two types of piezocomposites were developed.

0-3 piezocomposites were fabricated several years ago by mixing PZT or PMN-PT polycrystalline powder and polymer. Here, PSC PMN-PT cubic templates were used as the piezoelectric phase. Their higher electromechanical properties (in particular for the thickness mode) are expected to improve the properties of the composites.

1-3 piezocomposites were also fabricated by a recently published lamination method [2] which is an alternative process to the "dice and fill" method (DFM) [3] and well adapted for large area samples.

In this paper, the new fabrication processes of these two kinds of piezocomposites are first described (Section 2). Then Section 3 gives the electromechanical properties of the fabricated samples. These results are compared to predictions using an homogenization method [4] (Section 4). Finally, three single element transducers were fabricated and characterized. They are based on 1-3 piezocomposites obtained by the lamination and "dice and fill" methods.

2. Composite fabrication

2.1 0-3 Piezocomposites

0-3 piezocomposites consist in a mixture of isolated piezoelectric particles in a polymer matrix. Here, the novelty is to use single crystal particles instead of standard polycrystalline ceramic grains. The fabrication and properties of piezoelectric inclusions are briefly described and the fabrication process is detailed.

2.1.1. Micro PMN-35PT single crystal synthesis

(1-x)PMN-xPT cubic single crystals with composition close to $x=0.35$ were obtained by the flux method [5]. Their density is 8060 kg/m^3 and they are selected according to their sizes by sieving. Fig. 1 shows the selected cubic single crystals with sizes in the range 20-40 μm .

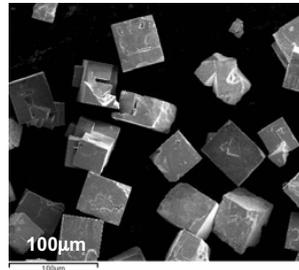


Fig.1 SEM photograph of selected cubic single crystal particles.

For the fabrication of 0-3 piezocomposites, the selected sizes range from 20 to 100 μm .

2.1.2. Fabrication process

Three polymers were tested for the matrix and tri-ethyleneglycol-dimethacrylate (TEGDM) was retained for its high fluidity and low polymerization time (lower than 10 mn at room temperature). TEGDM is deposited on a glass plate and cubic single crystals are added and mixed to obtain a highly loaded material. A second glass plate is used to press the mixture and the plate is turned (in a circle motion) to evenly distribute the cubic single crystals, optimize their alignment and minimize the porosity. With this method a density up to 6000 kg/m^3 can be obtained, corresponding to a single crystal volume fraction of around 60%. The size of the piezoelectric inclusions has a large influence on the highest load content and orientation efficiency of these cubic elements. The highest density and

orientation degree are obtained for the smallest size range (20–40 μm , Figure 1). The final thickness also has a great influence on electromechanical performance of the sample. Fig. 2 represents the Lotgering factor (which is closely related [6] to the degree of orientation of the cubic particles) as a function of depth in a 200 μm thick 0-3 piezocomposite (with a volume fraction around 60% and 20 μm piezoelectric cube size). This factor was obtained from X-ray diffraction spectra, the upper face of the 0-3 composite being successively polished. Near the two faces, the degree of orientation is high (80 and 93%), but this factor decreases rapidly in the sample. This phenomenon can be minimized by decreasing the thickness of the sample (i.e. by minimizing the ratio between the size of the cubic inclusion and the thickness of the final composite).

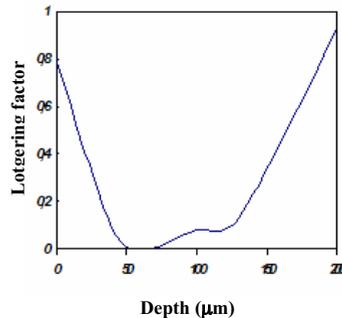


Fig.2 Lotgering factor as a function of depth in a 200 μm thick 0-3 piezocomposite.

