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EFFECT OF PARTICLE SIZE IN THE COMPRESSIBILITY AND DENSITY OF PZT POWDER

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Abstract. *PZT is one of the most used piezoelectric materials in many applications because of its great electric proprieties. The manufacturing process of PZT should produce pieces with high density, small grains, and stable chemical composition. However, to achieve such quality, it is necessary to obtain optimal sintering conditions, minimizing lead loss and excessive grain growth. One possible solution is to increase powder reactivity by reducing particle size through milling. The purpose of this paper is to evaluate a possible drawback of the solution: the worst compressibility of thinner powder. PZT powder was mixed with PVB and milled in two different conditions (ball milling and vibratory milling). The compressibility of the two batches was evaluated through mechanical testing. The chemical composition of the batches was compared with the original powder to verify if there was any contamination in the milling process. The batch which was processed through vibratory milling presented a smaller average particle size. However, its packing was compromised by the narrower distribution of particle size. Therefore, although this batch would probably be sintered at lower temperatures, reducing problems of lead loss, it has lower green density, thus, more porosity. The chemical composition was not significantly changed by milling.*

Keywords: *Ceramic manufacturing, Vibratory milling, Ball milling, Lead titanate – lead zirconate.*

1. INTRODUCTION

Piezoelectric components have many applications such as precision actuators, microphones, hydrophones, high-voltage generators, energy harvesting systems, accelerometers, sonar, and ultrasound imaging (Richerson, 2005). Among many piezoelectric polycrystalline materials, lead zirconate-lead titanate (PZT) is one of the most commonly used, mainly because of its excellent piezoelectric properties, high Curie point and a wide range of properties achieved by small changes in composition (Li et al., 2012). PZT pieces can be produced in a variety of shapes, from simple disks and cylinders to more complex shapes with multiple features (Moulson and Herbert, 2003; Sherman and Butler, 2016). A PZT piece should have high density (ideally no porosity), small grains, and homogenous chemical composition (Moulson and Herbert, 2003). PZT can be produced through the same manufacturing routes as other ceramic powder materials. It should be pressed, followed by sintering, and sometimes also machined before or after sintering (Moulson and Herbert, 2003; Richerson, 2005). However, some major issues of manufacturing should be addressed in order to produce functional PZT pieces with complex shapes.

First of all, green pieces (pieces that have not been thermally treated) should have enough strength to withstand handling and green machining (Richerson, 2005). Parts made of PZT powder alone do not meet this requirement. For increased mechanical strength, mixing a binder with the powder is necessary. Binders are usually polymer molecules or other types of organic matter that are adsorbed and bridge between ceramic particles providing a binding action (Reed, 1995; Richerson, 2005). The proper amount of binder improves mechanical strength in the green piece. During sintering, these additives are removed in the organic burnout-stage (Richerson, 2005).

Second, the green piece should have a high and homogenous green density and the correct dimensions. If the green density is low or if the piece has large pores, sintering might not completely remove all porosity, compromising the mechanical and piezoelectric properties of the piece (Reed, 1995). Also, density variation throughout the piece should be small. Density gradients higher than 1%/mm might introduce cracks on the material during sintering (Zipse, 1997). The shape and friction of the mold have an essential role in the density homogeneity of the pressed part (Richerson, 2005). Furthermore, it is necessary to design a mold that produces a green piece within the correct green dimensions. During sintering, the piece will shrink. Therefore it is necessary to offset the green dimensions from the final dimensions. Designing the mold based on trial-and-error consumes much time and money. Simulation technics are a useful solution to predict the dimensions and density distribution of a pressed piece, achieving a better mold design in a

shorter time (Morais et al., 2016). To be able to simulate the powder mechanical behavior during compression, it is necessary to select an appropriate material model and calibrate it through mechanical tests (Morais et al., 2016). In the case powders, one of the key parameters of a constitutive model is the hardening law, that relates the applied pressure with the density or inelastic volumetric strain (Han et al., 2008; Melo et al., 2018).

