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Magnesia induced coagulation of aqueous PZT powder suspensions for direct coagulation casting

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Abstract

Coagulation characteristics of poly(acrylate) dispersed PZT powder suspensions by MgO coagulating agent have been studied. The PZT powder suspensions undergoes coagulation at MgO concentrations much lower than the equivalent amount to react with the dispersant indicating a major shift in the coagulation mechanism from the corresponding alumina powder suspensions. Unlike in alumina powder suspensions, the Mg^{2+} ions generated from the MgO reacts with the ammonium poly(acrylate) adsorbed on particle surface that result in cross-linking of PZT particles by Mg^{2+} through the ammonium poly(acrylate) molecules. The particle bridging induces faster coagulation of the slurry cast in a mould as required for an ideal DCC process. The compressive strength and stability against oscillatory stresses of the wet-coagulated bodies increased with increase in number of cross-links between the particles. The PZT green bodies prepared by the DCC process sintered to near theoretical density and the MgO added as coagulating agent (~0.1 wt%) had only minor influence on its piezoelectric characteristics.

Keywords: A. Shaping; C. Strength; D. MgO; PZT; Direct coagulation casting

1. Introduction

Direct coagulation casting (DCC) is a relatively new ceramic shape forming process from concentrated ceramic powder suspensions [1–18]. The process has created more interest among the researchers as it is completely free from the use of polymeric binders. In DCC, concentrated ceramic powder suspensions cast in a mould is set in to rigid gel, by *in situ* coagulation, which can be removed from the mould immediately after gelation. *In situ* coagulation of ceramic powder suspensions has been achieved either by shifting the pH of the medium towards the iso-electric point of the ceramic powder by time delayed *in situ* generation of acid or base from water-soluble precursor molecules or by compressing the electric double layer by *in situ* generation of excess electrolyte [1–18]. Enzyme catalyzed *in situ* hydrolysis of urea has been used to increase both the pH (due to ammonia) and concentration of electrolytes like ammonium carbonates and ammonium bi-carbonate that coagulate powder suspensions of alumina, zirconia, silicon carbide and silicon nitride [1–12]. Coagulation by *in situ* generation of acid from water-soluble precursor molecules such as acid anhydrides, esters, lactones, and hydroxy aluminium acetate has also been reported for setting of ceramic powder suspensions prepared in alkaline pH range or using ploy (electrolyte) dispersants [13–18].

Recently we have reported a novel coagulation method for direct coagulation casting of alumina suspensions prepared using ammonium poly(acrylate) dispersant using MgO as coagulating agent [19–23]. In this, Mg^{2+} generated from the sparingly soluble MgO reacts with the un-adsorbed ammonium poly(acrylate) in the dispersion medium and form precipitate of Mg-poly(acrylate). This leads to desorption of ammonium poly(acrylate) from the alumina particle surface. Desorption of ammonium poly(acrylate) from particle surface resulted in insufficient dispersant surface coverage and hence coagulation of the suspensions. The reactions leading to coagulation of alumina suspensions is as shown

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below:

$$\text{Amm. poly(acrylate)}_{(\text{aqueous})} \rightleftarrows \text{Amm. poly(acrylate)}_{(\text{adsorbed on alumina})}$$

$$MgO + H_2O \rightleftarrows Mg^{2+} + 2OH^-$$

$$\text{Amm.poly(acrylate)}_{(\text{aqueous})} + Mg^{2+} \rightarrow \text{Mg-poly(acrylate)}_{(s)} + NH^{4+}$$

It has been reported that incorporation of small amount (<1 vol.%) of MgO increased the mechanical properties of PZT ceramics without deteriorating its piezoelectric properties [24]. This encouraged us to study the coagulation of PZT powder suspensions using MgO as the coagulating agent. It is evidenced from this study that the coagulation of PZT slurries prepared using poly(acrylate) dispersant by MgO follows mechanism different from that of alumina.

2. Experimental

PZT-5H powder of average particle size 0.64 μm (measured using Malvern Master Size Analyzer 2000, UK) and surface area 6.2 m^2/g (measured using surface area analyzer, Sorptomatic 1990, Thermo Fennigan, Italy) was procured from Sparkler Ceramics, Pune, India. A 35 wt% aqueous solution of ammonium poly(acrylate) (Darvan-C, Vanderbilt Company Inc., Norwalk) was used as the dispersing agent. Analytical reagent grade light MgO powder (Thomas Baker, Mumbai) was used as the coagulating agent. Distilled water was used for preparation of slurries. Polyvinyl alcohol (PVA) binder of average molecular weight 14 000 was procured from S.D. Fine Chemicals, Mumbai, India.