Finally, evaporated gold electrodes were deposited on the two faces and samples were poled at 60°C in an oil bath with an electric field between 4 and 10 kV/mm. Fig. 3 shows a representative highly loaded 0-3 piezocomposite (sample 1 in Table 1).



Fig.3 0-3 piezocomposite made with cubic PMN-28PT piezoelectric single crystal and TEGDM polymer (sample 1).

2.2 1-3 piezocomposites

1-3 piezocomposites fabricated with two different techniques have been evaluated. First, polycrystalline PMN-34.5PT ceramic and an epoxy resin (this polymer is used in this connectivity) were used for the two phases. Fig. 4 shows the two fabricated samples by the standard "dice and fill" method (a) and by the lamination technique (b) which is described in [2]. The thickness of the two samples is slightly different (Table 1) but the periodic structure is

similar (the lateral dimensions of the ceramic rods are around $500\mu\text{m}$ and the pitch of the structure is between 800 and $900\mu\text{m}$).

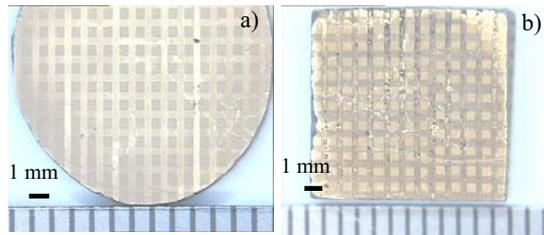


Fig.4 1-3 piezocomposites made by a) "dice and fill" method (sample 2, Table 1) and b) by the lamination technique (sample 3, Table 1) with epoxy resin for the inert phase and PMN-34.5PT for the polycrystalline piezoelectric ceramic phase.

A third 1-3 piezocomposite sample was fabricated by lamination technique using a commercial PMN-28PT piezoelectric single crystal (sample 4) with a slightly higher piezoelectric material volume fraction than the other samples. The three 1-3 piezocomposite samples were electroded with 400nm of gold on the two faces and poled at room temperature at 1.1kV/mm for the composites based on PMN-34.5PT and 600V/mm for sample 4.

3. Characterization

Knowing the electrode area, thickness and density of the different samples, a fit of the experimental electrical impedance (measured with a HP4395A impedance analyzer and its impedance test kit) of the piezoelectric element in free resonator conditions [7] allows the properties related to the thickness mode to be determined. Complex electrical impedance curves of two samples are represented in Fig. 5 around the fundamental resonance. All the characteristics obtained for the four samples are summarized in Table 1.

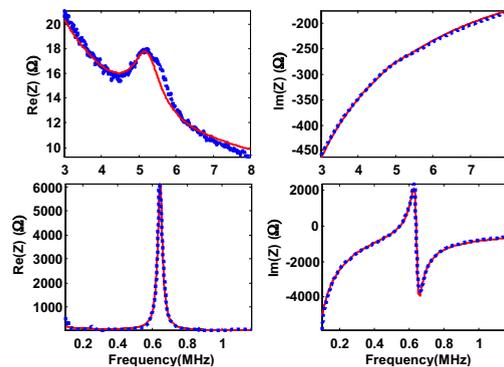


Fig.5 Experimental (blue points) and theoretical (red solid lines) complex electrical impedance measured in air of a) 0-3 piezocomposite (sample 1) and b) 1-3 piezocomposite (sample 4).

Table 1. Characteristics of 0-3 and 1-3 piezocomposites.

