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Gelation of water-based PZT slurries in the presence of ammonium polyacrylate using agarose

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Abstract

Gel casting is a suitable near net shape-forming technique based on the solidification of aqueous suspensions for the production of green parts with interesting economic and environmental benefits. In the present work, PZT-5 suspensions in aqueous media were successfully prepared using ammonium polyacrylate (PAA-NH_4) as the dispersing agent. The gelation of the 46–48 vol.% PZT suspensions in aqueous media based on agarose was studied by measuring the height of the samples before and after demoulding. The study found that the suitable amount condition for development of the green parts made was achieved at 0.082–0.19 wt.% agarose (based on dry solid). The density of the green body produced at the optimum content of agarose was determined. A very uniform part with green density of 52% and 55% before and after drying, respectively, was developed. Small shrinkage was measured after drying and heat treating at 550 °C. Sintered samples at 1250 and 1285 °C showed a theoretical density of 99% with an even smaller shrinkage of 16.2%. The dielectric constant and longitudinal piezoelectric charge coefficients, d_{33}, of the selected samples were 2550 and 680 pC/N, respectively.

Keywords: PZT; Gel casting; Aqueous media; Agarose; Sintering

1. Introduction

Piezoelectricity is the ability of selected materials to polarize in response to applied mechanical stress (direct effect) and to develop strain when exposed to an electric field (converse effect). Piezoelectric ceramics such as lead zirconate titanate (PZT) are used in many transducer applications, including medical imaging, igniters and micromotors. This is due to the high dielectric constant, charge coefficient (d_{33}) and electromechanical coupling coefficient (k), as well as the low dielectric loss of these materials. Success in the practical implementation of electroceramics depends not only on their performance characteristics but also on their processability and cost-effectiveness. Improved electromechanical properties of PZT can be achieved by controlling its three-dimensional geometry.[1–3]

In general, the processing of advanced ceramic components usually requires an expensive multi-step fabrication processes to achieve the desired product performance. Among several technical solutions to the high production cost of the ceramic components, the development of near net shape-forming accompanied by an engineered microstructure of the ultimate product without defects and homogeneous grain boundaries is the most promising approaches. Therefore, forming a ceramic component in a shape near the final dimensions is an efficient way to reduce both the time and the cost of the post machining.

Several methods for forming piezoelectric materials have been proposed such as fused deposition of ceramics, tape casting, and injection moulding.[4–6] In these methods, the ceramic phase is dispersed in a non-aqueous solvent and a significant amount of organic binders are added to support the structure. The use of the organic and polymer materials causes a series of problems (e.g. geometry distortion and microstructure defects, pollution of the environment) and increase the cost. However, little attention was paid to aqueous-based PZT tape casting.[7] Recently, the water-based direct (gel) casting method is

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recognized as a promising technological route for fabrication of optimal performance near net shape.[8–11] In this technique, the powder is dispersed in aqueous media (water) and the amount of polymer used for dispersion or consolidation is very low. The green body with the desired shape which is made by this method can be easily dried, machined virtually without the time-consuming binder burnout step. Also, the gel casting method is a suitable way for manufacturing materials which have complex and intricate features. Despite these advantages, little attention has been paid to using direct casting methods, particularly in particular gel casting for the fabrication of piezoelectric parts.[12–16] These works focus on the dispersing of PZT in deionized water using tri-ammonium citrate (TAC) as the dispersant agent and achieving the gelation by in situ polymerization of acrylamide ($C_2H_3CONH_2$, AM) monomer and N,N-methylenebisacrylamide ($(C_2H_3CONH)_2CH_2$, MBAM) cross-linker in the presence of N,N,N′,N′-tetramethylethylenediamine (TEMED) as catalyst and $(NH_4)_2S_2O_8$ as initiator. Unfortunately, the acrylamide monomer that is widely used in this process is harmful to the nervous system. In addition, the polymerization of the monomer makes the ceramic suspension difficult to control.[17,18] Therefore, offering an of environmentally friendly material to gel PZT slurry is very attractive. In this term, environmentally friendly natural polymers such as agarose, gelatine and agar have been successfully applied in the water-based injection moulding and gel casting of alumina and zirconia. The polymer solutions of these kinds of polymers in hot water can gelate under suitable conditions and the molecular chains attract each other to form a three-dimensional network by van der Walls forces and hydrogen bonds.[19] Despite of these advantages, there was no mention in the literature of studies with PZT ceramics using agarose in the literature.[17] Therefore, this work focuses on the preparation of PZT slurry in aqueous media and its gelation using agarose as a natural polymer. One of the requirements for the successful application of this technique is the preparation of a well-dispersed suspension with maximum solid loading. This cannot be achieved without a better understanding of the elctrokinetics and rheology of this system to control its stability and fluidity, particularly at high solids loading.

A number of factors such as the molecular weight and molecular structure of the polymer, charging effect, ionic strength, adsorption density and thickness of the adsorbed layer have been recognized to affect the rheological behavior of electrosterically stabilized colloidal dispersions.[20] The issues of stability control and the importance of the rheological properties of the suspensions were considered in earlier publications.[21,22] The rheological behavior of the system can give some insight into the interaction between particles, the polymer and the media. Furthermore the strength of the interactions can be estimated with information at various shear rate conditions. Several models have been developed that can be applied to describe the relationship between the relative viscosity of the dispersion and the volume fraction of solids in the system.[23,24] A well-known equation is provided by the Krieger–Dougherty's model:

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \tag{1}$$

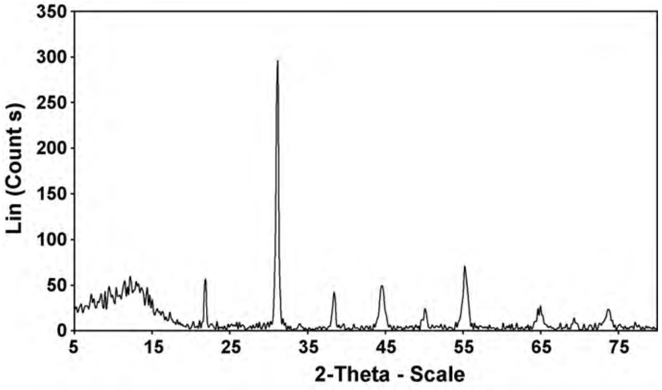


Fig. 1. XRD pattern of the investigated PZT powder.

where η_r is the relative viscosity of the suspension with respect to the suspending fluid at a given shear rate, ϕ is the volume fraction of solids, ϕ_m is the maximum packing fraction of solids and $[\eta]$ is the intrinsic viscosity of the suspension.