PZT slurries (50 vol.%) were prepared by tumbling the PZT powder, water and various amounts of the dispersing agent in polyethylene containers along with zirconia grinding media for 12 h. Viscosity of the slurries was measured using a Brookfield viscometer (RVT model) using a small sample adapter and cylindrical spindles (SC 21 and SC 28) to find out the dispersant concentration required for optimum dispersion of the powder. Various amounts of MgO powder was added to the PZT slurries prepared at dispersant concentration of 0.43 wt% and mixed thoroughly by continuing the tumbling process at room temperature. The amount of dispersant and MgO used was based on the PZT powder. Viscosity variation of the slurries with time after the addition of MgO was measured using SC-28 spindle at a shear rate of 2.8 s^{-1}. In order to study the effect of cooling on coagulation, the slurries were cooled in an ice bath to a temperature of ∼5 °C before addition of MgO powder. After the addition of MgO powder, the slurries were mechanically stirred for 1 h by keeping in the same ice bath and viscosity was monitored at regular intervals. Effect of heating on coagulation of the slurries was studied by measuring the viscosity of the slurries at 60 °C using a thermosel assembly along with Brookfield viscometer. The slurries used to study the effect of heating were mixed thoroughly with MgO powder by mechanical stirring for 20 min by keeping in an ice bath.

The load–displacement behavior of the wet-coagulated bodies (gels) was measured using a universal testing machine (Hounsfield, S-sires, UK) at a cross-head speed of 2 mm/min. Cylindrical coagulated bodies of 22 mm diameter and 45 mm length used for compressive strength measurement were prepared by coagulation of the PZT slurries using various MgO concentrations in closed stainless steel moulds. The coagulated bodies were aged overnight and removed from the mould immediately before the testing. The compressive strength (defined as the yield stress) and bulk modulus of the coagulated bodies was determined from the load–displacement graph [7,9]. Stability of the wet-coagulated bodies against oscillatory stresses is qualitatively evaluated by vibration test reported by Balzer et al. [7]. The wet-coagulated bodies immediately after removal from the mould were subjected to vibration on the vibration unit of a sieving tower for 2 min. The coagulated bodies prepared at various MgO concentrations have been subjected to vibration of same amplitude and deformations of the bodies, if any, were noticed visually.

The coagulated bodies were dried at room temperature (∼30 °C) at 75% relative humidity. The humidity condition was created inside a desiccator using saturated sodium chloride solution. Cylindrical pellets were also prepared by pressing the PZT powder suing 2 wt% PVA binders for comparison. Both the green bodies prepared by coagulation casting and powder pressing were heated up to 600 °C at a rate of 3 °C/min to remove the organic matter. The green bodies were then sintered at 1290 °C for 2 h. Lead oxide atmosphere was created during sintering to compensate any lead loss. Density of the sintered samples was determined by Archimedes method. Microstructure of the sintered ceramics was observed on fractured surfaces using a Scanning Electron Microscope (SEM). The sintered PZT ceramics prepared by the DCC process and powder pressing were cut in to cylindrical discs of 3 mm thickness using a precision dicing machine and coated with silver paste (Central Electronics Ltd., New Delhi, India) on top and bottom surfaces. The silver coated samples were annealed at 750 °C for 30 min. The silver coated samples were immersed in a silicon oil bath at 100 °C and poled by applying a dc field of 20 kV/cm for 20 min. Capacitance and loss factor of the samples were measured using impedance analyzer (4294 A Agilent Technologies, Palo Alto, CA) at a frequency of 1 kHz and at room temperature. The piezoelectric charge coefficient (d_{33}) of the samples was measured using Berlincourt piezometer (Take Control Piezometer Systems, PM25, UK).

3. Results and discussion

Fig. 1 shows viscosity of 50 vol.% PZT powder slurries prepared at various dispersant concentrations. Viscosity of the slurries decreased with increase in dispersant concentration and reached a minimum value at 0.26 wt% of the dispersant. Further addition of dispersant up to 1 wt% did not increase the slurry viscosity considerably. That is, well dispersed suspension of the powder is achieved at minimum dispersant concentration of 0.26 wt% and addition of higher amount of dispersant up to 1 wt% did not adversely affect the dispersion of the powder.