Sample #	0-3composite		1-3 composites	
	1	2	3	4
method	MX	DFM	LM	LM
polymer	TEGDM	EP	EP	EP
Piezo-material	PSC PMN-28PT	PMN-34.5PT	PMN-34.5PT	PSC PMN-28PT
e (mm)	0.24	2.3	2.9	2.7
S (mm ²)	28.3	129	118	400
v _f (%)	60	32	30	40
ρ (kg/m ³)	5600	3360	3495	3830
ε ₃₃ ^S /ε ₀	94	505	580	470
v _l (m/s)	2540	3755	3705	3485
f _a (kHz)	5225	830	643	638
k _t (%)	6	62	57	74

Method: MX (mix and press), DFM (dice and fill), LM (lamination); Polymer : TEGDM (Tri(ethyleneglycol)dimethacrylate); EP (epoxy resin); piezo-material: PMN-28PT (single crystal), PMN-34.5PT (polycrystalline); e: thickness; S: area of the upper electrode; v_f: volume fraction of the piezoelectric material; ρ: density; ε₃₃^S/ε₀: dielectric constant; v_l: longitudinal wave velocity; f_a: anti-resonant frequency; k_t: thickness coupling factor.

4. Modelling and Discussion

Homogenization method [4, 8] is used to calculate the effective properties of the composite materials. This method is based on a decomposition of a cubic unit cell containing a single inclusion which is adapted to change the connectivity (here 0-3 and 1-3). The data used for these simulations is given in Table 2 for the inert phase and Table 3 for the piezoelectric phase. Two plates of each polymer were specifically fabricated (with a thickness of 2 mm) to measure longitudinal and shear wave velocities by transmission method using transducers which have a center frequency at 1 MHz. Thus, elastic parameters were deduced.

Table 2. Characteristics of the two polymers used.

Polymer	ρ (kg/m ³)	c ₁₁ (GPa)	c ₁₂ (GPa)	c ₄₄ (GPa)	ε/ε ₀
TEGDM	1200	7.22	3.84	1.69	5
Epoxy resin	1100	7.84	3.90	1.97	3

ρ: density; c₁₁, c₁₂ and c₄₄: elastic constants; ε₃₃/ε₀: dielectric constant;

In Table 3, the database of the PMN-34.5PT ceramic used for the simulation and taken from [9] are recalled. For the single crystal parameters, all the tensor components are not available. Moreover, the content of PT is not exactly known in the cubic particles and uncertainty exists on the theoretical parameters used. The database used in Table 3 is taken from [10, 11] for a PMN-33PT (nearest composition available) and the parameters mentioned in italic are

deduced from a direct characterization of the thickness mode of a disk (pure PMN-28PT) used for the 1-3 piezocomposite fabrication (sample 4).

Table 3. Characteristics of the two piezoelectric materials used for simulation.

Polymer	PMN-34.5PT	PMN-28PT
ρ (kg/m ³)	8060	8060
c_{11}^E (GPa)	174.7	115.4
c_{12}^E (GPa)	116.6	103.4
c_{13}^E (GPa)	119.3	102.6
c_{33}^E (GPa)	154.8	114.1
c_{44}^E (GPa)	26.7	68.9
c_{66}^E (GPa)	29.0	65.8
$\epsilon_{11}^S/\epsilon_0$	2373	925
$\epsilon_{33}^S/\epsilon_0$	2825	813
e_{13} (C/m ²)	-6.4	-3.4
e_{15} (C/m ²)	17.1	10.1
e_{33} (C/m ²)	27.3	20.5

ρ : density; $c_{11}^E, c_{12}^E, c_{13}^E, c_{33}^E, c_{44}^E, c_{66}^E$: elastic constants at constant electric field; $\epsilon_{11}^S/\epsilon_0, \epsilon_{33}^S/\epsilon_0$: dielectric constant at constant strain; e_{13}, e_{15}, e_{33} : piezoelectric coefficients.

For the 0-3 piezocomposite (sample 1), the (k_t) is low but higher than the simulated value for the 0-3 connectivity. With a volume fraction at around 60%, several cubic particles are in contact, which creates locally a 3-3 connectivity and thus increases the (k_t) value. But the poling efficiency in this configuration is low (due to the large difference between the dielectric constants of the two phases) and has been quantified with FE method (ATILA code): the voltage received by the piezoelectric particles is only a few volts (less than 10 V) for an electrical field of several kV/mm even if the polymer volume fraction is very low. Fig. 6 presents the homogenized thickness coupling factors as a function of piezoelectric phase volume fraction for all the studied combinations.