Finally, sintering should produce a PZT piece with refined and homogenous grains and low porosity while maintaining its chemical stoichiometry. One major concern during sintering is caused by the volatility of the lead present in the PZT (Moulson and Herbert, 2003). When sintering at low temperatures (or short time), the sintering process occurs incompletely, not removing all porosity, resulting in a piece with low density (Reed, 1995). On the other hand, sintering at high temperatures (or a long time) can result in excessive lead loss and undesired grain growth. One possible solution to enhance densification and reduce lead loss is enhancing powder reactivity through reducing particle size (Maiwa et al, 2005). The main driving force of sintering mechanisms is the reduction of the total free energy associated with the surface of the particles. Hence, a powder with more surface area is more active and easier to densify (Reed, 1995; Richerson, 2005). Therefore, particle size plays a key role during sintering. The smaller the particle, the higher the sintering rate. A finer-particle-size powder can be sintered more rapidly at a lower temperature than a coarser powder (Richerson, 2005). Milling can produce a very active powder that is easier to densify. It has been reported that the temperature of sintering of PZT can be effectively reduced by reducing particle size through grinding. (Maiwa et al., 2005; Ochiai et al., 2008; Xiao et al., 2018). However, the particle size distribution is also critical. Particles that are all of one size are difficult to pack efficiently and generate compacts with high porosity. Such compacts will undergo a high percentage of shrinkage and yet will retain significant porosity. (Richerson, 2005) On the contrary, a broader distribution with smaller particles distributed in the interstices of packed larger particles will reduce the porosity and pore size. (Reed, 1995). Figure 1 compares a narrow particle distribution with and a large one.

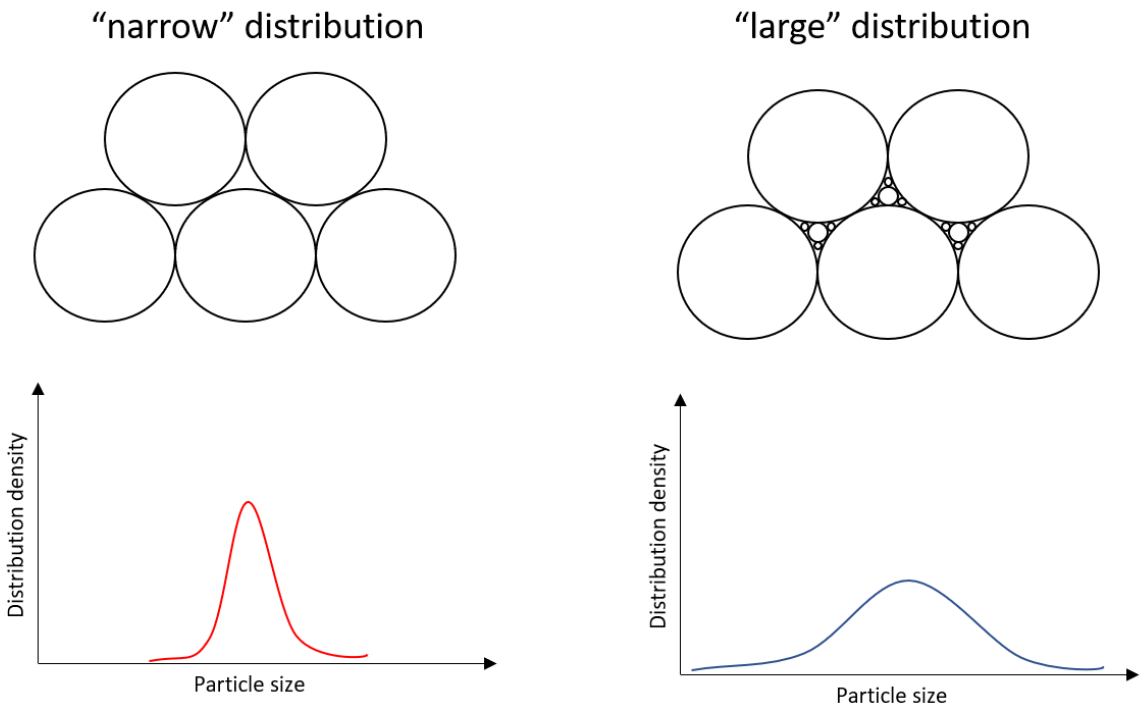


Figure 1. Effect of standard deviation of particle size in packing and porosity.