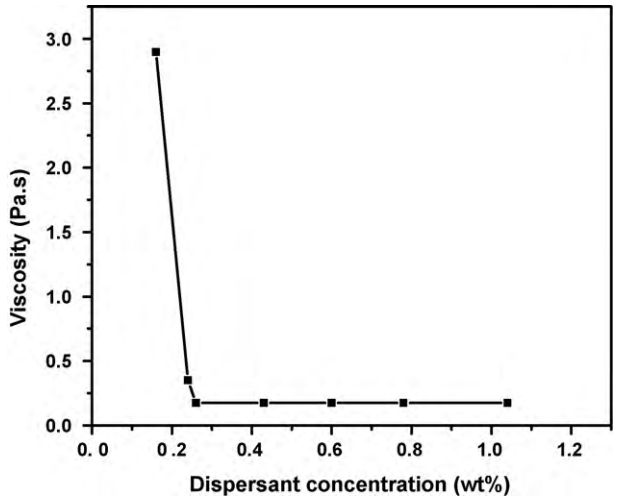

Fig. 1. Viscosity of 50 vol.% PZT powder slurries prepared at various dispersant concentrations (spindle-SC-21, shear rate-9.3 s^{-1}).

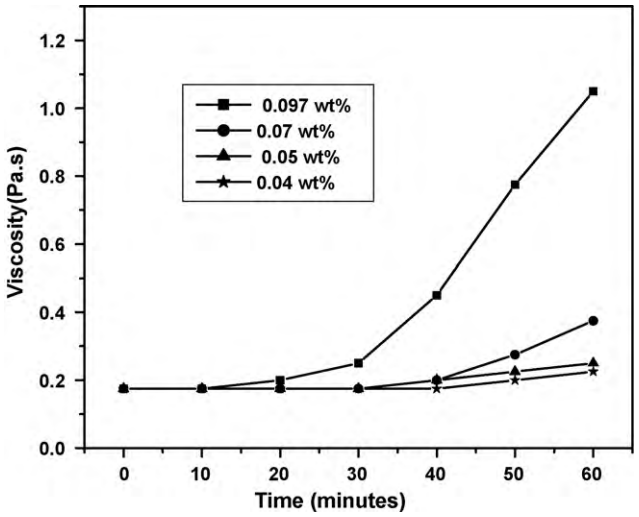

Fig. 3. Viscosity variation with time of 50 vol.% PZT slurries containing various amounts of MgO at low temperature of ∼5 °C (spindle-SC-21, shear rate-9.3 s^{-1}).

Fig. 2 shows effect of addition of various amounts of MgO on viscosity variation with time at room temperature (∼30 °C) of 50 vol.% PZT powder suspensions prepared at dispersant concentration of 0.43 wt%. Addition of 0.03 wt% of MgO produced only a small increase in viscosity of the PZT suspensions from 0.25 to 1.5 Pa s in 180 min. However, addition of 0.04 wt% of MgO increased the viscosity of the PZT suspension slowly in the initial 30 min and then rapidly with time. The slurry reached a gel-like consistency (viscosity above 40 Pa s) in 175 min. Incorporation of higher amounts of MgO increased the viscosity of the suspensions at a faster rate. The PZT powder suspensions containing MgO concentrations 0.05, 0.07 and 0.097 wt% reached gel-like consistency in 50, 15 and 10 min, respectively.

In a direct coagulation casting process, the slurry viscosity should remain more or less unchanged for sufficient time after the addition of coagulating agent to facilitate mixing, degassing and casting operations [1,17]. However, after casting, the slurry should form a stiff gel that can be removed from the mould immediately after gelation to provide higher production rate [1,17]. In the present case, the slurry viscosity remains in the range of 0.25–1.5 Pa s for 30 and 10 min at MgO concentrations of 0.04 and 0.05 wt%, respectively at room temperature. That is, the slurry provides enough time to perform the casting operation only at MgO concentration of 0.04 wt% at room temperature. At MgO concentration of 0.05 wt% mould filling become difficult unless casting of the slurry to be carried out very fast. However, at MgO concentration of 0.07 and 0.097 wt% slurry viscosity increased so rapidly that the casting becomes very difficult at room temperature.

