0-3 PIEZO-ELECTRIC COMPOSITES DESIGN TO THE SHAPE CONTROL OF STRUCTURES

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SUMMARY: A description of the way to process 0-3 piezo-composite materials is presented. In particular, it is about the utilisation of a separation technique, taking advantage of the centrifugal force. The aim is to increase the amount of piezoelectric ceramic powder of the mixture with centrifugation. This process leads to a non-homogeneous two-ply material. The top of the sample is made of a clear resin ply and the bottom of a more compact layer. Another purpose of this work, is to show the good agreement of experimental results with those existing in literature, in terms of dielectric properties of the composite. A comparison between polyester and epoxy based piezo-composites is performed. This material could be helpful for the creation of an *in-situ* actuator, for the shape control of resin based composite structures.

KEYWORDS: 0-3 Piezo-composites, Smart materials, Centrifugation, Piezo-electric ceramics, Sedimentation, Processing, Shape control.

INTRODUCTION

Effective structures operating in as severe environments as space must respect all geometric tolerances. In substitution of very stiff materials usually employed, smart composites can be used. Smart materials include passive materials (such as classical composites) and an actuator, which can produce a strain in the opposite sense of the environmental loading, in order to get a small value for the global strain of the structure. Several kinds of actuators can be used: SMA, piezo-electric ceramics...

Often, electroactive materials as 0-3 connectivity piezo-composites, have some peculiarities rendering them very appealing for purposes of active control and for use in transducers [1], for example in underwater and biomedical imaging applications. Another use can be as *in-situ* stress transducers: for instance, they can be placed inside a laminate, to evaluate its state of internal stress or the eventual presence of damage (Non-Destructive Testing). The attractive features are a smaller acoustical impedance and a greater shape flexibility, i.e. a higher global compliance, with respect to monolithic PZT or $BaTiO_3$. This work is dedicated to 0-3 piezo-composites.

The electromechanical behaviour of 0-3 piezo-composites has been analysed in several ways. The concept of connectivity was established by Newnham [2], to provide a microstructural characterisation, i. e. to describe the interspatial relationships in a multiphasic material. These models of series and parallel connectivity are very useful, as they give a superior and an inferior limit for piezoelectric coefficients and other electromechanical properties of the composite. These theories work well as upper and lower limits, when the behaviour of the material is studied in function of the volume fraction of the active inclusions. A theory nearer to the notion of homogenisation is that suggested by Furukawa [3]. He considers as a representative unit of a material, composed of spherical piezoelectric inclusions embedded in a matrix, a sphere recovered by a shell of resin; the ensemble is then covered with a homogeneous medium, having the macroscopic properties of a composite. More recently and with a quite similar viewpoint, a finite element procedure has been proposed [4], allowing to simulate the coupled electroelastic response of an actuator made of a 1-3 piezo-composite material. Their results allow the computation of the engineering constant of the composite, being considered again as a homogeneous medium at a macroscopic level. Pastor J. [5] has also studied the electromechanical behaviour of 1-3 piezo-composites by using homogenisation. Other authors extended the dilute, self-consistent and Mori Tanaka micromechanics theories, to consider the coupled behaviour of piezoelectric composites [6].

Electromechanical behaviour of 0-3 piezo-composites.

The constitutive laws of piezoelectric materials can be extended to 0-3 piezo-composites:

$$\epsilon_i = S_{ij} \cdot \sigma_j + d_{ij} \cdot E_k \tag{1}$$

In this local relation ϵ_i is the strain, σ_j is the stress E_k is the electric field, S_{ij} is the compliance of the material at constant electric field and d_{ij} is the piezoelectric parameter at constant stress. In order to get good actuation strains, the best material is that having the highest d_{ij}. In Eqn (1) the elastic and piezoelectric parameters are homogenised. In reality, these parameters are depending on the shape of active inclusions, on their volume fraction and on the electromechanical properties of the components.