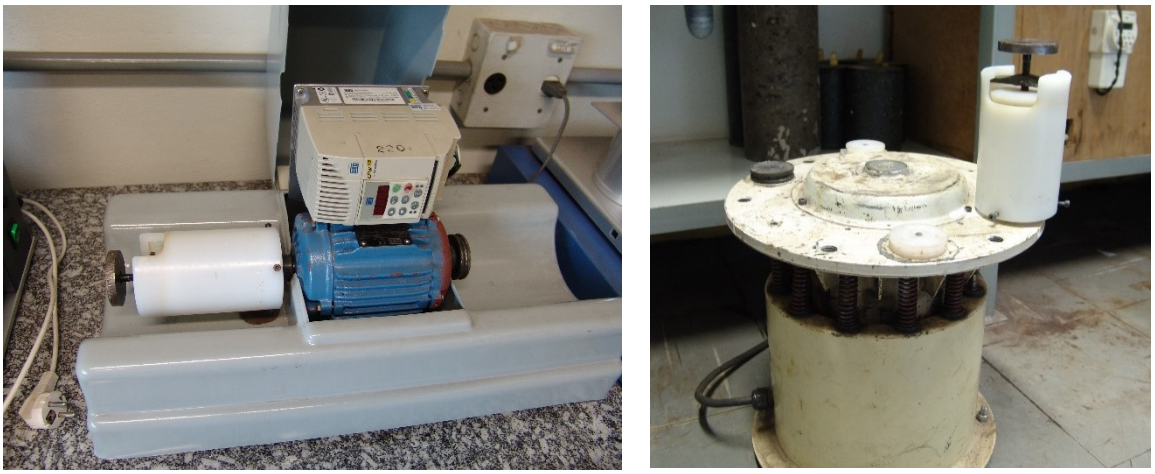
The purpose of this paper is to evaluate the effect of reducing particle size in the compressibility behavior of a PZT powder. The results should guide the decision of optimal particle size that will combine good compressibility and high reactivity, resulting in a high-quality PZT sintered part. Also, the compressibility tests are suited for finite element model calibration, allowing better design of the mold and, consequently, enhancing the part final quality.

2. MATERIALS AND METHODS

The methodology can be summarized in four points: 2.1 - Two powder batches were prepared with different particle size distribution; 2.2 – The particle size distribution of the powder batches were measured; 2.3 – The compressibility of the powder batches were evaluated and compared; 2.4 - The chemical composition was also compared to identify eventual contaminations caused by the milling process.

2.1 Powder preparation

The PZT powder type I (Sparkler Ceramics Pvt. Ltd. grade: SP-4) was initially received without binder or any other additives. Two batches (A and B) were prepared with the same formulation: 160g of PZT powder; 80 ml of isopropyl alcohol (1:4 in volume PZT/volume alcohol); 0.64g (0.4%wt) of ethylene glycol as lubricant and 0.08g (0.05%wt) of poly (vinyl butyral) (PVB) as dispersant. The slurries were mixed in a ball mill (Fig. 2A) with zirconia balls (diameter 10 mm) for 24 hours at 140 rpm. For Batch A, 1.2g (0.75%wt) of PVB was added as a binder and mixed for more 2 hours in the ball mill. Batch B was placed in a vibratory mill (Fig. 2B) for 96h before adding the binder. Then, using a hot air blower, the alcoholic solvent of both batches was evaporated. The remaining powder agglomerates were granulated using a mortar and pestle and screened in a standard 80-mesh (137 μm). Finally, the batches were dried at 80ºC for 2 hours to remove any remaining liquid.