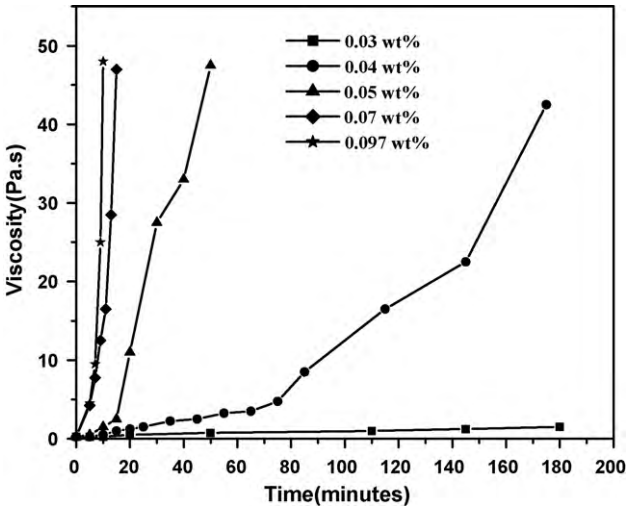

Fig. 2. Effect of addition of various amounts of MgO on viscosity variation with time at room temperature (∼30 °C) of 50 vol.% PZT powder suspensions prepared at dispersant concentration of 0.43 wt% (spindle-SC-28, shear rate-2.8 s^{-1}).

Fig. 3 shows effect of cooling on viscosity variation with time of PZT slurries containing various amounts of MgO. Slurries were mixed with MgO after cooling to a temperature of ∼5 °C in an ice bath. The slurries were kept in the ice bath through out the viscosity measurements. Viscosity measurements were taken using SC-21 spindle at a shear rate of 9.3 s^{-1}. The viscosity of the slurries remains unchanged for about 40 min at MgO concentrations of 0.04, 0.05 and 0.07 wt% and then increased slowly with time. The viscosity increased from initial value of 0.175 to 0.225, 0.25, and 0.35 Pa s in 1 h for slurries at MgO concentrations of 0.04, 0.05 and 0.07 wt%, respectively. However, at 0.097 wt% MgO, the slurry viscosity remains unchanged for only 10 min. Further, the viscosity increased slowly with time and reached a value of 1.05 Pa s at the end of 1 h. That is, mixing of the slurries with MgO at a low temperature of ∼5 °C keeps the viscosity of the slurries low for sufficiently long time to perform mixing, degassing and casting operations.

Fig. 4 shows effect of heating on viscosity variation with time of PZT slurries containing various amounts of MgO. The slurries were mixed thoroughly with MgO at a temperature of ∼5 °C by mechanical stirring for 20 min before starting the viscosity measurements. Viscosity measurements were taken

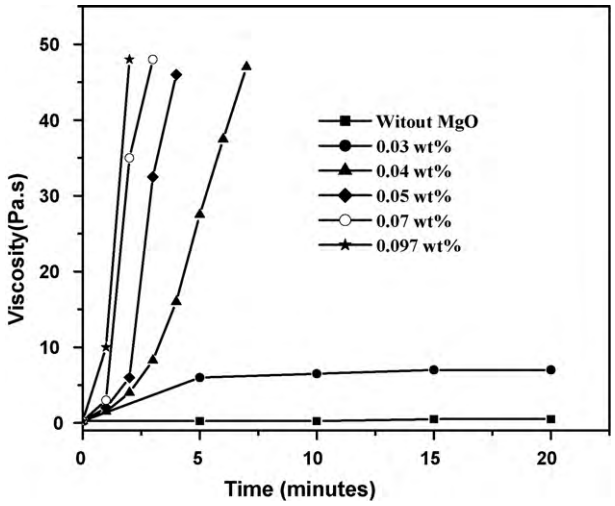

Fig. 4. Viscosity variation with time of 50 vol.% PZT slurries containing various amounts of MgO at 60 °C (spindle-SC-28, shear rate-2.8 s^{-1}).