The objective of this work can be summarized into three phases termed: (1) investigation the electrokinetic and rheological behavior of aqueous PZT suspensions in the presence of ammonium salt of polyacrylic acid (PAA-NH_4) in order to prepare well-dispersed slurries with high solid loading, (2) gel casting of high solid loading slurry by using Agarose, and (3) sintering and characterization of the green body.

2. Materials and experimental procedure

2.1. Materials

The PZT-5H powder (PZT-5H, 610-HD) used in this work was obtained from TRS Technologies, USA. Powder composed of lead zirconate titanate with formula of $Pb_{0.58}Ti_{0.4}O_3$ was used, with the XRD pattern shown in Fig. 1. The average particle size of the powder was 1.5 μm. Ammonium salt of polyacrylic acid with an average molecular weight of 4000–10,000 and concentration of 22 wt.% was used as the dispersing agent (Texchem Egypt Co., Egypt). Agarose was used as the coagulant agent (Aldrich, SD Fine-Chem Ltd).

2.2. Experimental procedure

2.2.1. Zeta-potential and turbidity measurements

Electrokinetic studies were performed on two sets of PZT suspensions prepared in ultra pure water and in a solution containing 1.1 wt.% PAA-NH_4 (based on dry solids). The pH of the first and second set of samples was adjusted to different values from 4 up to 10 using Fisher brand HCl and aqueous NH_3, respectively. Samples were prepared by adjusting the pH and mixed by using a shaker for 1 h. After mixing, the pH was measured and adjusted. Zeta-potential measurements were determined with Zetaasier (Malvern Instruments, UK). The sample was loaded into the cell of the instrument and the mean of the zeta potential of the particles was determined at room temperature (25 °C).The turbidity of the dispersed PZT powder (16.13 vol.%) in water as a function of PAA-NH_4 content was measured using a microprocessor turbidity meter (Hanna Instruments, HI 93703) following the manufacture's structure.

2.2.2. Rheological studies

Steady shear viscosities of the samples were determined as a function of shear rate using a Bohlin Rheometer (Bohlin Instruments Ltd., UK) with a cone-and-plate geometry. Experiments were performed at 25 °C. In all experiments, a cone of radius 40 mm with a cone angle of 4.0° (a gap size of 150 μm) was used. The dependence of shear viscosity on dispersant dosage was studied using dispersions of 16.13 vol.% PZT particles prepared over a range of PAA-NH_4 dosage, from 0.22 wt.% (based on dry solids) to 0.66 wt.% (based on dry solids). These samples were prepared by mixing the suspension constituents in a planetary mill with a high purity zirconia grinding ball for a period of 1 h. at 150 rpm. The pH of suspensions was around 8.45 ± 0.01. The effect of solids loading on shear viscosity was studied using samples of volume fractions ranging from 5.2 to 48.46 vol.% PZT using 0.44 wt.% PAA-NH_4 (based on dry solids) as the dispersant at a pH of 8.45 ± 0.01 and which were then milled using the aforementioned procedure.

2.2.3. Gel optimization

Gel strength was determined qualitatively to optimize agarose content and time. PZT was dispersed in deionized water in the presence of 0.44 wt.% of PAA-NH_4 (based on dry solids) at pH 8.45 ± 0.01. Agarose powder with 0.014–0.19 wt.% (based on dry solids) was added to the slurries after mixing in ball mill for 24 h. The slurries were heated to 85 °C in a water bath. The slurries were kept at a constant 85 °C in the water bath with strong shaking for 15 min. The slurries debubbled in a vacuum oven at room temperature for 5 min. They were then cast into a non-porous PVC mould and covered to prevent the evaporation of water. After 8 h, the cast products were demoulded and their handling was examined by the determination of the height stability as reported.[25]

2.2.4. Green body preparation and its sintering

The green body was prepared according to the optimum conditions using the aforementioned procedure. The binder was removed by putting the dried parts in the oven and raising their temperatures at rate of 3 °C/min up to 500 °C. The part was kept for 3 h at 500 °C and then cooled at the same rate to room temperature. The PZT part was then placed in an alumina crucible containing ball milled equimolecular mixture of PbO and ZrO_2 in order to maintain the stoichiometry of the sintered object. The crucible was covered by sealed alumina plates using refractory cement. The crucibles and its ingredients were placed in an electric muffle furnace. The temperature was raised from room temperature up to 1250 °C at a rate of 210 °C/h, then kept at 1250 °C for 2 h, then cooled using the same rate to room temperature. The same firing program was applied to fire the samples at 1285 °C.

2.2.5. Characterization of the green and sintered body

Density of green part was determined by dividing weight by volume. However, from the sintered parts, density was determined by Archimedes' method. The fracture surface of both parts whether green or sintered were investigated by field emission scanning electron microscopy (FESEM, LEO (ZEISS) 982).