A) B)

Figure 2. A) Picture of the ball mill. B) Picture of the vibratory mill.

2.2 Particle size measurement

The effect of the vibratory milling on the particle size was evaluated through three samples: Sample 0h (after 24h of ball milling – Batch A); Sample 48h (after 48h of vibratory milling); and Sample 96h (after 96h of vibratory milling – Batch B). Figure 3 summarizes the process used to obtain the samples and the batches A and B. The particle size of the samples was analyzed at a SediGraph III Plus. The measurement principle selected was X-Ray monitored gravity sedimentation and the calculation method used was the Stokes sedimentation and Beer's law of extinction. All analyses were conducted at 35ºC.

2.3 Hardening test and density evaluation

The hardening test is necessary to calibrate constitutive models such as the modified Drucker-Prager/cap used in finite element software (Melo et al., 2018; Morais et al., 2016). The hardening curve relates the applied hydrostatic pressure with the correspondent density (or with the volumetric plastic strain). The compression behavior is related to the size distribution, shape, and elastic/plastic behavior of the particles (Reed, 1995; Richerson, 2005). To obtain the curve, first, the powder was uniaxially pressed at 10 MPa in a cylindrical die with 41 mm of internal diameter. The initial height of the powder filled in the die was 13 mm. Then, the mass of the pressed disc was measured in a conventional balance. The disc was placed inside an elastomeric evacuated sealed bag and isostatically pressed at the following pressures stages: 20, 40, 60, 80, 120, 160 and 200 MPa. After each stage, the sample was depressurized, had its dimensions measured, and its volume calculated before proceeding to the next stage. The density at each stage was calculated considering the disc mass after the uniaxial pressing.

Another condition was also tested to compare the compression behavior of the processed powders. Twenty-four discs (12 of each batch) were pressed uniaxially at 40 MPa inside an 8 mm inner diameter die, followed by isostatic pressing at 200 MPa. The dimensions and mass of each disk were measured, and their densities were calculated.

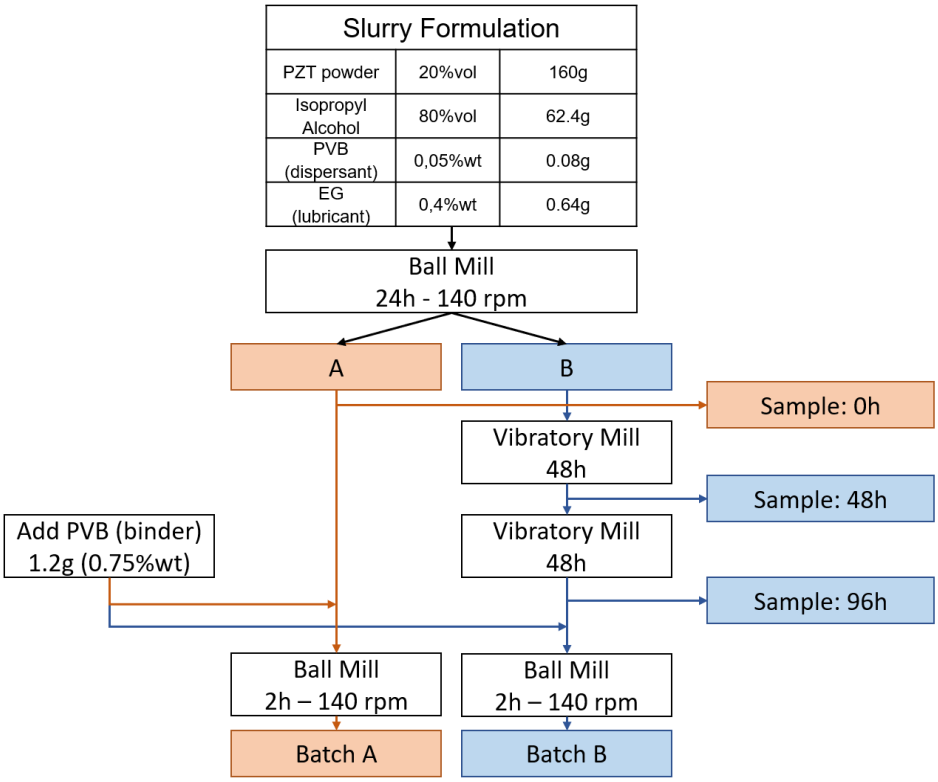


Figure 3. The process used to obtain batches A and B and the samples 0h, 48h, and 96h.