If we follow the parallel connectivity theory for these materials, developed by Newnham [2] and giving the following expression for d_{33}:

$$d_{33} = \frac{\left(v_P \cdot d_{33P} \cdot S_{33M} + (1-v_P) \cdot d_{33M} \cdot S_{33P}\right)}{\left(v_P \cdot S_{33M} + (1-v_P) \cdot S_{33P}\right)} \tag{2}$$

where matrix properties are designated with the index M, while those of the particles with the index P. It is then shown that letting the Young modulus of the resin vary between 1 and 3 GPa and the volume fraction v_p of the powder between 0.6 and 0.9, the best piezoelectric coefficients d_{33} for this model can be achieved by using a rather soft resin, according to Fig.1:
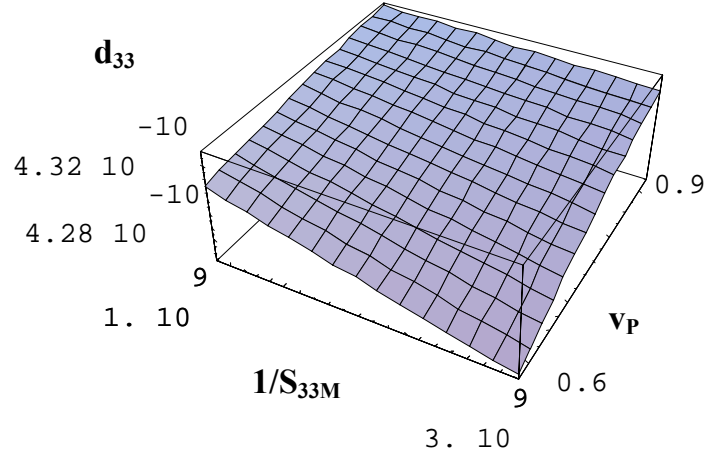
Fig.1: The coefficient d_{33} as a function of the volume fraction of piezo-electric ceramics and of the Young modulus of the resin

We can suppose to apply a mechanical load to the sample. Due to electroelastic coupling, the load will create an electric displacement D_i. It follows that the higher potential gradient occurs in the portion of the composite having the lower permittivity [4], as seen in this other local relation:

$$D_i = d_{ij}\sigma_j + \varepsilon_{ik} \cdot E_k \qquad (3)$$

Permittivity is always much lower in resins than in ceramic powders: this means that high electric fields are needed to activate the composite. So it is generally quite difficult to build an actuator with this type of composite, unless a very important amount of piezoelectric inclusions is present in the composite.

Piezo-electricity and dielectricity

As dielectric constant is synonymous with dielectric susceptibility X for high relative permittivity ε_r materials, it is the dielectric susceptibility, which is referred to:

$$[X] = [\varepsilon_r] - [I] \qquad (4)$$

Eqns 4) and 5) are global relations. If the electric field E is kept constant in Eqn. 5, it is seen that the composite material having the lowest dielectric constant has the worst polarisation P:

$$\{P\} = \varepsilon_0 \cdot [X] \cdot \{E\} \qquad (5)$$

with ε_0 being the free space permittivity. This is another way to explain why problems are encountered to activate the composite material.
The electric displacement D is proportional to the intensity of the polarisation:

$$\{D\} = \{P\} + \varepsilon_0 \cdot \{E\} \qquad (6)$$

The Berlincourt piezo-meter measures the electric charge on the surface of the sample, created by the action of dynamical load of compression, at a given frequency (see Eqn 3). It means that it calculates the following ratio:

$$d_{33} = \frac{D_3}{\sigma_{33}} \tag{7}$$

σ_{33} being the component of the stress tensor and D_3 that of the electric displacement vector in the direction of the applied load.