The top and bottom surface of the sintered sample were polished and electroded with silver paste, followed by firing at 550 °C for 15 min. The room temperature polarization–field (*P*-*E*) hysteresis loops were measured with a Sawyer–Tower circuit that was operated at 50 Hz (Radiant Technologies Inc.). Poling was performed under an electric field intensity of 20 kV/cm for 15 min in silicon oil at 60 °C. The piezoelectric charge coefficient, d_{33}, was measured directly from a Berlincourt Piezometer (Channel products, Inc.) at 100 Hz. At least ten readings, from different locations of both top and bottom surface were made and averaged. Capacitance and dielectric loss were measured at room temperature and 1 kHz using an HP 4194 A impedance/grain phase analyzer (HP, Palo Alto, CA). The relative permittivity was calculated according to the formula:

$$\varepsilon_r = \frac{Ct}{A\varepsilon_0} \qquad (2)$$

where ε_r is the relative permittivity, *C* is the capacitance, *t* is the thickness of the sample, *A* is the area and ε_0 is the permittivity of air and is equal to 8.854×10^{-12} F/m.

3. Results and discussion

3.1. Electrokinetic studies

Satisfactory aqueous dispersions can be prepared by dispersing the powder in an aqueous medium having a pH adjusted far away from the point of zero charge.[26] This condition is likely to ensure sufficient electrostatic stabilization due to the development of charge onto the surface of solids. The results reported here are for aqueous dispersions of PZT particles using PAA-NH_4 as a dispersing agent. An interesting feature about this system is that the isoelectric point for PZT (in the absence of dispersant) is in the pH range of 4–5. As the pH of the suspension is increased from a value of 4 to a value of 10, the surface charge of PZT will change from a positive to a negative value. In this pH range, the dissociation of ammonium carboxylate groups (R-$COONH_4$) of PAA-NH_4 occurs.[27] As it is known, PAA-NH_4 in basic aqueous solutions (at high pH values) is negatively charged and stretched because of the repulsive forces between the negatively charged segments of the polymer. This type of behavior is strongly affected by the pH of solvent and ionic strength. Polymer or organic molecules having –$COONH_4$ or –COONa are typically considered good dispersants for powders. In such polyelectrolytes, electrostatic attraction and electrostatic repulsion can be obtained at low and high levels of pH levels respectively.

The variation of zeta potential of PZT as a function of pH is shown in Fig. 2. It is evident that the ζ-potential of PZT in the presence or absence of PAA-NH_4 remains negative over the range of pH. However, the ζ-potential reaches above −35 mV at pH > 8 in the absence of PAA-NH_4. However, a shift in IEP was not observed. In spite of that, negative charges on the surface of particles are expected to be strongly affected by pH and the

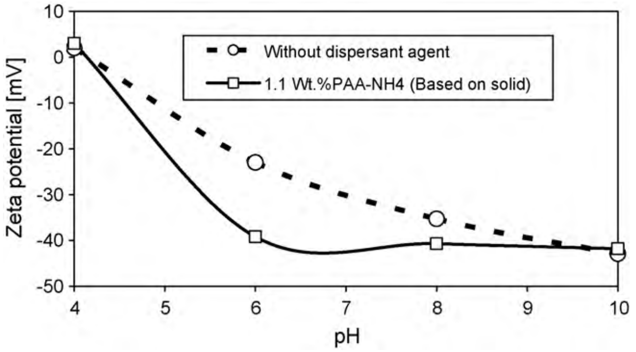


Fig. 2. The variation of zeta potential of PZT suspension as a function of pH.

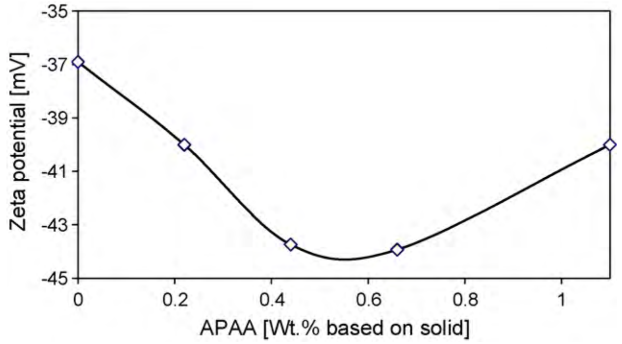


Fig. 3. The variation of zeta potential of PZT suspension at pH of 8.45 ± 0.01 as a function of $PAA-NH_4$.

$PAA-NH_4$. As stated above, in this condition, stable aqueous colloidal dispersions of ceramic powders can be achieved through the generation of highly charged surfaces which can be achieved by adjusting the pH far away from the IEP through strong double layer repulsion. Further experiments were conducted at $pH > 8$ (8.4) extending the acceptable range for dispersing the particles. Different APAA ($PAA-NH_4$) contents were considered and the ζ-potential of the PZT particle was measured as shown in Fig. 3. It was observed that increasing the content of $PAA-NH_4$ up to 0.66 wt.% (based on dry solids), the particle surface charge attains high negative values (the ζ-potential was ∼−44 mV). The turbidity of the suspensions, Fig. 4, was in good agreement with the zeta-potential results. Turbidity reached a steady state starting from 0.44 wt.% $PAA-NH_4$ (based on solids) up to 0.66 wt.% $PAA-NH_4$ (based on dry solids).

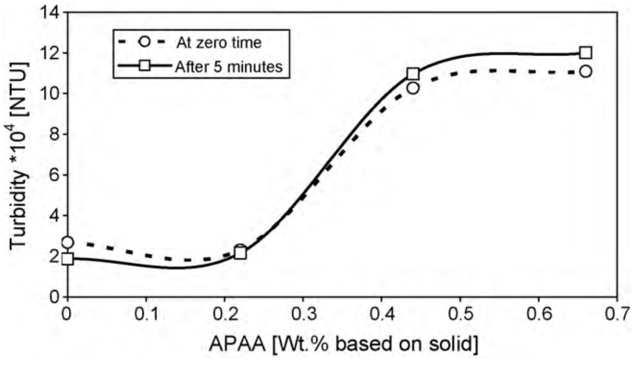


Fig. 4. The variation of turbidity of PZT suspension at pH of 8.45 ± 0.01 as a function of $PAA-NH_4$.