2.4 X-Ray spectrometry

The powder preparation process should not change the chemical composition of the original powder significantly. Otherwise, the piezoelectric and mechanical proprieties of the final product would be changed. In order to evaluate if the grinding process changed the composition of the powders, one sample of the original powder and one sample of each batch powder was analyzed in an Energy Dispersive X-Ray Spectrometer (Shimadzu EDX-720). The 10 mm collimator was used in a vacuum atmosphere to analyze all material spectrum lines.

3. RESULTS AND DISCUSSION

The powder preparation processing produced 149.4g of batch A and 153.1g of batch B. The batches presented distinct visual differences. Batch B showed lighter color and finer texture than batch A and the original powder without binder. The original powder presented some agglomerates and worse flowability than the processed powders. The differences between the batches and the original powder can be observed in Fig. 4.

Figure 4. Visual difference between powder as received and batches A and B.

3.1 Particle size distribution

Figure 4 presents the cumulative mass distribution of the particle diameter of the powder processed only through ball milling (Sample 0h – batch A); 48h of vibratory milling and 96h of vibratory milling (batch B). The histogram for the particle size distribution can be observed in Fig. 5.

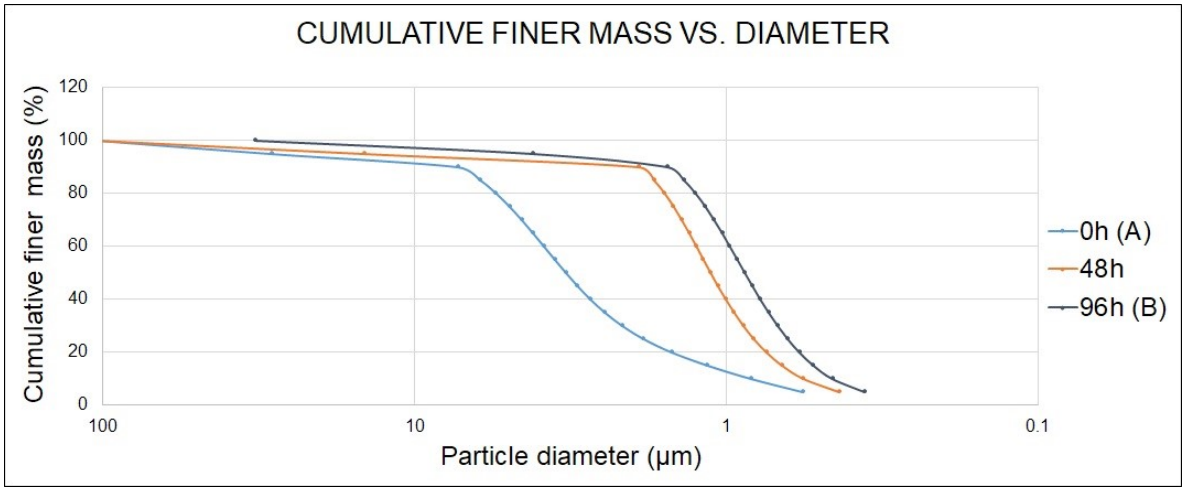


Figure 4. Cumulative finer mass percentage of particle diameter.

It can be observed that vibration milling reduced the particle size considerably, increasing the percentage of submicron particles. Also, the shape of the distribution changed. The Sample 0h presented a wider distribution of particles sizes, while the samples 48h e 96h had a narrower distribution. Therefore, vibration milling reduced not only the average particle size but also size dispersion. This result agreed with the literature (Reed, 1995).