Processing

The way to process samples is rather original. It is based on the use of the centrifugal force while, till now, the most common way to fabricate 0-3 active composites was the hot rolling technique: the piezoelectric ceramic powder was hot laminated after melting with a thermoplastic or a thermosetting resin [3], [7], [8]. Even though we didn't get thin samples, with respect to sedimentation and to the preceding technique, we didn't need to use spatulas; we didn't even need to apply vacuum degassing procedures to prepare our mixtures, as we can expel porosity very easily. The mixture, still homogeneous, is put in a suitable mould of cylindrical form and closed in a centrifugal or in a lathe. The action and the aim of the centrifugal force are destroying the homogeneity of the mixture, giving rise to a two-ply specimen and evacuating porosity. The process begins by mixing thoroughly the piezo-electric powder and the resin. The diameter of the specimen is 20 mm and the height is 6 mm.
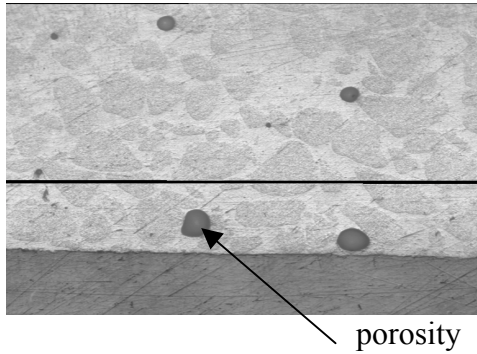

porosity

big amount of resin

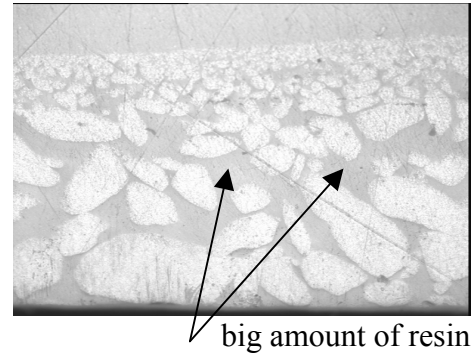Fig. 2: sedimentation: porosity is found in the black spots

Fig. 3: settling by centrifugation in a lathe: large areas of resin are due to empilement of particles and aggregates of particles

We initially used a lathe that easily removed air: Figs. 2-3 show some micrographs taken with an optical microscope ($1\text{cm} \cong 230 \ \mu m$). Unfortunately, its limited acceleration values, only reaching 220 $\vec{\text{g}}$ $\left(\|\vec{\text{g}}\| = 9.81 \ \text{ms}^{-2} \right)$, were not sufficient to separate particles from the resins we used. Looking for a way to avoid that particles superpose them the ones on the others, a device has been designed and created, producing shear vibration, so to stir them and make large resin areas disappear (Fig. 4). But it didn't still improve enough the results in terms of amount of solid inclusions.