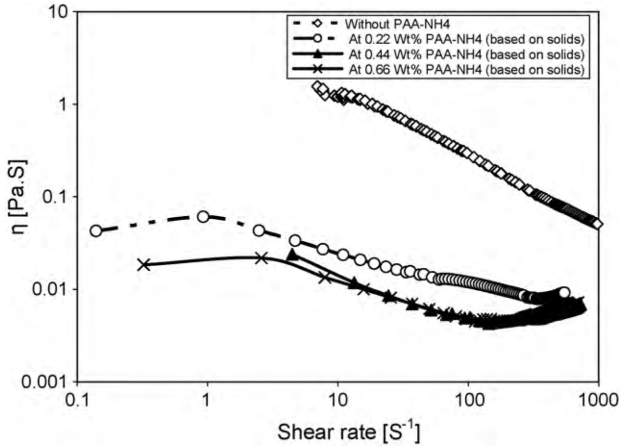


Fig. 5. Viscosity of PZT suspension in aqueous media with various dosages of $PAA-NH_4$ as a function of shear rate.

Therefore, the results of a high negative charge coupled with higher turbidity when compared with dispersed PZT in the absence of $PAA-NH_4$ indicate the best conditions for the preparation of a PZT dispersion in aqueous media: pH 8.4 and in presence of 0.44 wt.% $PAA-NH_4$ (based on solids).

3.2. Rheological behavior results

3.2.1. Variation of viscosity with $PAA-NH_4$ dosage

The effect of a dispersing agent on the rheological properties of suspensions is attributed to the charges on the adsorbed polyelectrolyte molecules. The adsorbed polyelectrolyte molecules induce a combination of electrostatic and stearic repulsive forces between the suspended particles and consequently affect the viscous behavior of the system. The effect of the concentration of a dispersing agent on the viscosity of PZT suspensions of 16.13 vol.% is presented in Fig. 5. This diagram shows viscosity as a function of shear rate at different concentrations of the dispersant agent, at 25 °C and pH 8.45 ± 0.01. It is observed that at all levels of PZT dosage, the sample exhibited shear thinning behavior at an intermediate shear rate approach a Newtonian plateau at higher shear rate values.

Fig. 6 represents the viscosity data as a function of the concentration of PZT at a shear rate level of $50\,s^{-1}$ for PZT suspensions with 16.13 vol.%. As it can be observed, there is an initial decrease in viscosity of the dispersion with increasing $PAA-NH_4$ concentration up to 0.44 wt.% (based on dry solids). Beyond 0.44 wt.% the viscosity of the dispersion increases with increasing $PAA-NH_4$ concentration. The lower viscosity values of the suspensions can be explained in terms of insufficient electrostatic repulsion forces to overcome the van der Waals attractions at lower concentrations (less than 0.44 wt.%). As the surface coverage of adsorbant increases, the repulsion forces increase accordingly and eventually attain a level that is strong enough to overcome the van der Waals forces.[28] At this coverage level (0.44 wt.% $PAA-NH_4$), the suspension is dominated by repulsive forces, thus it is stabilized and consequently the

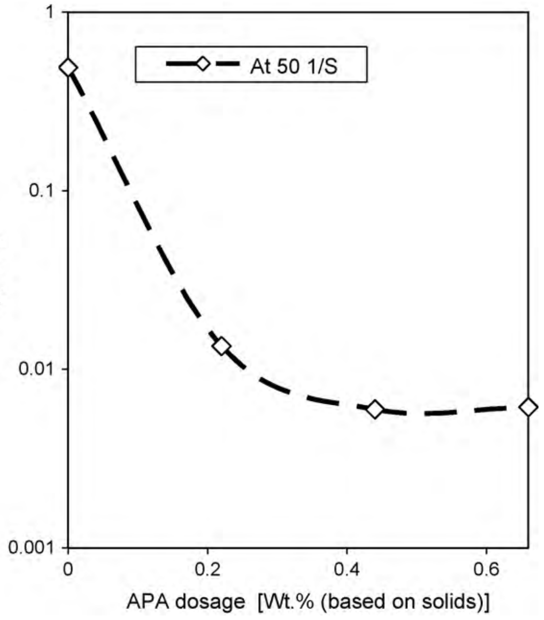


Fig. 6. Viscosity of PZT suspension as a function of PAA-NH$_4$ dosage (based on dry solids) at shear rate of 50 s^{-1}.

viscosity decreases. The further addition of PAA-NH$_4$ leads to the increase of viscosity due to the existence of excess amount of PAA-NH$_4$, which does not adsorb on the surface and therefore the high electrolyte content causes the compression of the double layer and the surface-to-surface distance becomes smaller, causing weaker repulsion to be obtained.[28] On the basis of the results presented above, well-dispersed PZT suspensions can be prepared from the addition of 0.44 wt.% PAA-NH$_4$.

3.2.2. *Effect of solid loading*

Using dispersions of higher solid loading in the preparation of ceramic green bodies has a very important role on the quality of the final products. The higher the solid loading, the lower the liquid content of the slurry. This condition will lead to a green body of higher packing factor or higher density, which also minimizes the shrinkage of the green body. This result is possible only if the sample at high levels of solid loading maintain its stability without sedimentation and aggregation of the particles at high levels of solid loading and also maintains on acceptable viscosity for easy casting.[29]

Fig. 7 represents the viscosity as a function of shear rate and volume fraction of the particles for aqueous PZT suspensions containing 0.44 wt.% PAA-NH$_4$ (based on dry solids) as a dispersing agent. The viscosity changes with both the shear rate and volume fraction of the particles. At low or higher volume fraction of the particles and moderate shear rates, the viscosity falls monotonically with the increasing shear rate and does not appear to approach a final limiting value at higher shear rates. However, at a volume fraction less than 23 vol.% and high shear rate, Newtonian behavior was observed. There are at least a two orders of magnitude change in viscosity as the solid loading is increased from 5.2 to 48.46 vol.%. It is evident that the differences in viscosity at various volume fractions are more significant at low shear rates which are due to the fact that interparticle forces are dominant and control the viscosity of the suspension.

