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Fabrication of lead zirconate titanate ceramic fibers by gelation of sodium alginate

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Abstract

A novel ceramic fiber processing method by gelation of Na-alginate, a natural innoxious polymer, is reported. The ion exchange reaction between Na and Ca, and associated gelation process is utilized to fabricate lead zirconate titanate piezoelectric ceramic fibers using a Na-alginate based ceramic suspension. Effects of solid loading, viscosity of the starting sodium alginate and its amount in the slurry, and the chelator content were investigated as main parameters in obtaining uniform, dense fibers. Slurries with 64 wt% solid loading containing 1.0–1.5 wt% low or 0.5 wt% medium viscosity Na-alginate and 0.25–1.0 wt% chelator resulted in dense fibers with uniform shapes and dimensions. Electrical measurements taken from pellets prepared from reprocessed slurry and fibers indicate a decrease in the properties with increasing Na-alginate content of the slurry. However, the dielectric constant and piezoelectric charge coefficient values prove that this is a viable process to produce piezoelectric ceramic fibers.

Keywords: B. Fibers; D. PZT; Suspensions; Gelation

1. Introduction

Composite materials provide engineered properties by combining the best aspects of the constituents while minimizing their undesired features. Research on piezoceramic–polymer composites (piezocomposites) with various connectivity types, described by Newnham et al. [1], was first started in the late 1970s [2]. Among these, the most widely studied, understood and utilized two-phase piezocomposite is the 1–3 piezocomposites where individual piezoelectric ceramic rods, or fibers, aligned in a direction parallel to the poling direction, are surrounded by a polymer matrix. The rod diameter, rod spacing, composite thickness, volume percent of rods, and polymer compliance all influence the performance of these composites [3].

There are three major processes developed to produce piezoceramic fibers; extrusion [4], viscous suspension spinning process (VSSP) [5] and sol–gel method [6]. Additionally, injection moulding became a mass production method to prepare 1–3 piezocomposites [7]. The main differences between these processes are the precursors used in obtaining the green fibers and the way the green fibers are shaped prior to sintering. The variations in the processing conditions may create differences in the shape and microstructure of the fibers which in turn influences the mechanical and electrical properties of the resultant products.

In this paper, details of fabrication of lead zirconate titanate (PZT) fibers using a novel process involving extrusion and gelation of a sodium alginate based PZT slurry are reported. Sodium alginate is a gelling polysaccharide that is generally obtained from brown kelp. It is soluble in water at room temperature and forms a three-dimensional network by chemical gelation in the presence of multivalent cations. Compared to other synthetic monomers that are used in coagulation of ceramic suspensions such as acrylamide, alginate is a non-toxic natural polymer. It is also more cost effective than other natural polymers without toxicity, such as agarose and gelatine. Therefore, alginates are being employed in traditional ceramic forming techniques, such as dry moulding, extrusion, slip casting to provide plasticity, workability, suspension stability, and suitable wet and dry strength. Sodium alginate was also used in gel-

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casting, tape-casting and solid free form fabrication techniques to produce ceramics [8,9].

The alginate gelation process have been used previously by Konishi et al. [10] to obtain Y-Ba-Cu-O based superconductor ceramic fibers, and by Shimizu and Takada [11] to prepare Bi-based superconductor ceramic fibers. In both of these studies, the biosorption of divalent metal ions from a solution by Na-alginate through metal ion exchange was used to obtain the stoichiometric ceramic composition. The preparation of the fiber form was achieved through gelation of the material due to the cross-linking of carboxyl groups in the presence of divalent metal ions.

However, in our study a novel route was pursued to prepare the fibers; a water based slurry prepared from a commercial lead zirconate titanate—$Pb(Zr_{0.52}Ti_{0.48})O_3$ (denoted as PZT) powder was used as the starting material and Na-alginate was used as the main fiber forming agent in the extrusion of the ceramic fibers. The optimum conditions to obtain the PZT fibers, the effect of the Na-alginate viscosity and tri-ammonium citrate content on the macro and microstructure of the fibers, and finally the electrical properties of the material are discussed.

