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Influence of carbon black on slurry compositions for tape cast porous piezoelectric ceramics

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Abstract

Functionally graded porous piezoceramics are of interest for ultrasonic applications as the gradual decrease of acoustical impedance improves the transfer of acoustic energy to water or biological tissues, assuring at the same time an high piezoelectric response. This ceramic architecture can be easily produced by tape casting as long as each step of the production process (slurry formulation, lamination and thermal treatments) is fully optimized. A thorough discussion on the process of slurry optimization is here reported. The Carbon Black (CB) was chosen as pore former agent and slurry formulations with CB concentration ranging between 3 and 43 vol% referred to the ceramic powder were optimized. Linear relationships between CB and solvent, binder and plasticizers amounts were found. The additional polymer (AP) required to optimize the slurry formulations was found to proportionally increase with CB amount. The abovementioned linear relationships were shown to allow an easy planning of the slurry composition to obtain defects-free green tapes for any CB concentration in the range considered.

Keywords: Suspensions; Tape casting; PZTN; Carbon black

1. Introduction

Lead Zirconate Titanate (PZT) is one of the most widely used material for ultrasonic transducer applications [1–3]. The addition of small amounts of Nb ion (<5 mol%) can improve PZT performances at the same time increasing its dielectric constant and decreasing its Curie temperature. The composition $Pb_{0.988}(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3$ was considered in this work. As a consequence of a lower acoustic impedance (Z) [6,7], the transfer of acoustical energy to water [4] or biological tissues [5] is additionally improved when the material is porous. A low Z value, in fact, reduces the mismatch between the device and the media through which the signal is transmitted or received, leading to a more efficient acoustic wave transfer [8]. On the other hand introducing porosity reduces the electromechanical coupling (k) and piezoelectric charge (d) coefficients in the thickness mode and therefore lowers the piezoelectric response in respect to the dense material.

A porous Functionally Graded Material (FGM) allows to match the requirement of an high response, typical of dense piezoceramic, to a good compatibility with the investigated media given by a porous material.

Tape casting is the most used technique for the production of multilayer functionally graded ceramics. Casting, lamination, debinding and sintering are necessary steps of the process and any variation in each of them can affect the final product.

For the production of engineered porous layers, tape casting is generally combined with the so-called sacrificial template technique. Organic or inorganic particulates (pore formers) are mixed into the ceramic slurry before casting and then eliminated during the thermal treatments leaving stable voids in the sintered ceramics [9]. Carbon black (CB) is one of the most used pore forming agents for its particle morphology and size [10–12]. The porosity gradient is formed *in situ* by sintering layer-stacked green tapes with stepwise-varied contents of CB. We have recently published the results of the lamination and the thermal treatments needed to produce porous functionally graded PZTN material [13], but the method followed to optimize the slurries' compositions was not considered there.

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In this work the systematic approach followed for the optimization of the tape-cast-slurry formulations with increasing CB concentration is therefore discussed.

2. Experimental

The procedure followed to prepare the porous graded material is reported in Fig. 1. PZTN powders [$Pb_{0.988}(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3$] with average particle size of 0.6 μm and specific surface area of 3.0 m^2/g (BET Flowsorb II 2300 Micromeritics) were produced using the mixed oxides route. Carbon Black (CB, N99, Thermax-Cancarb), with average particle size of 1 μm and specific surface area of 10.0 m^2/g, was used as sacrificial pore-forming agent.

The stability of the slurry without pore former was optimized considering different deflocculants [glycerine trioleate (GTO), 4-idroxy-benzoic acid (IBA), 4-aminobenzoic acid (ABA), furoic acid (FA), lauric acid (LA), polyvinylpyrrolidone (PVP)] following the procedure reported by Galassi et al. [14]. The sedimentation tests were performed with 1.0 vol% suspensions of the powder in the azeotropic mixture of ethyl alcohol and methyl ethyl ketone. The concentration of each deflocculant was fixed at 1.3 wt% respect to the powder as reported for a similar system [14].