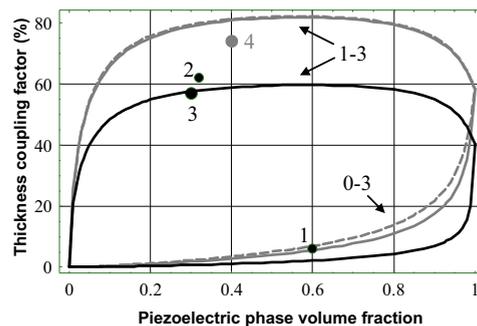


Fig.6 Thickness coupling factor (k_t) as a function of the piezoelectric phase volume fraction for the two connectivities studied (0-3 and 1-3): PMN-34.5PT/TEGDM (solid black lines), PMN-28PT/TEGDM (dashed gray lines), PMN-28PT/epoxy (solid gray lines). The points are the experimental results of the four samples.

For a v_f of 60%, assuming that the poling is perfect (this is the case for the simulations in Fig. 6.), (k_t) can be significantly improved by using a PSC phase. For the combinations PMN-34.5PT/TEGDM and PMN-28PT/TEGDM, (k_t) values are respectively 3% and 7%.

For the 1-3 piezocomposites, similar results are obtained for samples 2 and 3, which confirms the efficiency of the lamination technique. Measurements are in fair agreement with the theoretical results. Sample 4 exhibits high performance, which has already been observed in [2], but, experimental results are lower than the theoretical prediction. This difference is probably due to the uncertainty of the PMN-28PT parameters used for the simulation.

5. Transducers

Three ultrasonic transducers were fabricated with samples 2, 3 and 4. The backing was fabricated with an epoxy resin loaded with tungsten particles (the corresponding volume fraction is around 30% for an acoustical impedance around 8 MRa). The backings are directly moulded and polymerized on the 1-3 piezoelectric samples. No matching layer has been added. The pulse echo responses were measured in a water tank on a metallic target. Experimental set-up is exactly the same for the three transducers. Fig. 7 shows the pulse echo response of the transducer with the 1-3 piezocomposite obtained by the lamination technique based on PSC.

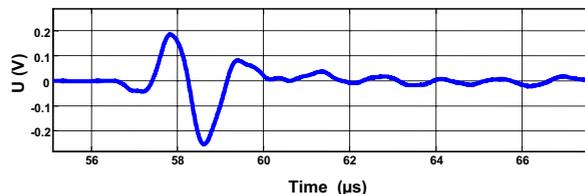


Fig.7 Electro acoustic response of the transducer made with sample 4.

The transducer performance is summarized in Table 4. Results show that the transducer properties are lower for lamination technique than “dice and fill” method (samples 2 and 3), but by using a PSC material, sensitivity and bandwidth become comparable.

Table 4. Transducer characteristics.

	f_c (kHz)	S (dB)	BW (-6dB) (%)	BW (-20dB) (%)
Sample 2	840	0	75	120
Sample 3	610	-8.4	50	105
Sample 4	550	-2	70	165

f_c : center frequency; S: relative sensitivity (normalised with sample 4); BW(-6dB): relative bandwidth at -6dB; BW(-20dB): relative bandwidth at -20dB.

6. Conclusion

New 0-3 piezocomposites were fabricated using PSC phase. Theoretical predictions showed that the thickness coupling factor should be more than twice that of a composite based on standard PZT. Performance of 1-3 piezocomposites fabricated by lamination technique, well adapted for large area samples, are comparable to those obtained by “dice and fill” method. Their integration in a transducer shows that the corresponding sensitivity decreases of few dB.

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