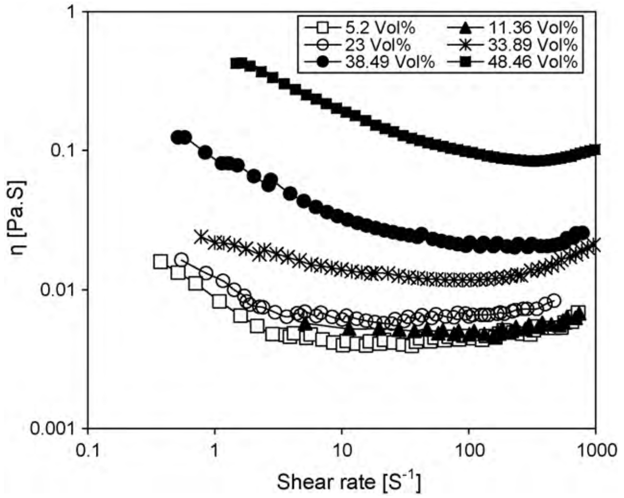


Fig. 7. Viscosity of different volume fraction of PZT suspensions with 0.44 wt.% PAA-NH$_4$ (based on dry solids) as a function of shear rate.

The relative viscosity of PZT suspensions at two different shear rates, 10 and 500 s^{-1}, as a function of volume fraction are presented in Figs. 8 and 9. Relative viscosities were simulated as a function of volume fraction of the particles using Krieger–Dougherty's equation. Using this model, relative viscosities at shear rates of 10 and 500 s^{-1} can be expressed respectively as:

(a) at 10 s^{-1}:

$$\eta_r = \left(1 - \frac{\phi}{0.65}\right)^{(-6.01\times 0.65)} \tag{3}$$

(b) 500 s^{-1}:

$$\eta_r = \left(1 - \frac{\phi}{0.73}\right)^{(-5.775\times 0.73)} \tag{4}$$

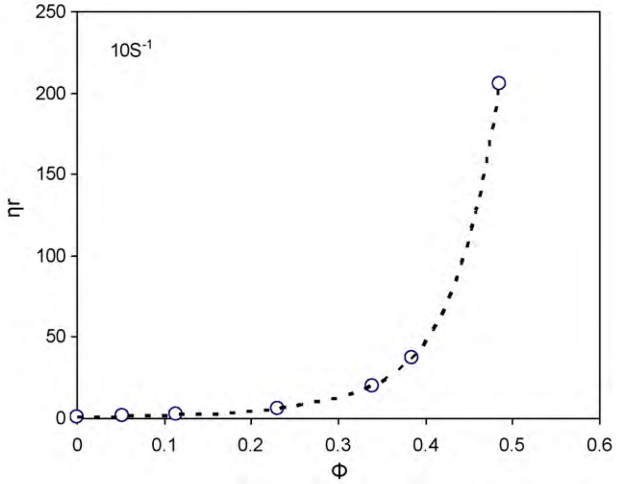


Fig. 8. Relative viscosity of PZT suspension as a function of volume fraction at 1000 s^{-1}.

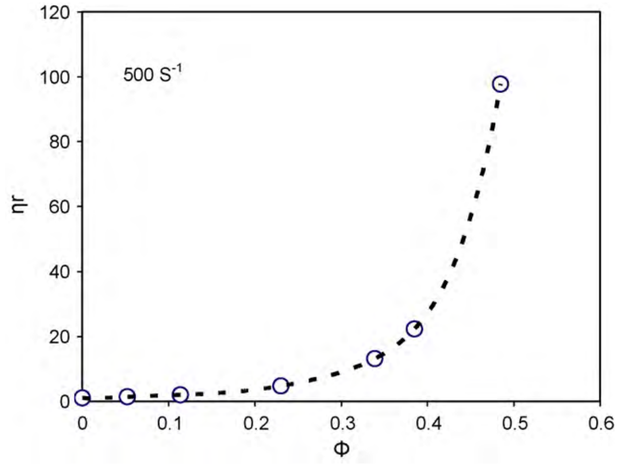


Fig. 9. Relative viscosity of PZT suspension as a function of volume fraction at $500\,s^{-1}$.

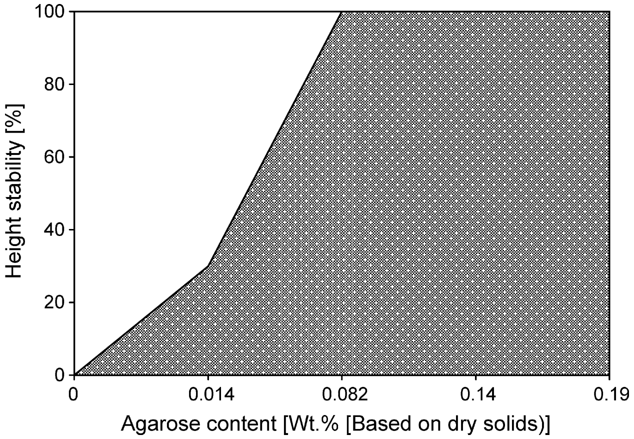


Fig. 10. Effect of the agarose amount on the height stability of 48.46 vol.% PZT suspension in aqueous medium at pH 8.45 ± 0.01 as function of temperature with soaking time 8 h.