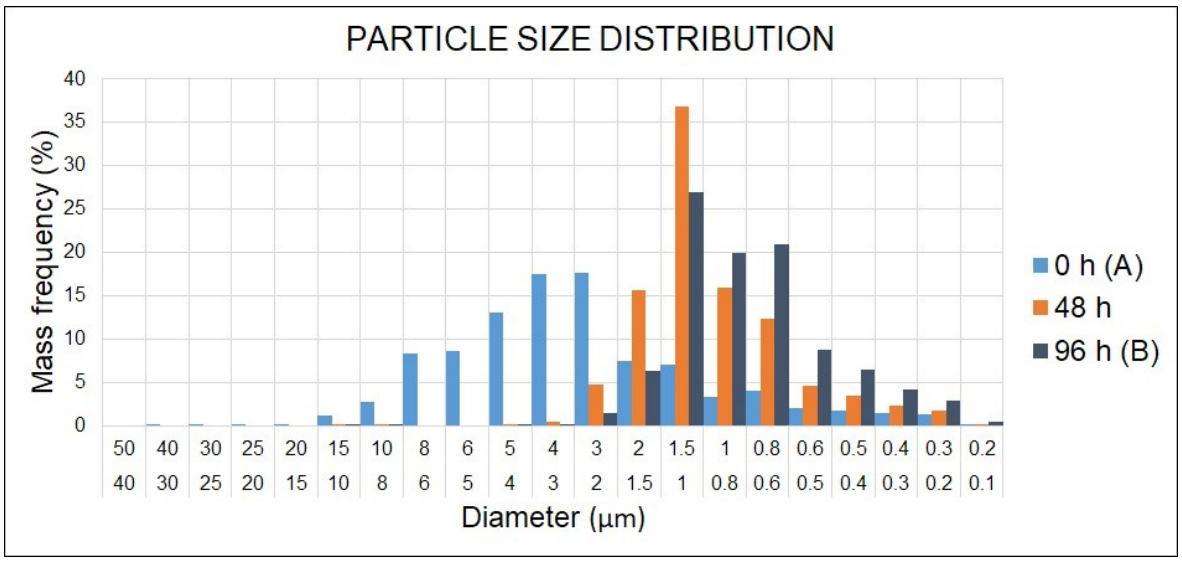


Figure 5. Particle size distribution.

3.2 Hardening curve and density results

The hardening curve of a sample of batch A and batch B is presented in Fig 6. It was observed that the density-pressure relation could be approximately described with a logarithmic fit. Hence, the density of the compact does not increase in the same proportion as the pressure. Furthermore, the batch A sample achieved 5.2 g/cm^3, which corresponds to 65% of theoretical material density (8 g/cm^3), a high value for green ceramic compacts. Increasing the pressure would require more resistant equipment that would probably not result in a significantly higher density. It should be highlighted that the binder was enough to keep the shape of the samples and had enough mechanical strength to withstand handling and measurement.

The density of the pressed disks is presented on Tab. 1. The disks from batch B presented an average density 5% lower than batch A samples. This result was also observed in the hardening curve. It can be explained by the particle size distribution of both batches. The particle size dispersion is related to the packing arrangement. As previously explained, a wider distribution is expected to have better packing because the small particles may fit in the interstices of larger particles (Reed, 1995).