The formulations with different CB content (from 0 to 43 vol% with respect to the PZTN powders) were prepared by adding to the ceramic powders the desired amounts of solvent (azeotropic mixture of ethyl alcohol and methyl ethyl ketone, Sigma-Aldrich), deflocculant, binder (Butvar B98, Monsanto Co. St Louis, MO, USA) and plasticizers (PEG 400, Fluka, and Santicizer 160 Monsanto Co. St Louis, MO, USA). The ball milled suspension was deaerated under vacum and cast on a moving Mylar carrier (v = 6 mm/s) resulting, after solvent evaporation, in green tapes of about 100 μm thick.

3. Results and discussion

3.1. SEM analyses

The SEM micrographs of the starting PZTN and CB powders are shown in Fig. 2. PZTN powder is formed by micrometric rounded agglomerates with primary particles size of about 0.25 μm. On the other hand, the porous agglomerates of micrometric CB particles are easily broken down during the ball milling process, leading to powders with a broad particle size distribution [12].

3.2. Sedimentation tests

The sedimentation tests (Fig. 3a) indicate that only the three electrostatic deflocculants (FA, PVP and ABA) were effective in dispersing the suspensions, while the others produced a quasi-instantaneous sedimentation of the PZTN powder. The suspension stability in the azeotropic mixture (dielectric constant value of 20-25) induced by electrostatic deflocculants could then be ascribed to an electrostatic mechanism. However not all the electrostatic deflocculants have the same performances. The best dispersing effectiveness is reached by the heterocyclic compounds and/or by the deflocculants with a marked Bronsted-Lewis basic behavior (i.e. ABA). This action could be linked to the acid nature of the PZTN surface that interacts preferentially with basic sites [15].

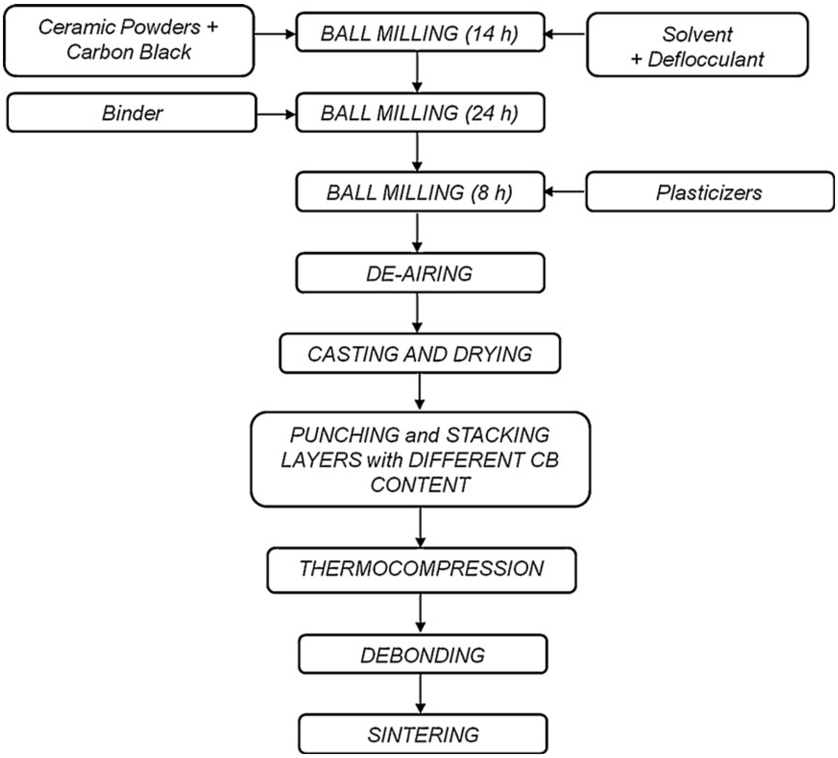

Fig. 1. Flow chart of the manufacturing process to produce porosity graded material.