The behavior of the suspension changes from liquid-like to solid-like as ϕ approaches the maximum packing fraction. Different values have been reported in the literature for the maximum packing fraction of suspensions of monodisperse particles. These results indicate that the maximum packing fraction may change significantly with purity, shape, pore size distribution, particle geometry arrangement, relative monodispersity of the particles and the level of accuracy of the experiments. Moreover, different models may predict different values for the maximum packing fraction of the same system. The maximum packing fraction, ϕ_m, appears to be shear rate-dependent, and an increase in ϕ_m with increasing shear rate is due to the fact that particles pack more closely under shear.[30]

The calculated values of $[\eta]$ for suspensions of PZT particles using the Krieger–Dougherty model gives higher values than the theoretical ones for suspensions of spherical particles ($[\eta] = 2.5$). It is known that the intrinsic viscosity of suspensions is affected by the shape and surface roughness of the particles. Since in our system the PZT particles are not exactly spherical, we believe that this may be a reason for the high value of the intrinsic viscosity of the suspension. Additionally, the polydispersity of the samples, as well as surface roughness, may also be responsible for the high intrinsic viscosity. The data presented in Figs. 8 and 9 indicate that the effect of solid loading on the relative viscosity of the system increases rapidly above 48.46 vol.%. This result indicates that the preparation and handling of the suspension will be difficult at higher levels of volume fraction of the particles. Therefore, in this work the ceramic suspension at 48.46 vol.% was chosen in order to avoid difficulties associated with highly viscous samples.

3.2.3. *Consolidation of maximum solid loading PZT slurry*

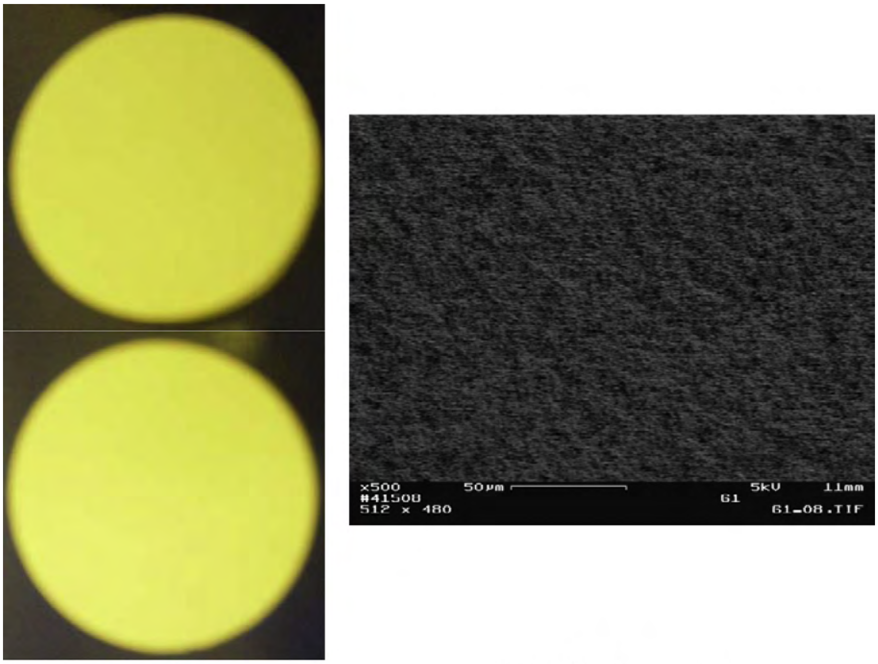
The preparation of the low viscosity and high solid loading suspension is required for gelation in order to facilitate the mould filling process, to increase the density and to minimize the shrinkage of the green body. Accordingly, the agarose content required to consolidate the suspension for preparing a ceramic green body was optimized. Fig. 10 shows the height stability of a PZT slurry dispersed in deionized water using 0.44 wt.% PAA-NH_4 (based on dry solids) as a function of agarose content. It was found that the height stability of the casted parts with less than 0.082 wt.% agarose (based on dry solid) was compromised because of insufficient strength. The stability condition of the parts was achieved at 0.082–0.19 wt.% agarose (based on dry solid). This means that the preparation of the PZT parts with 0.082–0.19 wt.% agarose (based on dry solid) is possible.

The use of an excessive concentration of gelating agent in a PZT suspension increases the viscosity of the slurry, prevents its casting and, consequently, leads to agglomeration. Therefore, a minimum concentration of agarose that gave 100% height stability was selected as a candidate for the manufacturing of a ceramic green part.

Based on the arguments stated above, a PZT ceramic green part was prepared by dispersing PZT powder in deionized water using PAA-NH_4 at pH 8.45 ± 0.01 and consolidated by addition of 0.082 wt.% agarose (based on dry solid).

Uniform and well-distributed green parts were made as seen in Fig. 11. The density of the green body was 52% (before drying). The magnitudes of shrinkage were 0.24% and 0.37% after drying and treating at 550 °C, respectively. Low magnitudes of shrinkage indicate that direct cast (gel) of PZT water-based suspensions can be used for manufacturing of near net shape. The sintered parts made at 1250 °C or 1285 °C gave higher shrinkage (16.2%) compared by the dried and treated parts at 550 °C. Although, this shrinkage value is considerably high, it is still lower than that observed in PZT parts formed by using a uni-axial press and sintered at 1285 °C (∼18%). The density of the dry parts at room temperature was 55% and reached ∼99% after sintering at both temperatures (1250 °C or 1285 °C). The porosities of both parts were less than 1%. The densification parameters confirmed the possibility of manufacturing near-fully dense parts using this technique. In addition, similarity in the densification parameters at both sintering temperatures would translate in a tangible economic benefit by choosing the lower temperature.