Fig. 4: centrifugation and vibration

We continued, then, experimental investigations with a centrifuge, whose values of acceleration can reach nearly 2200 $\vec{g}$. Electrodes for measurements of capacity were put during processing of the specimen. A little support, with a weight applied on a piston lying in the mould, avoided their deformation while polymerisation in the oven. Measures of the dielectric constant could be taken after polishing the sample.
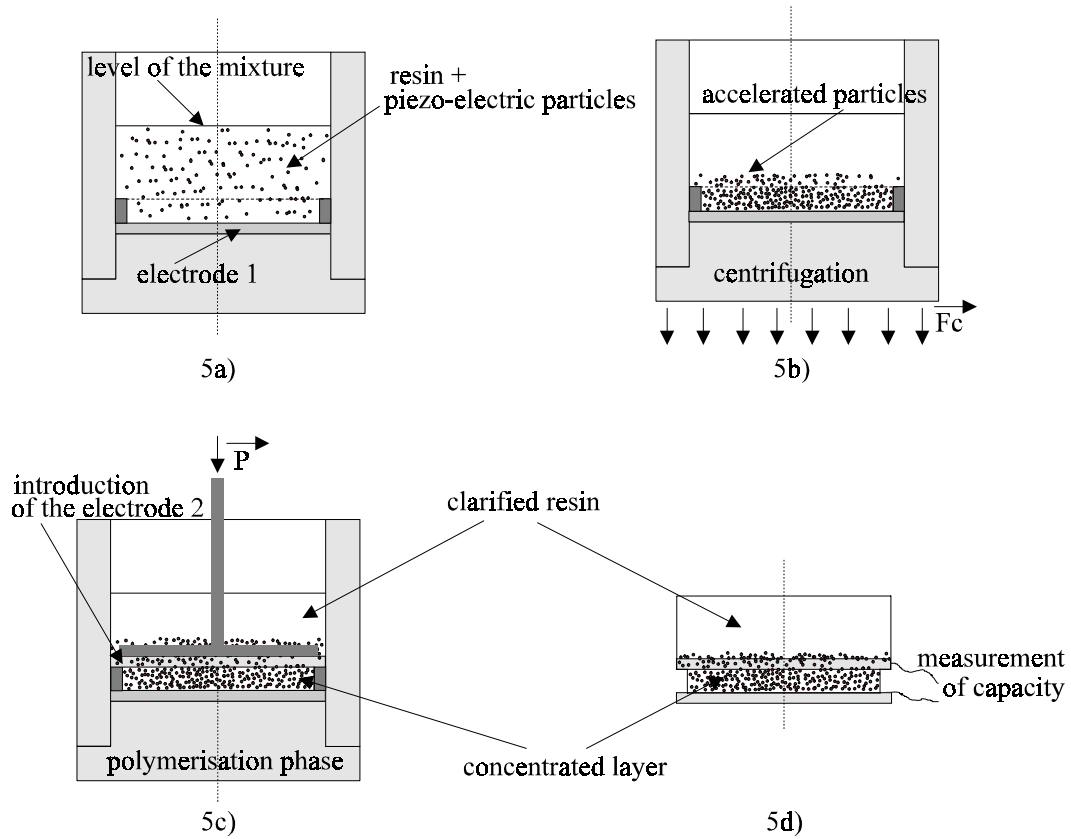

Fig. 5: 0-3 piezo-composite processing

Fig. 5a) shows the initial phase of the process. The electrode is a stainless steel sieve, the size of the grid being 300 μm and the diameter of the steel wire 50 μm. It is put on the bottom of the mould and a Teflon made ring is posed on it. Afterwards, the system is put in the centrifuge, to realise a sample made of two layers, as described in Fig. 5d), on which we can measure capacity. Fig. 5c) shows some details of the polymerisation phase: the second electrode is fit on the ring, inside the concentrated layer. Afterwards we apply a weight of nearly 200 g. on it, to avoid dilatation of the steel parts.

Choice of the materials

Our investigation has been focused on a few types of piezo-electric ceramics, the most part being PZT and $BaTiO_3$ powders and on two types of thermosetting resins (Polyester and Epoxy Stycast 1365-65). The aim of using two resins is also that of highlighting the influence of its viscosity on the separation/concentration process accomplished by centrifugation, as can be seen from the following expressions for the speed of the particle v_t [6]:

$$v_t = \frac{\omega^2 \cdot R \cdot D_P^2 \cdot (\rho_P - \rho)}{18\mu} \tag{8}$$

in the case of settling of dilute mixtures during centrifugation and

$$v_t = \frac{\omega^2 \cdot R \cdot D_P^2 \cdot (\rho_P - \rho) \cdot (\varepsilon^2 \cdot \psi_P)}{18\mu} \tag{9}$$