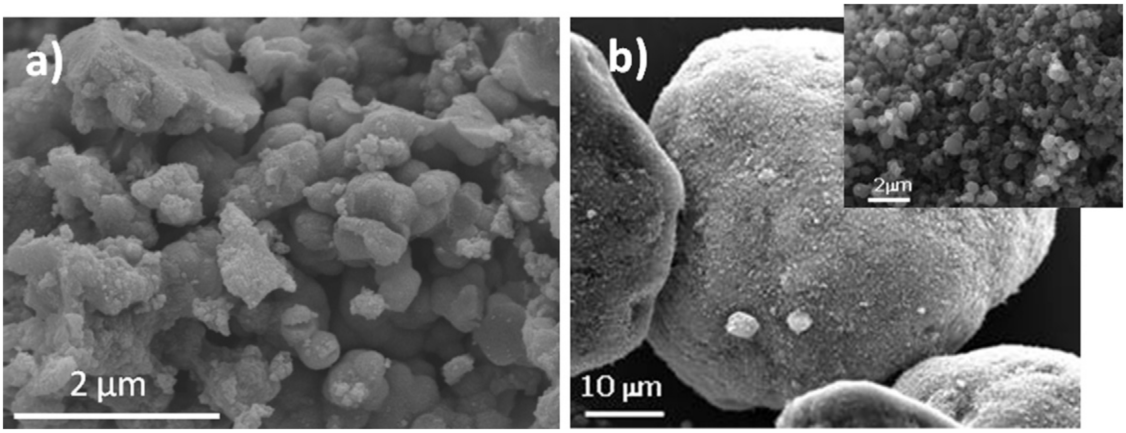

Fig. 2. SEM micrographs of the starting powders: (a) PZTN, (b) CB.

Tape casting tests using FA and ABA as deflocculants leaded however green tapes with defects like phase separation and cracks. These results could be explained considering that the main component in a slurry formulation (excluding the ceramic powder) is the binder. This compound is not generally added in the sedimentation tests to avoid competitive adsorption phenomena [16] that could shadow the real dispersion capability of the deflocculant. The binder used in this study is the polyvinyl butyral (or PVB). This polymer is formed by tailored proportion of hydroxyl, acetate and acetal groups, randomly distributed along the molecule. The alcoholic parts are the mostly responsible for the polymeric reticulation: the higher is the number of reticulation sites, the stronger would be the polymeric network formed (i.e. increasing of the binder glass transition temperature) [17]. In suspension, PVB could react with the active carboxylic groups of FA or ABA forming hydrogen bonds as schematized in Fig. 4. These two deflocculants efficiently functionalize the powder surface through Bronsted-Lewis acid-basic interactions, but they deactivate at the same time the hydroxyl groups of PVB hindering as a consequence the formation of a well reticulated polymeric network. For this reason the PVB is partially unable to create a suitable cross-linked powder-polymer network, leading to cracked green tapes.

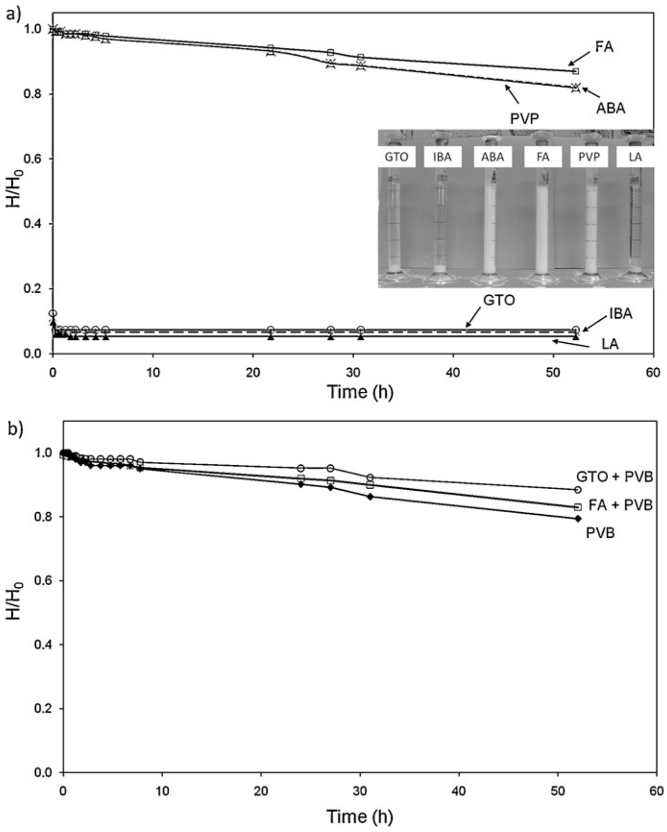

Fig. 3. Plots of the ratio between sediment height (H) and the suspension height at t = 0 (H_0) versus time for (a) deflocculants and (b) binder tested. In the insert a picture of the sedimentation cylinders after 52 h is shown.