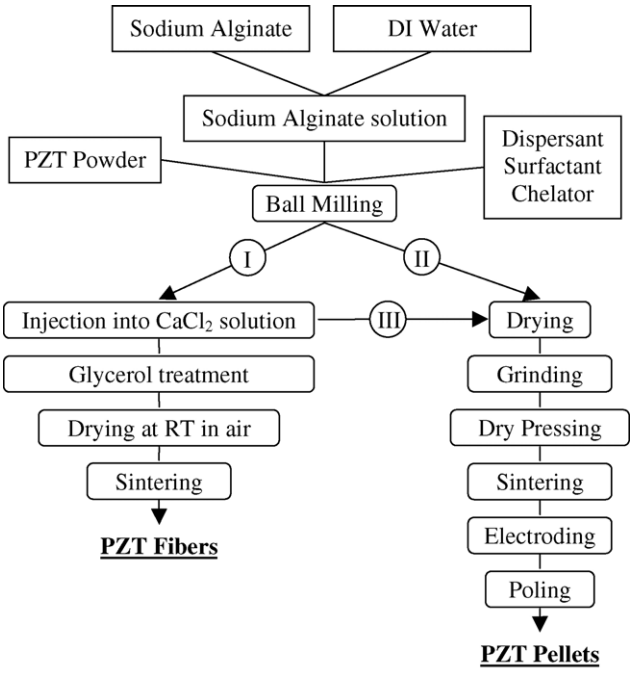

Fig. 1. Flow chart of the fiber and pellet forming process.

2. Experimental procedure

2.1. Starting materials

A commercial grade lead zirconate titanate powder (APC 850 from APC International Ltd.) with 2 wt% PVA binder was used in the PZT fiber preparation. Two different kinds of alginic acid sodium salt from brown algae (Sigma–Aldrich) were used as the Na-alginate source; one with a low viscosity (~250 cP at 2% soln.) and another with a medium viscosity (~3500 cP at 2% soln.). Calcium chloride dihydrate (Merck KGaA) was used for the ion exchange gelation process. Ammonium polyacrylate based Darvan 821 A (R.T. Vanderbilt Company, Inc.) was used as a dispersing agent to obtain a stable ceramic slurry. Surfynol 104E (Air Products and Chemicals, Inc.) was used as a surfactant to prevent foaming in the slurry. Tri-Ammonium citrate (Analar BDH Chemicals Ltd.) was used as a chelator to control the gelation time and ratio. Finally, Glycerol was used as a plasticizer to control the flexibility of the dried fibers.

2.2. Suspension preparation and fiber fabrication

The process flow chart is given in Fig. 1. Alginic acid sodium salt was dissolved in deionized water at 70 °C to form a solution. PZT powder was then added into this solution accompanied with dispersant (1.0 wt%), surfactant (0.065 wt%) and chelator. Chelator content was varied from 0.25 to 2.50 wt%. Detailed contents of the suspensions are given in Table 1. Excess water was added to obtain a low viscosity slurry for ball milling. It was then ball milled for 24 h using zirconia milling media to break up the agglomerates and obtain a uniform slurry. Ball milling was followed by removal of the excess water by heating while continuously stirring the slurry. The amount of additives and slurry preparation process

Table 1
PZT fiber processing conditions and uniformity of the products

Water/PZT	Alginate type[a] and content (wt%)	Tri-ammonium citrate (wt%)	Fiber[b]	Cross-sectional uniformity[c]
1:1	LV—0.50	–	×	N/A
	LV—1.00		×	N/A
	LV—1.25		×	N/A
	LV—0.50	–	×	N/A
	LV—1.00		✓	Diameter variation
	MV—0.50		✓	Uniform circular
	MV—1.00		×	N/A
1:2	MV—0.50	0.25	✓	Uniform circular
		0.50	✓	Ridges, circular
		0.75	✓	Ridges, ellipsoidal
		1.00	✓	Ridges, ellipsoidal
		1.25	✓	Ridges, ellipsoidal
		1.50	✓	Ribbon-like
	LV—1.00	0.25	✓	Diameter variation
		0.50	✓	Uniform circular
		0.75	✓	Ridges, circular
		1.00	✓	Ridges, circular
		1.25	✓	Ridges, circular
		1.50	✓	Ridges, ellipsoidal
	LV—1.50	0.50	✓	Diameter variation
		1.00	✓	Uniform circular
		1.50	✓	Uniform circular
		2.00	✓	Ridges, circular
		2.50	✓	Ridges, ellipsoidal