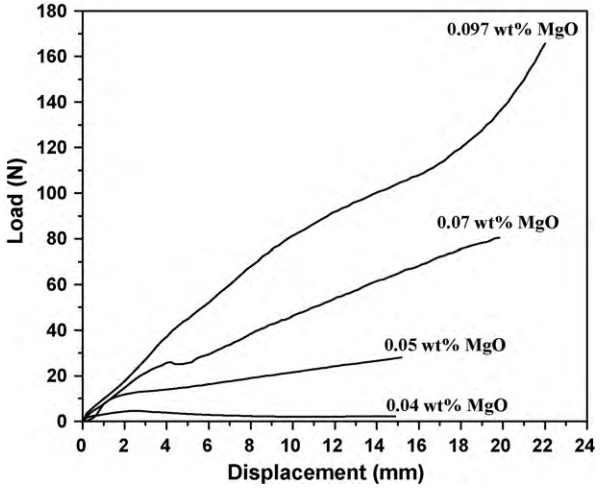

Fig. 6. Compressive load–displacement graph of the gelled bodies prepared from 50 vol.% PZT slurries containing various MgO concentrations.

using SC-28 spindle at a shear rate of 2.8 s^{-1}. The slurry without MgO showed a viscosity increase from 0.25 to 0.5 Pa s in 20 min at 60 °C. This small viscosity increase is attributed to loss of water due to evaporation. Viscosity of the PZT slurry containing 0.03 wt% MgO increased rapidly from 0.25 to 6 Pa s in 5 min. Further, the viscosity increased slowly with time and reached a value of 7 Pa s at the end of 20 min. At higher MgO concentrations the slurries rapidly reached gel-like consistency at 60 °C. The time required to reach gel-like consistency at MgO concentrations of 0.04, 05, 07 and 0.097 wt% are 7, 4, 3 and 2 min, respectively. That is, faster coagulation of the slurries after casting could be achieved by heating.

Fig. 5 shows viscosity at various shear rates of PZT DCC slurries containing various MgO concentrations. The slurries were mixed thoroughly with MgO at a temperature of ∼5 °C by mechanical stirring for 20 min before the viscosity measurements. The slurries in general showed shear thinning flow behavior. The slurries containing MgO concentration of 0.04, 0.05, and 0.07 wt% showed similar viscosity values. The viscosity values are in the range of 0.0825–0.225 Pa s at shear rate in the range of 93–4.65 s^{-1}. However, the slurries containing MgO concentration of 0.097 wt% showed slight higher viscosity and shear thinning flow behavior. The viscosity of the PZT slurry containing MgO concentration of 0.097 wt% is in the range of 0.1125–0.3 Pa s at shear rates in the range of 93–4.65 s^{-1}. However, the viscosity of the DCC slurries containing all the four MgO concentrations is sufficiently low to flow in to mould of any intricate shape.

The DCC slurries, prepared at MgO concentration in the range of 0.04–0.097 wt%, cast in closed stainless steel mould could be removed as coagulated bodies without any deformation after aging for 4–1 h, respectively at room temperature. However, the coagulation could be achieved at time less than 10 min by keeping the slurries cast in the mould in an oven at a temperature of 70 °C. Fig. 6 shows compressive load–displacement graph of the wet-coagulated bodies prepared from 50 vol.% PZT slurries containing various MgO concentrations. The wet-coagulated bodies prepared at 0.04 wt% MgO

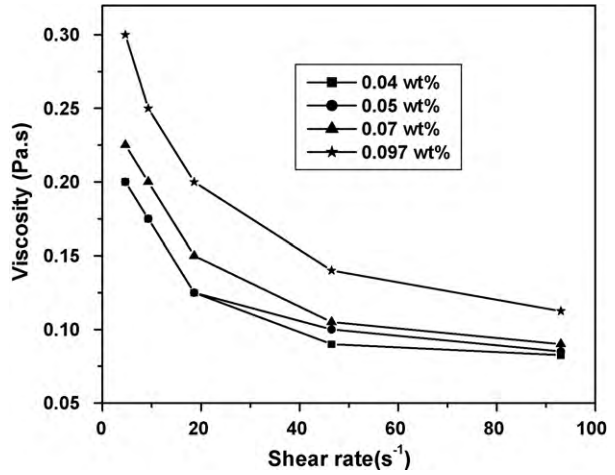

Fig. 5. Viscosity at various shear rates of PZT DCC slurries containing various MgO concentrations (spindle-SC-21).