in the case of hindered settling of concentrated mixtures, where $(\varepsilon^2 \cdot \psi_P)$ is a function of the volume fraction of the resin, always during centrifugation. D_P is the particle diameter, $\omega^2 \cdot R$ the acceleration of the centrifugal force, $\rho_P - \rho$ the difference between the densities of particles and of the resin, μ the dynamic viscosity of the resin. (8) and (9) are valid in the laminar flow region. With the lathe, only reaching 220 $\vec{g}$ as acceleration value, we couldn' t complete the separation of solids from polyester resin in thirty minutes: after this time polymerisation problems of polyester begin, leading to a considerable rise of viscosity. This renders the centrifugation useless from then on. Satisfactory results by using both resins, have been obtained with a centrifugal, reaching 2300 $\vec{g}$. Tests performed on mixtures containing the Epoxy Stycast 1365-65, revealed that this last one is more appropriate for purposes of solid/liquid separation. In fact it has a lower viscosity than Polyester and it polymerises with heat. So we had the chance of making the centrifuge work in continuous run during 2 hours or more, without augmentation of its viscosity. This allowed us to obtain a layer of clear, practically pure resin and another layer, whose content in solid inclusion is the maximum possible with a given initial volume fraction of ceramic powder. There is another reason why our choice has been oriented towards as soft resins as Stycast 1365. As already seen in Fig. 1, making the hypothesis that materials are parallel connected, the best results are achieved by using the softest resins. Also, we tested piezoelectric ceramic powders with different relative dielectric constants, going from 575 for PZT to 3300 for $BaTiO_3$.

Results and discussion

Eqns 4/7 explain the interest in measuring composite dielectric constants, before measuring piezoelectric coefficients. We verified that the best piezoelectric coefficients, i. e. the greatest dielectric constants of the composite, are obtained with piezoelectric powders having the lowest ε_r. Till now, the parameters we were able to change and vary were the powder volume fraction and the materials: in particular, this means to vary their properties, like the ratio of the dielectric constants and the Young modulus. This has been made by substitution of the components. It is the substitution of the resin that can impart the most important variation of rigidity to the composite, while it is the replacement of the ceramic powder that can impart a very important variation of the composite dielectric constant. This property is also very sensible to the content of piezo-electric powder. We verified the dielectric constant value of

the resins we used, to check the validity of our measures. What follows are our experimental results, preceded by the piezoelectric data of the components. We didn't use any polar resins.

Table 1: d_{33} coefficients of the component materials

Material	d_{33} (pC/N)
Stycast 1365-65	-
Polyester	-
PZT LS 43	175
PZT LS 39	230
PZT LS 47	433
PZT VS 129	300
BaTiO$_3$	520

Table 2: the relative dielectric constant $\bar{\varepsilon}_{r33}$ of the composite as a function of the piezoelectric ceramics and matrix permittivities, volume fraction and d_{33}.

Material	$\bar{\varepsilon}_{r33}$
Stycast 1365-65	4.01
Polyester	2
BaTiO$_3$	3300
PZT LS 47	2103
PZT VS 129	1700
PZT LS 39	636
PZT LS 43	575
BaTiO$_3$/Stycast. 40/60 vol %	6.80
PZT LS 47/Polyest. 33/67 vol %	15.19
PZT VS 129/Polyest. 29/71 vol %	14.87
PZT LS 39/Polyest. 31/69vol%	38.70
PZT LS 43/Polyest. 34/66vol%	69.27

The volume percentage of ceramic powder is that of the charged layer, after centrifugation. The initial homogeneous mixture has an amount of ceramic powder comprised between 10 and 20 %. To compare our measures, we referred to Table 3, where some results of permittivity available in literature [8] are shown, as functions of permittivities and of the volume fraction of the components, for electroactive 0-3 composites. ε' is the real component of the complex permittivity. The same order of magnitude for permittivities of composites is observed, when using components having a permittivity ratio of the same order of magnitude, with respect to Table 2.

Table 3: permittivity of Calcium-modified lead titanate (PTCa) 0-3 composites

Material	ε' (1KHz)
PTCa	209
Epikote 828	3.9
PTCa/Epikote 828 50/50vol%	17
PTCa/Epikote 828 55/45vol%	25
PTCa/Epikote 828 60/40vol%	36

It is clear, then, that the permittivities of the two materials must be as similar as possible, to attain good values for that of the composite. The results show a behaviour of the material being in agreement with some of those found in literature [4].