To avoid these deflocculant-binder interactions, new sedimentation and casting tests were performed using PVB either as dispersing agent and binder. If on one hand PVB-sedimentation curve (Fig. 3b) confirms its good dispersing capability, on the other hand casting tests result in cracked and stiff green tapes. This result was attributed to a not well optimized dispersing stage of the powder-PVB system that is known to be crucial to obtain suitable green tapes. Previous works [14,18] indicated GTO as the most suitable deflocculant for organic suspensions of similar systems. The data presented in the mentioned literature, apparently in contrast to the results reported in Fig. 3a, are probably a consequence of a synergic interaction between GTO (pure steric deflocculant) and PVB. To verify these hypotheses, sedimentation tests were performed using a combination of GTO and PVB (GTO/PVB equal to 40:60 wt%) as deflocculant and the results compared using the FA-PVB combination. The sedimentation curves (Fig. 3b) confirm that the GTO-PVB combination is the most effective in dispersing the PZTN suspension, whereas preliminary casting tests leaded to uniform crack-free green tapes. The dispersing mechanism and the nature of PZTN-GTO-PVB interaction established in the suspension will be object of further analyses. As a consequence of these results the GTO-PVB combination was used as deflocculant in the PZTN slurries with or without pore former.

3.3. Relationships between organic and CB content

The introduction of CB in the tape casting suspension must be counterbalanced by an increase of the organic content