SEM observation of the parts, Fig. 12, exhibited well-distributed and strongly packed grains. Such microstructure supports the densification results. The grain sizes of both parts did not exceed 2 μm. The part sintered at low temperature



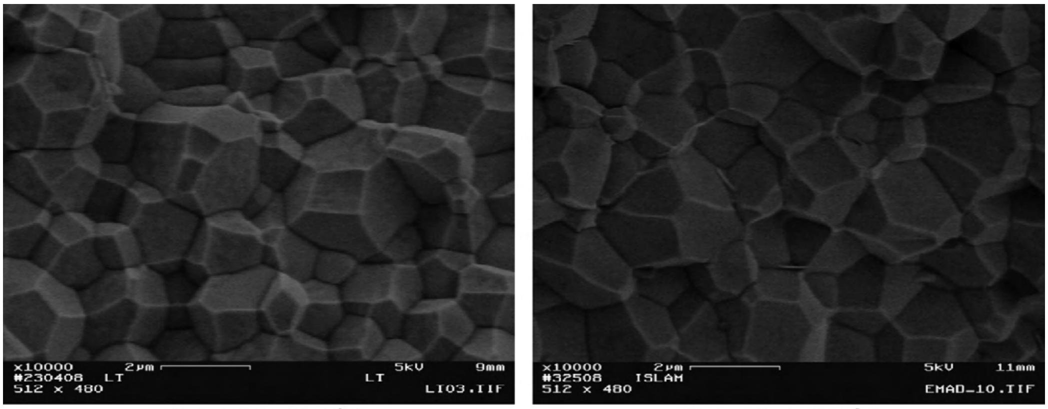
Part picture SEM of fracture surface

Fig. 11. Green parts.

showed several isometric closed crystal forms compared to the part sintered at high temperature, see Figs. 13 and 14. However, the part sintered at high temperature showed almost dodecahedral forms of five edged polygons as well as closed isometric forms.

The sintered gel cast parts did not show any piezoelectric properties before polarization. This is due to the chaotic orientation of the polar axes of the individual crystallites (grains) in it. In addition, the crystallites branched into domains (areas) with different directions of spontaneous polarization. However, with applied external electric field (E), as seen in Fig. 15, a reorientation of the spontaneous polarization along the field direction occurs. It was observed that the saturation polarization (P_s), remnant polarization (P_r) and coercive field (E_c) of both parts increased with increasing of E as shown in Table 1. However, there is no substantial difference between both parts. As a result of this, both parts acquired piezoelectric properties as shown in Table 2. With the increase of the external applied field (E) approaching the value of the coercive fields of the materials, a fast increase in piezoactivity is observed. With the further increase of E, the increase in piezoelectric charge (d_{33}) of both parts sintered at low and high temperatures is slowed down and stops in fields with intensity of approximately 7.14 and 8.05 kV/cm, respectively.

Lower dielectric constant (ε_r) and high dielectric loss ($\tan\delta$) of both samples was shown before poling compared to the poled parts as given in Table 3. This is due to the complex domain structure of these parts generated from different crystal (grain) sizes as demonstrated above by the microstructure. In such a microstructure, one or more domains may have been generated. However, with poling, a static distribution of the domains by coercive fields was applied. Although the poling made a



Sintered at 1250°C Sintered at 1285°C

Fig. 12. SEM of sintered gel cast parts.

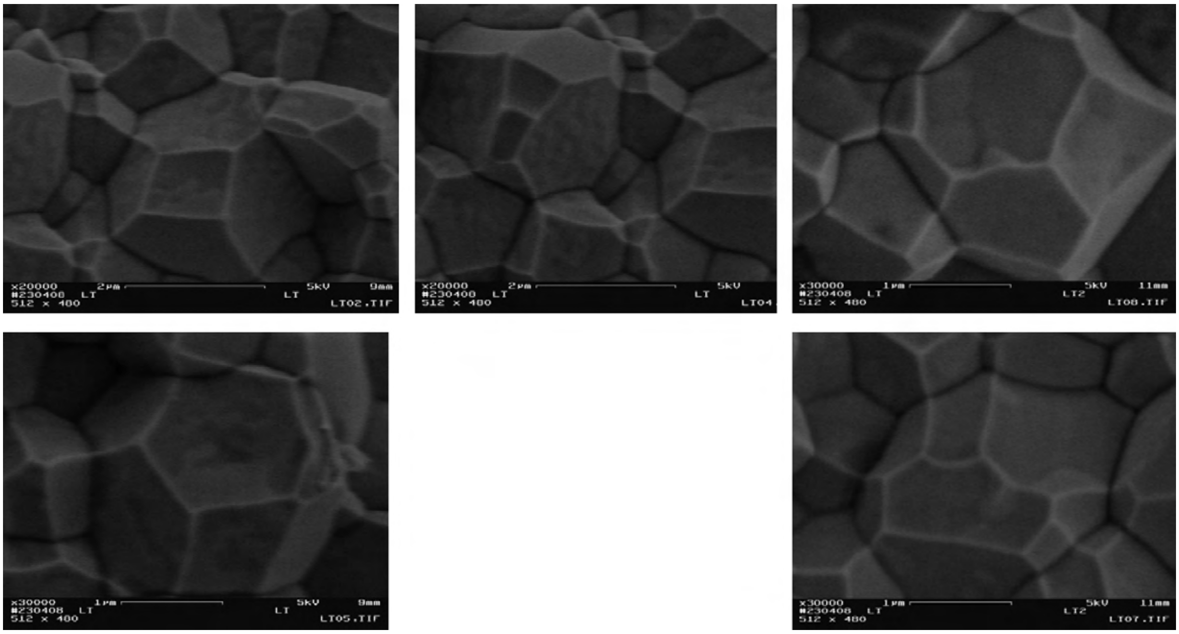


Fig. 13. Crystal forms of sintered part at 1250 °C.