[a] LV: low viscosity; MV: medium viscosity.
[b] ✓: successful fiber preparation; ×: fiber form cannot be obtained.
[c] N/A: not applicable.

are determined based on our previous work on gel-casting of PZT ceramics [12].

The PZT fibers were obtained by injecting the slurry through a nozzle with a 0.5 mm inner diameter into a $CaCl_2$ solution. The Ca ion concentration in the solution was matched to the Na-alginate concentration of the slurry. The fibers were kept in the solution for 60 min to achieve full gelation and then 10 min in Glycerol to give additional plasticity and flexibility to the dry fibers. The drying was done at room temperature under atmospheric conditions for 24 h. Removal of the organic ingredients from the fibers was carried out in two steps, at 200 and 600 °C for 30 min each, with a slow heating rate of 100 °C/h to prevent cracking during this process. Sintering was done at 1285 °C for 30 min in closed alumina crucibles on corrugated Pt foils. The heating rate was 200 °C/h. The high surface/volume ratio in PZT fibers requires a careful control of the PbO partial pressure during sintering. In order to compensate PbO losses and achieve a 100% PZT yield, sintering process was carried out in the presence of $PbZrO_3$ buffer powders. The cooling rate was left to the furnace characteristics.

The microstructural features of the sintered fibers were examined by scanning electron microscopy. The phase analysis was done using X-ray diffraction. Due to the difficulty in taking direct electrical measurements from single fibers an indirect method was used to characterize the electrical properties. The slurry was divided into three parts; the first part (Route I in Fig. 1) was used to obtain the sintered fibers for microstructural characterization and composite preparation, the second part slurry (Route II in Fig. 1) was dried without fiber preparation and ground to a fine powder (reprocessed unjelled slurry), the third part slurry (Route III in Fig. 1) was injected into the $CaCl_2$ solution, and the dried fibers were crushed and ground to a fine powder (reprocessed jelled fibers). Pellets were prepared from the ground powders obtained from the second and third routes by uniaxial pressing under 100 MPa. These pellets were then sintered under identical conditions with the fibers, electroded and characterized by dielectric and piezoelectric measurements.

3. Results and discussion

3.1. Principle of fiber gelation

The gelation of Na-alginate in the presence of divalent Ca ions takes place according to the chemical reaction given in Eq. (1).

$$2\text{Na-alginate} + Ca^{2+} \leftrightarrow \text{Ca-alginate} + 2Na^{+} \quad (1)$$

The exchange of Na^+ ions with Ca^{2+} ions causes cross-linking of the linear polymers creating a three-dimensional network and confining ceramics particles to form a consolidated green body. This reaction and resultant gelation usually proceed with a very fast rate, such that solidified agent and chelator are added into sodium alginate solution simultaneously, thus the gelation between calcium ions and sodium alginate is avoided in the initial stages in the alginate based gel-casting studies to allow enough time for moulding [8,13]. However, in our process this high gelation rate is the main mechanism that allows the injected slurry to assume and keep a fiber form in the $CaCl_2$ solution. Therefore, chelator is only used to control shape and uniformity of the fibers through control of the amount of free Ca ions that are present in the solution.