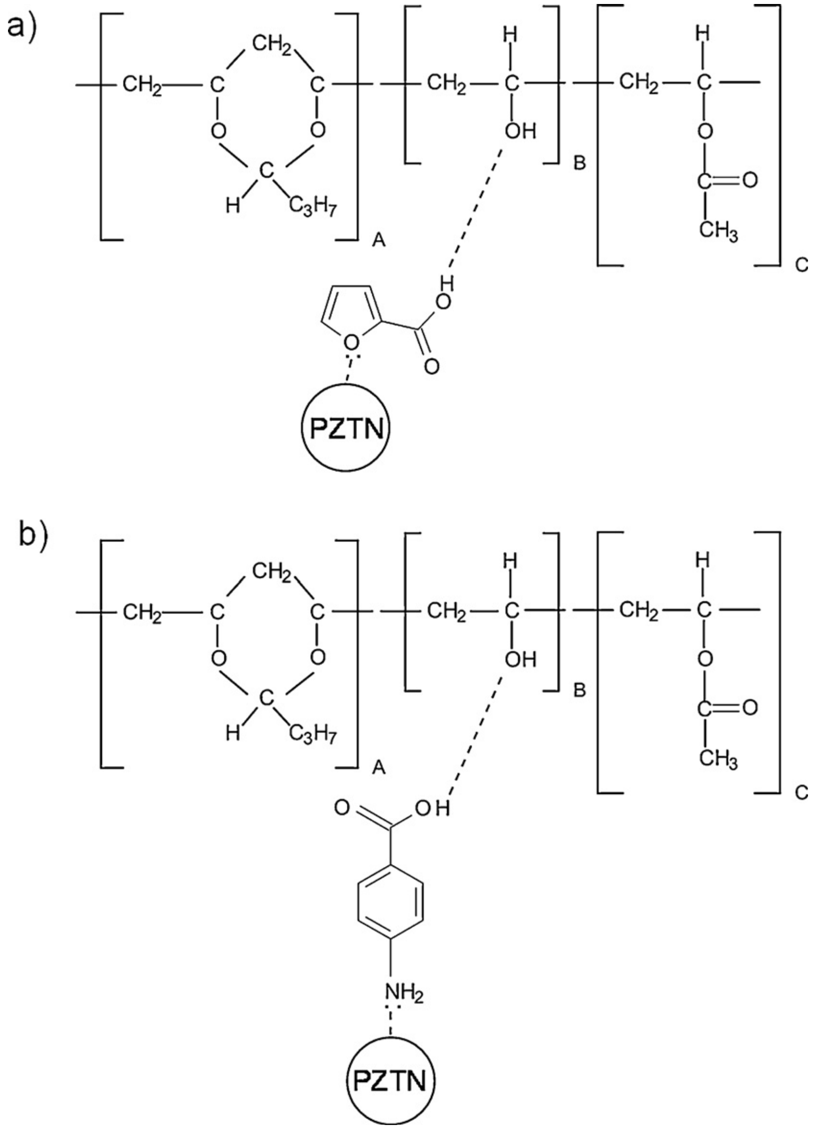

Fig. 4. Visualization of the possible interactions between (a) PVB-FA and (b) PVB-ABA.

(deflocculant, binder, plasticizers) in order to obtain defect-free green tapes [12]. The slurry formulation previously optimized without pore former was therefore modified changing the content of solvent and organic components. The CB amount was fixed respectively at 3 vol% and 43 vol% respect to ceramic powder for the tapes with the lower and highest porosity, following the indications of Piazza et al. [19] that show these pore former concentrations as the more appropriate to obtain an efficient FGM for ultrasonic applications.

The volume concentration of each organic compound in these two optimized slurries and in the one without CB, was plotted as a function of the CB content, resulting in linear relationships as reported in Fig. 5. These equations can be expressed as:

$$V_d = a_d \ V_{CB} + q_d = -0.18 \ V_{CB} + 5.2 \tag{1}$$

$$V_b = a_b \ V_{CB} + q_b = 0.05 \ V_{CB} + 37.2 \tag{2}$$

$$V_p = a_p \ V_{CB} + q_p = 0.71 \ V_{CB} + 12.0 \tag{3}$$

where V_d, V_b, V_p are the volumes of deflocculant, binder and plasticizers respectively and V_{CB} is the volume of carbon black in the green tapes. The linear equations reported in Fig. 5 led to formulate five more slurries with different CB concentration

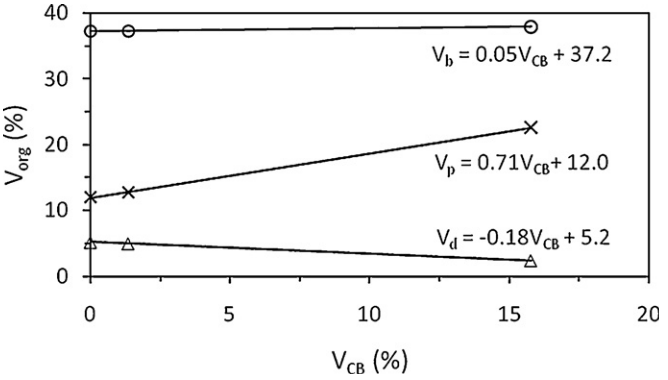

Fig. 5. Linear equations between deflocculant (V_d), binder (V_b) and plasticizers (V_p) volume and CB volume (V_{CB}).

Table 1
Composition of the green tapes at different CB concentrations.

Tape	PZTN (vol%)	Defloc. (vol%)	Binder (vol%)	Plast. (vol%)	CB (vol%)
0*	45.7	5.1	37.2	12.0	0.0
3*	43.7	4.9	37.2	12.8	1.4
9*	39.5	4.5	37.4	14.7	3.9
15*	35.7	4.0	37.5	16.5	6.3
20*	32.7	3.7	37.5	17.9	8.2
26*	29.3	3.3	37.6	19.5	10.3
33*	25.3	2.9	37.8	21.5	12.6
43*	21.3	2.4	37.9	22.6	15.8

* CB volume concentration referred to PZTN powder.

able to give crack-free green tapes (Table 1). The additional solvent amount, essentially needed to dissolve the PVB, was increased proportionally with the increasing of the binder concentration.