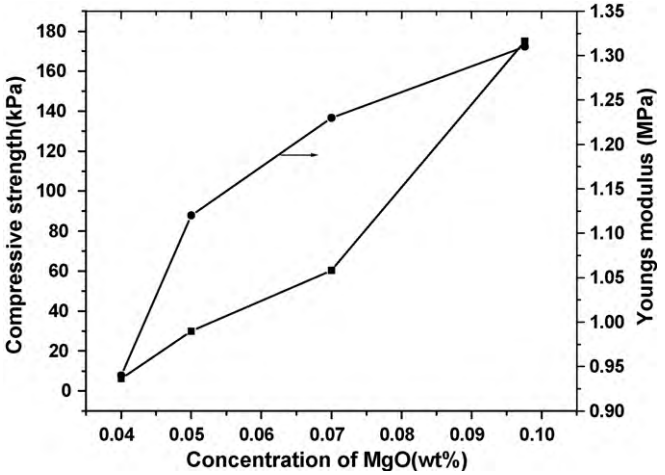

Fig. 7. Effect of MgO concentration on strength and Young's modulus of gels prepared from 50 vol.% PZT slurries.

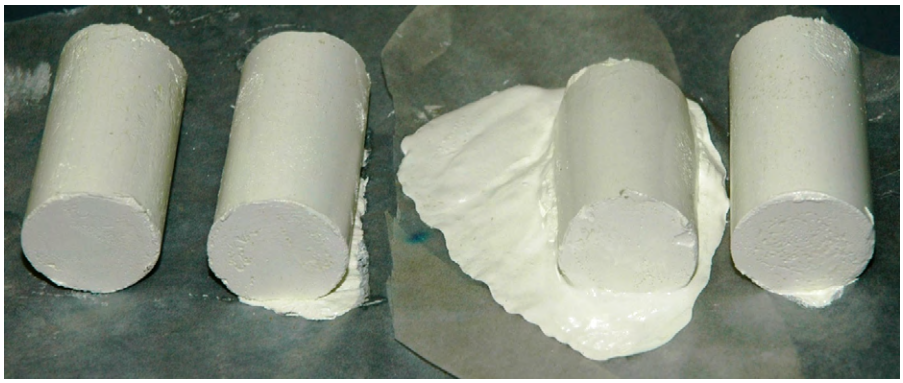

Fig. 8. Photograph showing the relative stability of the gels repaired at various MgO concentrations against the oscillatory stresses. Bodies after vibration test (from left) 0.07 wt% MgO, 0.05 wt% MgO, 0.04 wt% MgO, 0.04 wt% MgO (before vibration test).

showed elastic behavior at low compressive load and a characteristic yield point. Beyond the yield point, plastic deformation develops. As the MgO concentration increases, strain-hardening effect is observed beyond the yield point. The strain-hardening effect is remarkably high at MgO concentration of 0.097 wt%. The compressive strength (defined as yield stress) and Young's modulus values of the wet-coagulated bodies increased with increase in MgO concentration. The wet-coagulated bodies prepared from slurries containing MgO concentrations in the range of 0.04–0.097 wt% showed a compressive strength in the range of 6.2–175 kPa, respectively. The corresponding Young's modulus values are in the range of 0.94–1.31 MPa, respectively. Fig. 7 shows compressive strength and Young's modulus of the wet-coagulated bodies prepared from 50 vol.% slurries containing various amounts of MgO. Though the strength of wet-coagulated bodies prepared even at low MgO concentration of 0.04 wt% is enough to withstand its weight (no sagging was observed during aging), have poor capability to withstand oscillatory stresses. Fig. 8 shows photograph of the wet-coagulated bodies prepared at various MgO concentrations after the vibration test. The wet-coagulated body prepared at MgO concentration of 0.04 wt% started flow during the vibration test. However, the wet-coagulated body prepared at MgO concentration of 0.05 wt% showed only slight deformation at the bottom of the sample touching the vibrating surface. No deformation has been observed for the wet-coagulated body prepared at MgO concentrations of 0.07 and 0.097 wt% during the vibration test.

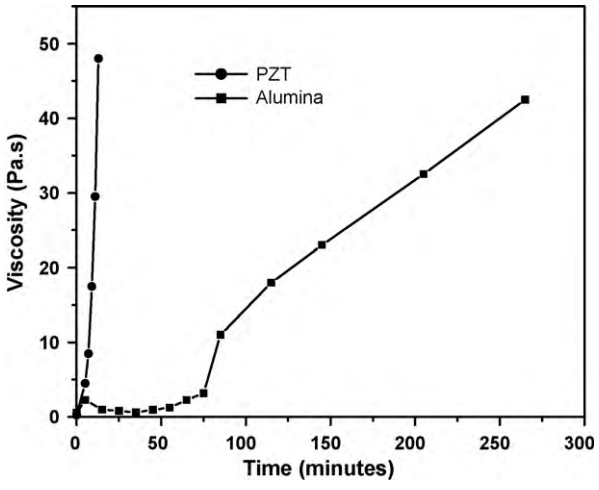

Fig. 9. Viscosity variation with time of 50 vol.% PZT and alumina suspensions prepared at 0.85 wt% dispersant on the addition of 0.192 wt% of MgO at room temperature (spindle-SC-28, shear rate-2.8 s^{-1}).