Some S.E.M. micrographs have been taken, to calculate the concentration of the compact layers, with the aid of software analysing them and to show the granulometric profile along the thickness:
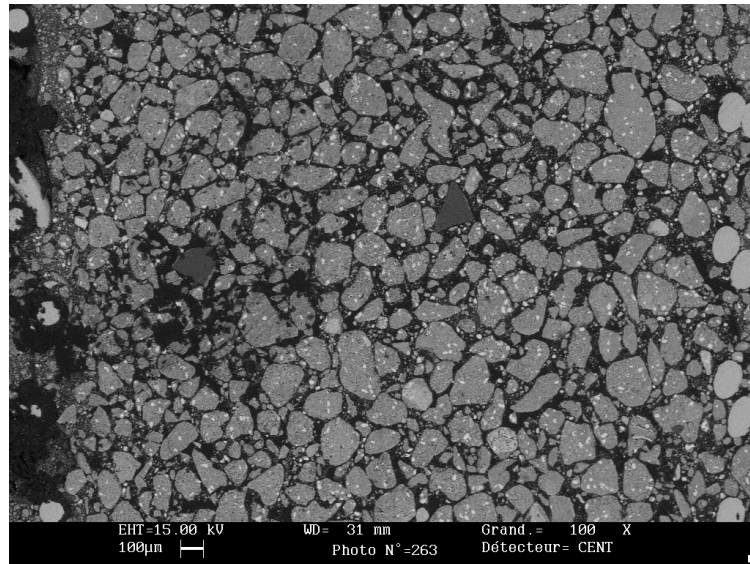

Fig.7: S.E.M micrograph of a 0-3 piezo-composite, BaTiO$_3$ -epoxy,
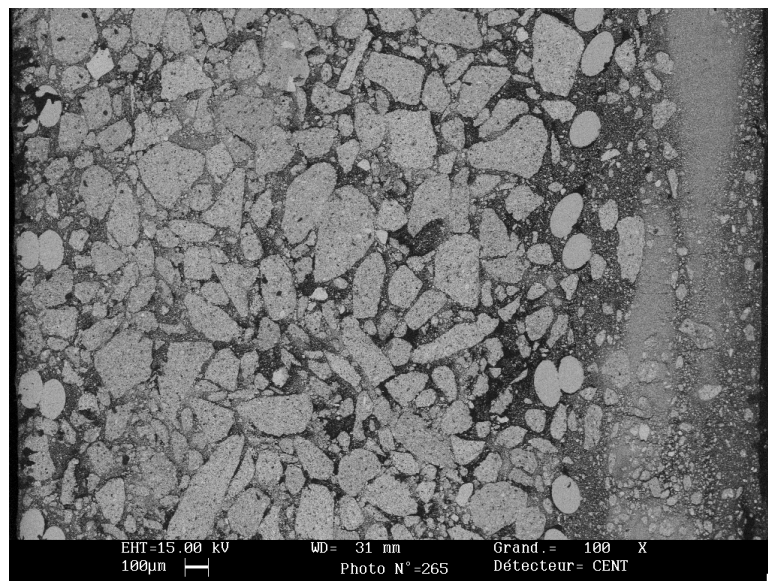after centrifugation (2 hours), layer between the electrodes

Fig.8: S.E.M micrograph of a 0-3 piezo-composite, PZT -epoxy,
after centrifugation (2 hours), layer between the electrodes

In the preceding images, the sections of the steel wires are clearly seen, where measures of capacity has been taken, after polishing the specimens. The steel sieves that we used as electrodes were perfectly inside the concentrated layer and parallel, so that measurements were performed in a correct manner, i.e. in absence of clear resin between the sieves.

Conclusions

We successfully applied a processing technique to 0-3 piezo-composites, based on the use of the centrifugal force, so that we didn' t need any vacuum degassing techniques to build our material. We obtained some experimental results, that we compared with those existing in literature, being numerical only in part, of these composites as functions of concentration in piezo-electric ceramics and of the ratio of dielectric constants of the component materials. The comparison showed that they are in agreement with literature [8], [4].
The connectivity theories for the calculation of the electro-mechanical properties of these composites don't take well into account the effects of the ratio of dielectric constants of the components on the piezo-electricity of the composite.

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