The value of angular coefficient of the straight lines corresponding to equations 1, 2 and 3 suggests that the CB addition does not equally influence the additional organic amount needed to optimize the slurries formulations. Although as expected the binder has to be increased when CB is introduced into the slurries, it is the concentration of plasticizers the most affected by the pore former content. Because the plasticizers are introduced to impart flexibility, workability, or distensibility to the binder [20], even a small increase in its concentration requires an adequate content of plasticizers to obtain a strong and flexibile green tape. On the contrary, slurries with higher concentrations of CB require less amount of dispersant. This compound is used to effectively disperse the ceramic powder. Sedimentation tests however showed that CB does not need a deflocculant agent for its dispersion, due to its surface chemistry and low density. Therefore the same amount of inorganic part of the slurry (PZTN + CB) needs less dispersant when the CB concentration increases (negative slope of the corresponding equation).

The additional amount of organics needed to adapt a slurry formulation to the addition of a pore former is indicated by Corbin et al. [9] as the "additional polymer ratio" (AP). The AP value can be calculated by the following equation:

$$AP = \frac{[VP - VC \cdot (VP_0/VC_0)]}{VT} \tag{4}$$

where *VP* and *VC* are respectively the volume of polymer (deflocculant + binder + plasticizers) and ceramic powder in each CB/PZTN formulation, VP_0 and VC_0 are respectively the volume of polymer and ceramic powder in the optimized PZTN tape without CB, and *VT* is the total green volume. Using the equation 1, 2 and 3, VP can be expressed as a function of V_{CB}:

$$VP = V_{CB}(a_d + a_b + a_p) + (q_d + q_b + q_p) \tag{5}$$

On the other hand

$$VC = VT - (VP + V_{CB}) \tag{6}$$

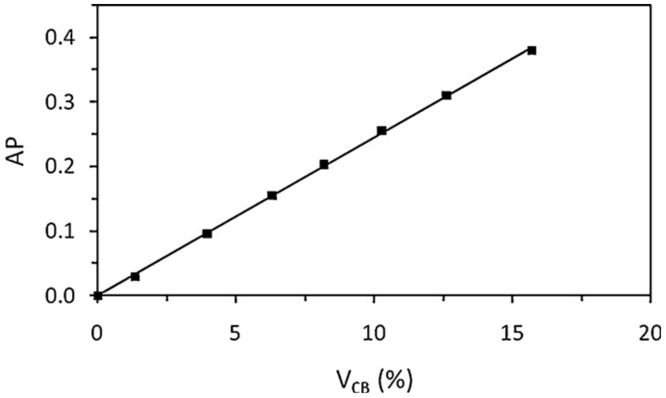

Fig. 6. Additional polymer ratio (AP) needed for different CB content.

Considering that VP_0/VC_0 is equal to 54.3/45.7 and VT = 100, the equation 4 for the different CB concentration leads to the following linear relationship between AP and V_{CB}

$$AP = 0.025\, V_{CB} \tag{7}$$

These results not only confirmed that an additional polymer must be added when CB is introduced in a tape casting slurry, but also pointed out the linear dependence existing between AP and V_{CB} (Fig. 6).

3.4. Relationship between the organic content and the specific surface area

The organic additives introduced in a ceramic slurry strongly interact with the powder surface [16], therefore AP can be related to the total Specific Surface Area (SSA_t) associated to the inorganic powders of each green tape. The SSA_t values include both the SSA of ceramic and of CB powders according to the following equation:

$$SSA_t = \frac{Wt\%_{PZTN} \cdot SSA_{PZTN} + Wt\%_{CB} \cdot SSA_{CB}}{Wt\%_{PZTN} + Wt\%_{CB}} \tag{8}$$

where $Wt\%_{PZTN}$ and $Wt\%_{CB}$ are respectively the PZTN and CB weight percent in the green tape, whereas SSA_{PZTN} and SSA_{CB} are the specific surface area of PZTN (3.0 m^2/g) and CB (10 m^2/g). When an inorganic pore former with higher SSA substitutes the ceramic powders, an increase of the SSA_t is expected. The % variation of the total specific surface area (ΔSSA_t) induced can be calculated using the equation 9:

$$\Delta SSA_t = \frac{SSA_t - SSA_{PZTN}}{SSA_{PZTN}} \cdot 100 \tag{9}$$

The relationship between ΔSSA_t and AP is shown in Fig. 7. To an increase of ΔSSA_t corresponds a quasi-proportional increase of AP. The small deviation from the linearity is thought to be due to a non-proportionality between ΔSSA_t and one or more organic additives considered in the AP value. To better understand this behaviour, ΔSSA_t was related to the green-volume percent variation (ΔV_{org}) of each organic compound present (deflocculant, binder, plasticizers). In particular ΔV_{org}