3.2. Factors affecting the macro and microstructure of fibers

In our study, the final aim is to obtain piezoelectric ceramic fibers. These fibers are not expected to bear any significant mechanical load in field applications, but they would rather act as active sensing elements in a composite, transforming acoustical signals or minute mechanical vibrations into electrical signals or vice versa. Therefore, the most important properties of the PZT fibers are: (i) uniform shapes and dimensions which control their vibration modes and their electromechanical coupling efficiencies; (ii) a dense and defect free microstructure which has an influence on their dielectric strength; (iii) electrical properties which are mainly related to the materials used.

In this study, one of the main parameters in obtaining fibers was found to be the solid loading of the slurry. As presented in Table 1, processing runs with slurries containing 1:1 water to powder ratio (50 wt% PZT powder) did not yield fibers due to the low viscosity of the slurry whereas slurries with 1:2 water to powder ratio (64 wt% PZT powder) resulted in successful fiber preparation with up to 0.5 m length and 200–300 μm diameter (Fig. 2a). The microstructures of the fibers were found to be usually dense but with a small amount of micron size pinholes that are believed to result from the burn-out of the organics (Fig. 2b). The grain size was found to be fairly uniform and vary between 1 and 5 μm.

The uniformity of the shape and dimensions of fibers (macrostructure) were found to be controlled mainly by the viscosity and concentration of the alginate solution, as well as the chelator content of the slurry. Our experiments (Table 1) showed that the optimum Na-alginate solution concentration to prepare fiber forms are 1 and 1.5 wt% for low viscosity and 0.5 wt% for medium viscosity Na-alginate. Na-alginate concentrations beyond these limits yield slurries with either too low viscosity to allow fiber formation and slurry simply disperses in the $CaCl_2$ solution, or too high viscosity such that slurry cannot be extruded from the nozzle. As the alginate content of the slurry increased the diameter of the fibers tend to vary along the length. This is shown in Fig. 2c and d where fibers prepared from 0.5 wt% alginate slurry have a constant diameter whereas fibers prepared from 1.5 wt% alginate content have diameters varying along the fiber length. This diameter variation is believed to be due to the increasing viscosity of the slurry by increasing alginate content, and associated difficulty in extruding the slurry from the nozzle.

The chelator content of the slurry was found to be critical for the shape and symmetry of cross-section of fibers. Tri