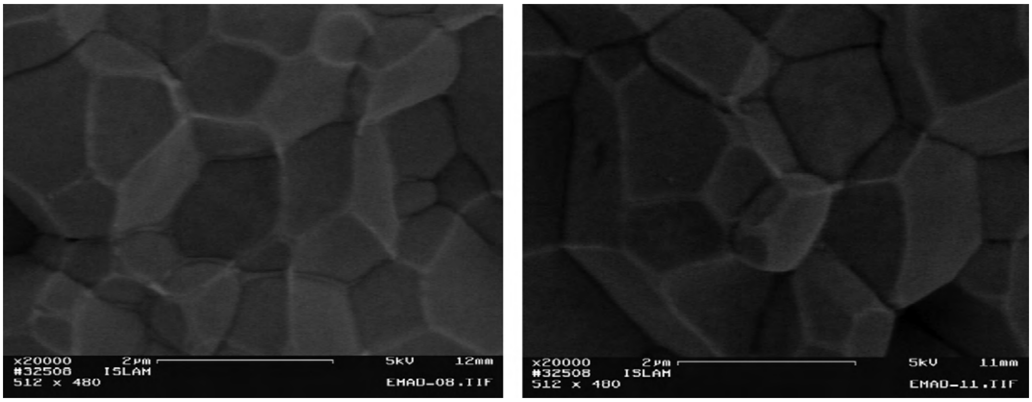


Fig. 14. Crystal forms of sintered part at 1285 °C.

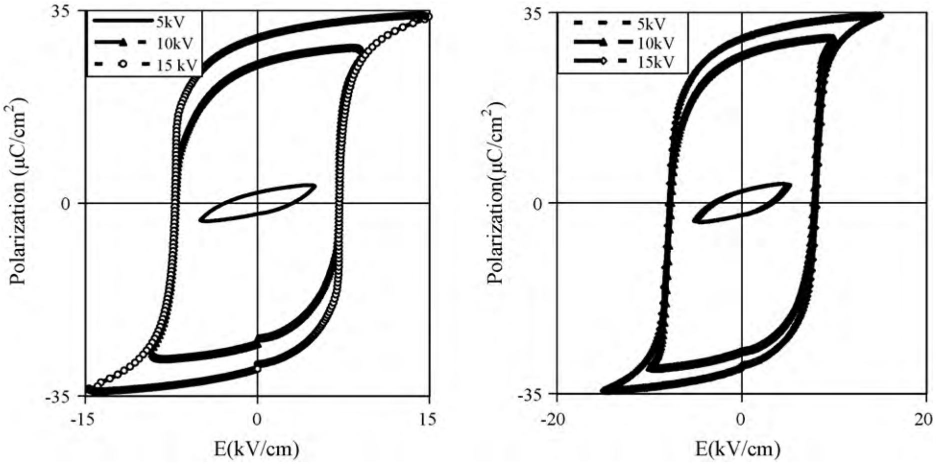


Fig. 15. Dielectric hystersis cycle of sintered parts at 1250 °C and 1285 °C (left: 1250 °C, right: 1285 °C).

Table 1
Saturation and remnant polarization (P_s and P_r) and coercive field (E_c) of sintered samples at different temperature.

External applied electric field (E) (kV/cm)	Sintered part at 1250 °C			Sintered part at 1285 °C		
	P_s (μC/cm^2)	P_r (μC/cm^2)	E_c (kV/cm)	P_s (μC/cm^2)	P_r (μC/cm^2)	E_c (kV/cm)
5	3.31	1.93	3.039	3.48	2.01	3.2
10	28.24	25.31	7.09	30.34	27.14	7.75
15	34.13	30.034	7.14	34.46	30.22	8.05

Table 2
Piezoelectric charge coefficient of sintered samples at different temperature.

d_{33} of sintered parts at 1250 °C (pC/N)	d_{33} of sintered parts at 1285 °C (pC/N)
24	24
497	610
616	680

Table 3
Dielectric constant (ε_r) and dielectric loss (tan δ) measured at 1 kHz of sintered samples before and after regular poling.

Sintered part temperature (°C)	ε_r		tan δ (%)	
	Before poling	After poling	Before poling	After poling
1250	2026	2550	3.1	1.91
1285	2011	2552	3.18	1.95

significant improvement in both coefficients, however, ε_r is quite low compared by the technical data provided supplier. The decreasing of ε_r may be understood in terms of lower grain size (~2 μm).

4. Conclusions

The present work has demonstrated that it is possible to obtain well-dispersed PZT powders in water in the presence of ammonium polyacrylate (PAA-NH_4). Gelation of these water-based PZT slurries using agarose gives rather dense green ceramic bodies with a homogeneous microstructure. Studies of the electrokinetic phenomena, turbidity data and the rheological behavior of this system have allowed determining the optimum content of dispersant (PAA-NH_4) to be determined. The optimum conditions were found to be 0.44 wt.% PAA-NH_4 (based on solids) at 25 °C and pH 8.45 ± 0.01. The application of Krieger–Dougherty's model on the system illustrated that the maximum solid loading to prepare green ceramic parts to avoid difficulties associated with high viscous samples is 48.46 vol.%. The optimum content of the agarose to consolidate this system was 0.082 wt.% agarose (based on dry solid). FESEM of the obtained green body showed uniform microstructure free from large pores. The density of the green body was 52% (before drying) and 55% (after drying) with respect to the theoretical density. A low magnitude of shrinkage was recorded after drying and treating at 550 °C. Low shrinkage and near-fully dense (99%) ceramics with low porosity (<1%) were produced at both sintering temperatures (1250 and 1285 °C) and results were compared with those obtained with similar parts made by uni-axial press. Dielectric constant and longitudinal piezoelectric charge coefficients, d_{33}, of the selected samples were 2550 and 680 pC/N, respectively.

Based on these results, the implementation of direct (gel) casting technique on the manufacturing of PZT green parts is considered a promising technique in term of economic and environmental benefits. In addition, this technique will allow the manufacturing of fully or near-fully dense PZT parts with near net-shape of variable complexity with some advantages with respect to conventional techniques.

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