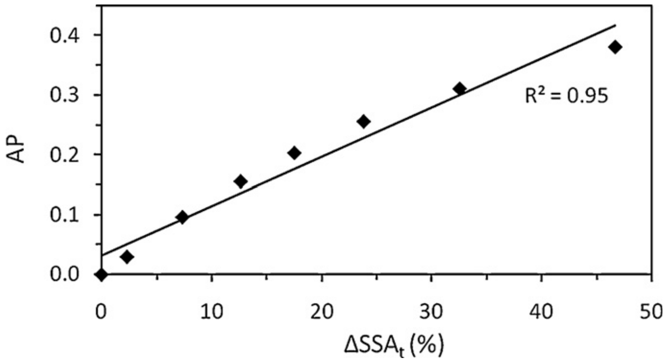

Fig. 7. Additional polymer ratio as a function of the total specific surface area variation.

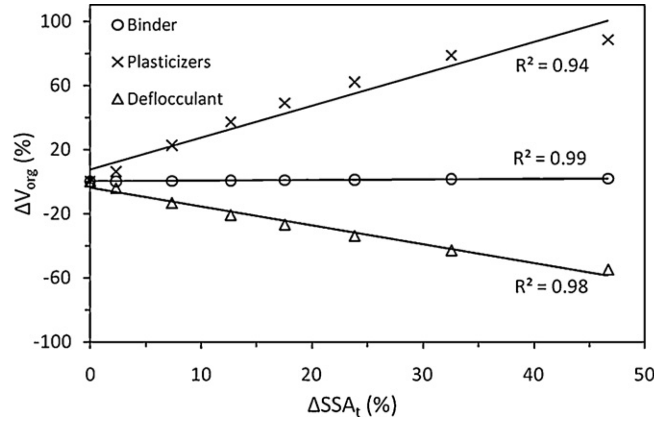

Fig. 8. Relationship between ΔSSA_t and the organic volume variation (ΔV_{org}) of plasticizers, binder and deflocculant.

for each green tape was calculated using the equation 10:

$$\Delta V_{org} = \frac{V_{org} - V_{org \leftrightarrows \leftrightarrows 0\%CB}}{V_{org0\%CE}} \cdot 100 \tag{10}$$

where V_{org} and $V_{org\ 0\%CB}$ are the volume of deflocculant, binder or plasticizers respectively in the green tapes with and without CB. Fig. 8 shows the relationship between ΔSSA_t and ΔV_{org}. While the volume variations of binder and deflocculant are directly proportional to ΔSSA_t, the volume variations of plasticizers shows a non-linear relationship. This could be explained considering that the deflocculant and the binder act on the powders surface whereas the plasticizers work on or around the binder polymer chains allowing their motion inside the tape matrix. Because the PVB chains are quite long (PM average 40-70000), even a small variation in the binder content needs a significant increase in plasticizers. The relation found between the volume variation of the latter reflects the trend of AP versus ΔSSA_t (Fig. 7). This shows that the trend of AP versus CB is mainly determined by the one of the plasticizers and confirms that the plasticizers are the most influenced by CB addition.

4. Conclusions

This work was focused on the optimization and rationalization of slurry formulations to produce a functionally graded porous piezoelectric ceramic.

This study showed that the stability of the suspensions required to produce homogeneous crack-free PZTN green tapes is dependent on the combined interaction of a steric deflocculant (GTO) with part of the binder.

It was demonstrated that increasing the CB concentration in the slurries, the additional polymer increased proportionally. Moreover, the organic additives are influenced in a different extent by CB addition. The additional polymer could be also associated to an increase of the total specific surface area of the inorganic powders (CB + PZTN), caused by the introduction of a pore former with high specific surface area.

The relationships found between the components of the tape casting slurry make easy to plan the formulations needed to obtain defects-free green tapes suitable for the subsequent processes with whatever CB amount in the range considered.

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