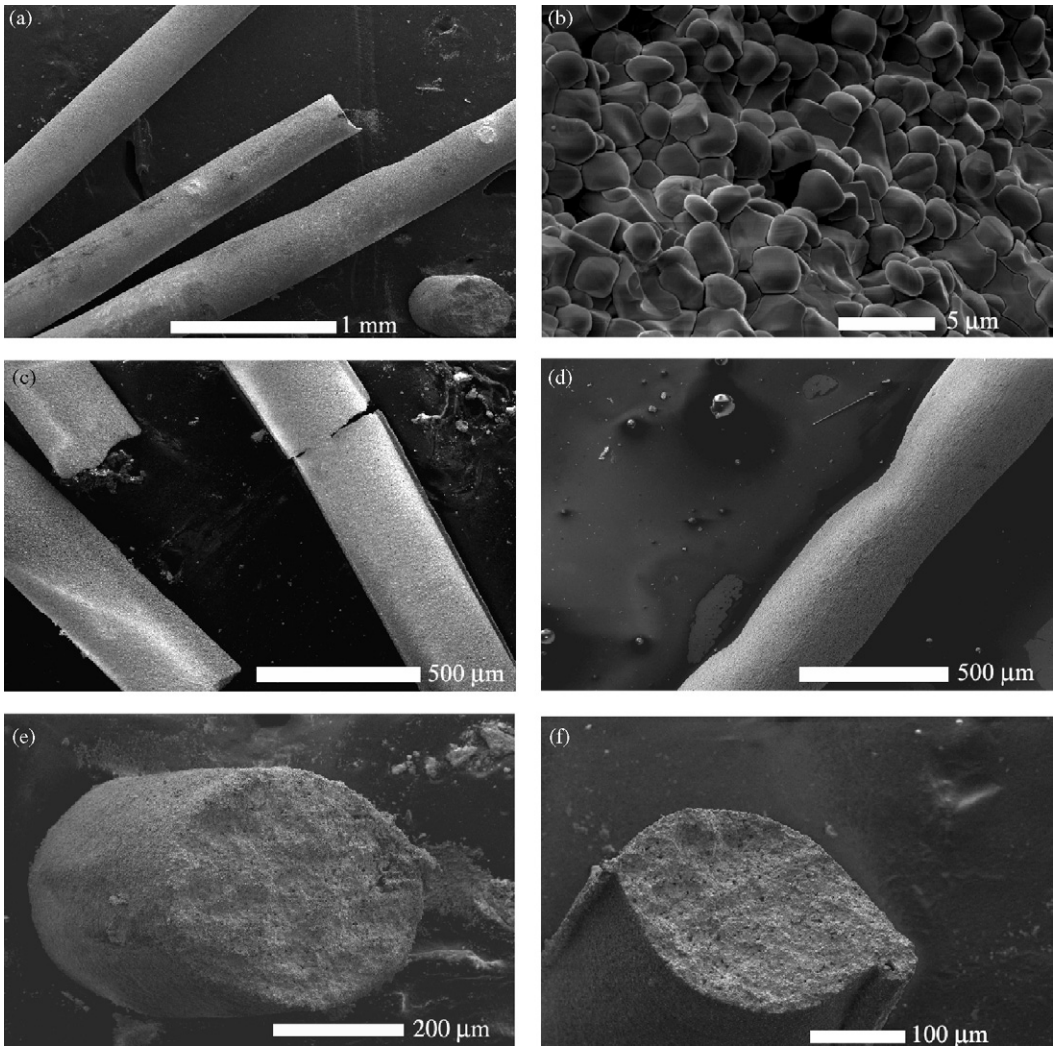

Fig. 2. SEM micrographs of PZT ceramic fibers: (a) general view; (b) microstructure; (c) fibers with uniform diameters; (d) fibers with varying diameters; (e) fibers with uniform circular cross-section; (f) fibers with ridges and ellipsoidal cross-section.

ammonium citrate $(NH_4)_3C_6H_5O_7$, was used as the chelator in our study. Chelator acts as a reagent that limits the content of free calcium ions in solution according to the chemical reaction given in Eq. (2).

$$2C_6H_5O_7^{3-} + 3Ca^{2+} \leftrightarrow Ca_3(C_6H_5O_7)_2 \quad (2)$$

When the amount of chelator increases in the slurry, it effectively decreases the amount of free calcium ions in the solution. This slows down the gelation rate and decreases the viscosity of the slurry. The chelator content was varied between 0.25 to 2.5 wt% in this study. As presented in Table 1, it was observed that low chelator content resulted in fibers with smooth surfaces and circular cross-sections (Fig. 2e) but increasing the chelator content beyond a certain limit caused fibers to float on the surface of the solution instead of staying submerged. This floating created fibers which have ellipsoidal cross-sections with ridge extensions on both sides, as shown in Fig. 2f. At the extreme case, ribbon-like fibers with very flat cross-sections were obtained. The exact chelator content required to obtain uniform fibers was found to depend on the Na-alginate content of the slurry and details are presented in Table 1. X-ray powder diffraction analysis of the sintered and crushed fibers is given in Fig. 3. The fibers have a polycrystalline perovskite structure.

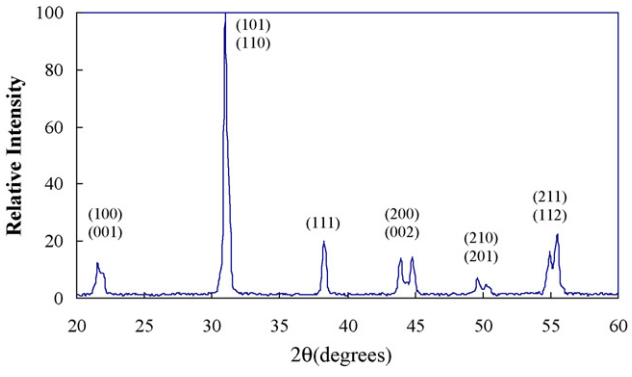

Fig. 3. XRD powder patterns of PZT ceramic fibers.