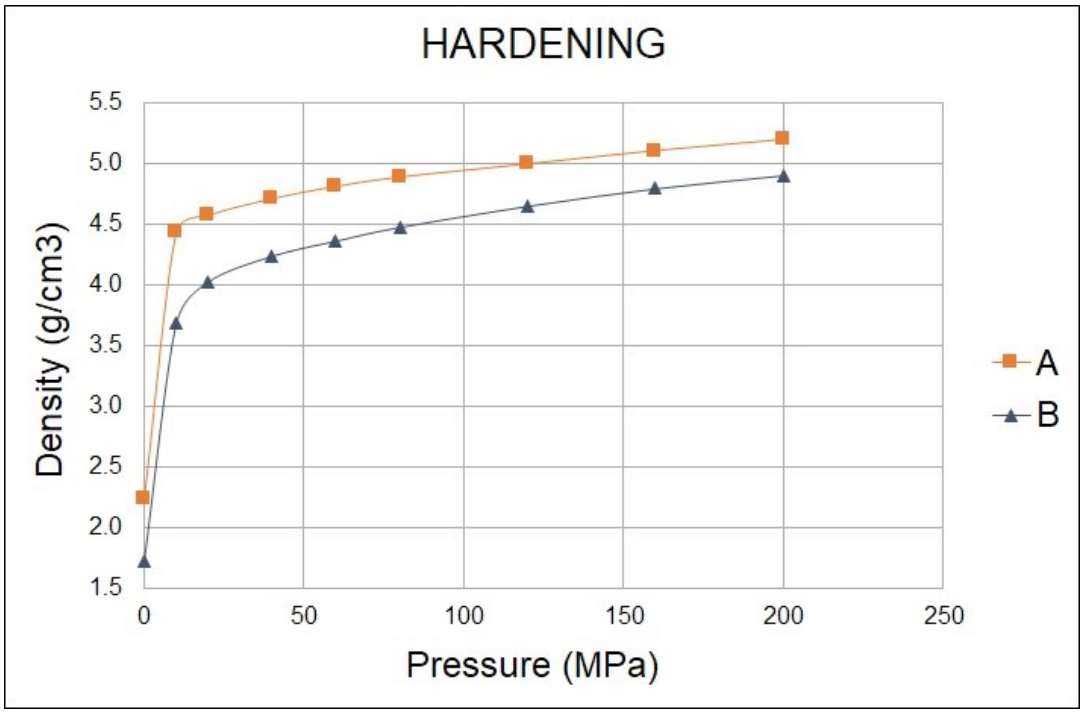


Figure 6. Hardening curve of batches A and B pressed isostatically.

Table 1. Density of disks of batch A and B isostatically pressed at 200 MPa.
Average results of 12 specimens for each batch.

Batch	Density (g/cm^3)	Standard Deviation (g/cm^3)
A	5.14	0.06
B	4.84	0.07

3.3 Chemical composition

The chemical analysis (presented on Tab. 2) revealed that the grinding process had not changed the chemical composition of the powder significantly, especially the Lead/Zirconium relation. Hence, regarding chemical composition, the processing route selected should not cause problems in the final product.

Table 2. X-Ray spectrometer results for mass percent of the principal constituent elements. Elements with mass percentage lower than 1% were omitted.

Element	Original Powder (%)	Batch A (%)	Batch B (%)
Pb	43.324	40.569	41.306
Zr	27.743	25.553	25.599
P	9.544	11.688	12.102
Ti	8.990	9.221	9.022
Cl	3.454	3.653	3.768
Si	2.770	4.815	3.631
Sr	3.011	2.814	2.829
Pb/Zr	**1.56**	**1.59**	**1.61**

4. CONCLUSIONS

The grinding process of the PZT powder significantly changed the particles average size and distribution, without considerably influencing the chemical composition. Batch B, which was processed through vibratory milling, presented smaller average particle size and low particle distribution. Although the superficial area and reactivity of the batch B were increased, the packing was compromised by the more uniform size of the particles. Hence, batch B has the advantage of better reactivity and probably can be sintered at lower temperatures, reducing problems of lead loss. However, batch A has the advantage of higher green density than batch B, with less porosity. In future works, samples of both batches should be sintered to evaluate which process condition will result in a sintered product with higher density, small grains, and fewer chemical alterations.

Furthermore, the hardening curves obtained can be used to calibrate a finite element model of the powder. This model will allow designing molds of complex shapes with better prediction of density distribution and shape.

5. ACKNOWLEDGMENTS

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