The mechanism of coagulation of alumina suspensions by MgO is reported in our previous publication [19]. In the case of alumina suspension, at higher ammonium poly(acrylate) concentration, viscosity remains more or less constant until majority of the un-adsorbed ammonium poly(yacrylate) present in the dispersion medium react with the Mg^{2+} ions produced from MgO [19]. Thereafter, the viscosity of the suspension increased with time and finally forms a gel due to desorption of ammonium poly(acrylate) from particle surface. Unlike alumina suspensions, the viscosity of the PZT suspensions increased with time immediately after the addition of MgO. Fig. 9 shows viscosity variation with time of 50 vol.% PZT and alumina suspensions prepared at 0.85 wt% dispersant on the addition of 0.192 wt% of MgO at room temperature. The amount of MgO added was equivalent to react with all COO^{-} groups present in the ammonium poly(acrylate). It appears that, in the case of PZT suspensions, the Mg^{2+} ions generated from the MgO react both with the un-adsorbed ammonium poly(acrylate) in the dispersion medium and the ammonium poly(acrylate) adsorbed on the PZT particle surface simultaneously. The reaction of Mg^{2+} with the ammonium poly(-acrylate) adsorbed on the particle surface resulted in bridging of the PZT particles. This bridging of PZT particles by Mg^{2+} ions through the ammonium poly(acrylate) adsorbed on the particles resulted in rapid viscosity increase and gelation of the suspension. Further, the wet-coagulated body prepared from 50 vol.% PZT suspension at dispersant concentration of 0.43 wt% and at MgO concentration of 0.097 wt% showed very high compressive strength (175 kPa) compared to the strength of wet-coagulated bodies (3.7 kPa) prepared from 50 vol.% alumina slurry at the same dispersant and MgO concentrations [21]. The higher strength of wet-coagulated bodies also suggests the cross-linking of PZT particles by Mg^{2+} ions through the ammonium poly(acrylate) adsorbed on the particle surface. Differences in mechanism of coagulation of

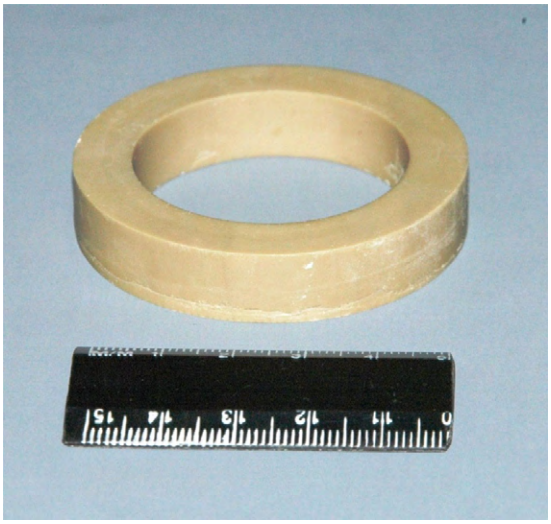

Fig. 10. Photograph of a sintered PZT ceramic ring fabricated by the DCC process.

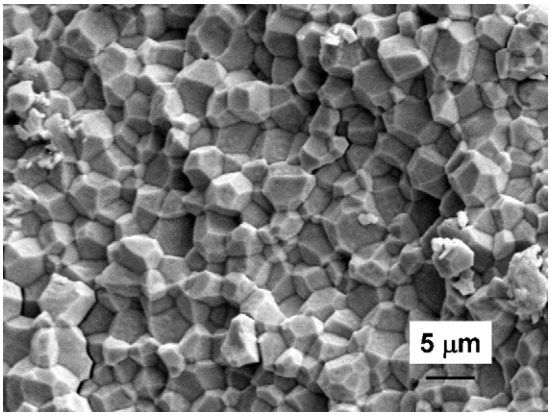

Fig. 11. SEM microstructure of fractured surface of PZT ceramic prepared by the DCC process (MgO concentration 0.1 wt% of PZT).