Table 2
Electrical properties of PZT pellets

	Alginate type[a] and content	Piezoelectric charge coefficient (pC/N)	Dielectric constant	Dielectric loss
Route II un-jelled	0.5 wt% MV	349	1804	0.013
	1.0 wt% LV	301	1658	0.013
	1.5 wt% LV	191	1297	0.011
Route III jelled	0.5 wt% MV	337	1576	0.011
	1.0 wt% LV	231	1127	0.011
	1.5 wt% LV	160	1209	0.012
Manufacturer's data		400	1750	0.014

[a] LV: low viscosity; MV: medium viscosity.

3.3. Electrical properties of the pellets

As indicated in the preceding section, electrical properties are mainly related to the materials used in obtaining the ceramic. And although commercial PZT powder is used in this study, the chemicals used in the fiber preparation and gelation process are expected to influence these properties. This is mainly due to the fact that Na-alginate contains Na ions and, as a result of the metal ion exchange reaction that occurs during the gelation process, Ca ions are also introduced into the ceramic body. All the organics that are used in the consolidation processes can be removed by binder burn-out procedures, however, Na and Ca ions will remain in the structure even after sintering. Na^+ may act as an acceptor and Ca^{2+} as an isovalent Pb-site dopant in the perovskite structure [3]. They may, therefore, influence the electrical properties of the PZT fibers.

The effect of these ions on the electrical properties of the material would, however, be difficult to determine directly on single fiber filaments, due to the electroding and poling problems, and dimensional and microstructural variations observed in the fibers. We, therefore, decided to determine their effect by preparing pellets from samples taken at two different points in the fiber fabrication process. As explained in Section 2.2 and shown in Fig. 1, Route II sample pellets are prepared from dried and ground un-jelled slurry and contains only Na-alginate, whereas Route III sample pellets are prepared from jelled and dried fibers and contains Ca^{2+} ions, in addition to the Na^+ ions. The pellets were determined to have a density of over 97% of the theoretical density. The results of the electrical measurements are presented in Table 2.

The exact amount of Na^+ and Ca^{2+} ions in the pellets have not been determined but the results presented in Table 2 suggest that increasing amount of Na-alginate in the slurry increases the amount of Na^+ and Ca^{2+} ions in the resultant ceramic body. This in turn influences the electrical properties adversely. Nevertheless, these properties are still respectably well and warrant the viability of using this process in fabricating PZT fibers.

4. Conclusions

Lead zirconate titanate piezoelectric ceramic fibers with 200–300 μm diameter, uniform shape and dimensions were successfully prepared using a novel alginate gelation process. Effects of solid loading, viscosity of the starting sodium alginate and its amount in the slurry, and the chelator content were investigated as main parameters in obtaining uniform, dense fibers.

Slurries with 64 wt% solid loading was found to be suitable for fiber processing. The optimum Na-alginate solution concentration to prepare fiber forms are determined to be 1 and 1.5 wt% for low viscosity, and 0.5 wt% for medium viscosity Na-alginate. Slurries with Na-alginate concentrations beyond these limits cannot be processed into fibers due to either too low or too high viscosity. Tri ammonium citrate $(NH_4)_3C_6H_5O_7$, was used as the chelator to control gelation rate and slurry viscosity through control of the amount of free calcium ions in the medium. Chelator contents between 0.25 and 1.0 wt% yielded fibers with smooth surfaces and circular cross-sections but increasing the chelator content beyond this limit caused fibers with deformed cross-sections. Electrical properties measured from pellets prepared from reprocessed slurry or fibers indicate that increasing Na-alginate content influences the properties adversely, however, the properties are still reasonably well to allow the use of these fibers.

Piezoelectric ceramic fibers with uniform, shapes, dimensions and microstructure were prepared with this novel forming process. Next step will be to fabricate 1–3 composites using these fibers.

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