Table 1
Piezoelectric characteristics of PZT ceramic prepared by DCC and powder pressing.

Sample	Dielectric constant (εr)	Loss factor (Tan δ)	Average D33 (pC/N)
DCC (with 0.097 wt% MgO)	3200	0.030	540
Powder pressing (without MgO)	3000	0.027	560

PZT powder suspensions from that of alumina are attributed to strong adsorption of ammonium poly(acrylate) on PZT particle surface compared to weak and highly reversible adsorption on alumina surface [19]. It appears that a fraction of the carboxylate groups in the dispersant forms complex with lead atoms present in the particle surface and the remaining extend in to the medium to provide electrosteric stabilization. The formation of this surface complexes results in strong adsorption of ammonium poly(acrylate) on PZT particles. This is further evidenced from the fact that ammonium poly(acrylate) dispersed aqueous suspensions of another lead containing ceramic powder, PMN-PT (in house prepared), also showed coagulation characteristics similar to the PZT suspensions upon the addition of MgO [25].

As the concentration of MgO increases the rate of reactions leading to the coagulation of the slurry increases due to higher amount of Mg^{2+} generated [20]. This leads to higher rate of viscosity increase of the suspension containing higher concentration of MgO at room temperature. It is well known that solubility increases with increase of temperature. Rapid coagulation (after casting) of the slurries on heating is because of higher rate of reactions leading to coagulation due to higher solubility of MgO at higher temperature [20].

The Mg^{2+} ions generated from 0.04 g MgO is equivalent to react only with nearly 40% of the COO^- groups present in the 0.43 g ammonium poly(acryl ate). However, Mg^{2+} ions generated from 0.097 g MgO is equivalent to react with all of the COO^- groups in 0.43 g ammonium poly(acrylate). That is, as the amount of MgO added in the slurry increases, the number of cross-linking between the PZT particles by Mg^{2+} ions through the poly(acrylate) adsorbed on the particle surface increases and the number of cross-links attains its maximum at 0.097 wt% MgO. Higher compressive strength and stability against oscillatory stresses of the wet-green bodies prepared at higher MgO concentration is due to this enhancement in number of the cross-links. This increase in wet strength might also be due to local rearrangement of particles due to syneresis of the polymer network [2]. This enhancement in number of cross-links at higher MgO concentration is further evidenced by the remarkable strain-hardening observed in gels prepared at 0.097 wt% MgO during compressive load–displacement measurements [26].

The strength and stability of the wet-coagulated body is sufficiently high for successful removal of a circular ring prepared by gelation of the slurry in a mould. The green PZT ring undergoes isotropic sintering shrinkage so that no deformation of shape was observed during sintering. Fig. 10 shows a PZT ceramic ring fabricated by the DCC process. Microstructure of the sintered PZT ceramic observed on a fractured surface shows intra-granular fracture. Average grain size calculated from the microstructure by linear intercept method is 3.5 μm. The PZT ceramic fabricated by powder pressing followed by sintering at 1290 °C showed more or less similar microstructure. Fig. 11 shows SEM microstructure of fractured surface of PZT ceramic prepared by the DCC process.

The piezoelectric characteristics of PZT ceramic prepared by the DCC process (0.097 wt% MgO) are given in Table 1. The dielectric constant, loss factor and average piezoelectric charge coefficient (d_{33}) value of the PZT ceramic prepared by the DCC process using 0.097 wt% MgO is 3000, 0.027 and 560 pC/N, respectively. The corresponding values for the PZT ceramic prepared without MgO by powder pressing are 3200, 0.030, and 540 pC/N, respectively. The results suggest that small amount of MgO added as coagulating agent have only minor effect on the piezoelectric properties of PZT ceramics.

4. Conclusion

Coagulation of aqueous PZT powder suspensions prepared using ammonium poly(acrylate) by MgO coagulating agent is by cross-linking of PZT particles by Mg^{2+} ions through the

ammonium poly(acrylate) molecules adsorbed on particle surface. The particle cross-linking facilitates faster coagulation of the slurries cast in a mould and provides higher strength and stability to the coagulated bodies which enable easy and early (within 1 h after casting) mould removal. The small amount (∼0.1 wt%) of MgO added as coagulating agent had only minor effect on the piezoelectric properties of the sintered PZT ceramics.

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