A comprehensive study on some binders for piezo-electric ceramics

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Binders play a vital role in formulating piezoelectric materials. A number of binders such as poly (vinyl alcohol) (PVA), methocel, starch, hydroxy propyl methyl cellulose (HPMC), hydroxy ethyl cellulose (HEC), poly vinyl pyrrolidone (PVP), gum-arabic, and poly ethylene glycol (PEG) have been studied for solubility, viscosity, pH, thermal behaviour and ash content incorporating them in a standard PZT formulation. Further, the resulting PZTs have been studied for green density, sintered density, shrinkage characteristics, microstructure, compressive strength and electrical properties. The generated data indicate that PVA is a potential candidate as a binder for this purpose.

Piezoelectric materials are special type of ceramics which under the influence of mechanical stress or strain generate piezoelectric charge. These materials have technological importance because of their versatility, reliability, low cost, and tailorability for desired applications.

Organic binders are very important additives for the processing of ceramics and provide green strength and plasticity to them. Such moulded bodies, once moulded, retain their shapes before the heat treatment. A good binder for ceramic applications provides high green strength, which is controlled by the polymer-to-polymer and polymer-to-ceramic interactions at a low usage level. The strength imparted by these binders varies with their molecular weights, e.g. waxes have low cohesive strengths (100 to 500 psi) whereas high molecular weight synthetic resins, e.g., PVA, etc., have high cohesive strengths (3000 to 10,000 psi) and impart strengths accordingly. The green strength results from bonding between particles induced by a binder and depends on binder quantity and its distribution. The green strength also depends on binder quantity and its distribution. After drying, packing ability of powder and intrinsic strength. The green strength of a ceramic compact is also important from the point of view of handling and machining.

For ideal bodies, green strengths are directly proportional to the cohesive or adhesive strengths of a binder. The applications requiring organic binders and demands placed on them have increased substantially as ceramics processing techniques have evolved. Further, mechanical performance of a binder is important to the compaction process as it provides satisfactory granule deformation, compact density, compact strength and compact separation from the punch and also burn out cleanly prior to sintering.

The green density is one of the most important parameters in the formation of ceramic articles. For a given ceramic powder, higher green density indicates better packing and results in less shrinkage during firing. The feed granules must deform, densify and adjourn into a monolithic compact with a uniform microstructure during granulation and consolidation of granulated powder.

The binders for ceramics are used in various processing techniques, e.g., dry pressing, injection moulding, tape casting, extrusion, slip casting. However, no systematic work is reported on the use of binders such as poly (vinyl alcohol) (PVA), methocel, starch, hydroxy propyl methyl cellulose (HPMC), hydroxy ethyl cellulose (HEC), poly vinyl pyrrolidone (PVP), gum-arabic, and poly ethylene glycol (PEG), etc., and other allied aspects. These binders have also been studied for properties such as solubility, viscosity, pH, thermal behaviour, and ash content. The aim of the present investigation is to study these binders in a standard PZT formulation and compare their properties such as green density, sintered density, shrinkage characteristics, microstructure, compressive strength and electrical properties, etc. The data generated on various binders and their effect in terms of various properties for standard PZT formulation are reported here.

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Experimental Procedure

Materials and binders

PZT ceramics mainly consisting of soft ferroelectric materials and binders, were obtained from various sources as:

- **Poly (vinyl alcohol) (PVA)** — White granules with specific gravity 1.26-1.31 and degree of hydrolysis 87-89%, were obtained from Gohsenol Ltd, Japan.

- **Methodcel** — White powder with specific gravity 1.39, refractive index 1.49 and M.P. 290-305°C was obtained from Fluka Ltd, Switzerland.

- **Starch** — Natural polymeric material having carbohydrate organic compound (moisture content 15.0% max.) was obtained from British Drug House (India) Ltd, Bombay.

- **Hydroxy propyl methyl cellulose (HPMC)** — Derivative of methyl cellulose with high surface activity and plastic flow properties, specific gravity 1.01 and pH ranging from 5 to 8.8 was obtained from DOW Chemicals Company, USA.

- **Hydroxy ethyl cellulose (HEC)** — Off white solid with sp. gravity 1.033, moisture content 5% (max.) and pH 6-7, was obtained from Interlab (India) Inc., Bombay.

- **Polvinyl pyridone (PVP)** — Molecular Weight 40,000 and glass transition temperature (T_g) 175°C, was obtained from Burogoyne Burdriges & Co. (India) Ltd, Bombay.

- **Gum arabic** — A natural binder with insoluble matter content 5% (max.) was obtained from Qualigens Fine Chemicals, Glaxo Ltd, Bombay.

- **Poly ethylene glycol (PEG)** — Solid granules with M.W. ~4000, density 1.212, and melting point 54-58°C was procured from Loba chemie Ltd, Bombay.

Sample preparation and characterization

This consists of several steps, i.e.: (i) Batch formulation (ii) Calcination (iii) Fine grinding (iv) Binder incorporation & granulation (v) Pressing (vi) Binder removal (vii) Sintering (viii) Lapping (ix) Electroding, and (x) Polarisation, as described in literature.

The PZT powder was granulated using different binders (3-8%) and used to prepare specimens of 20 mm dia and 1.5 mm thickness. The binder was subsequently removed over temperature 400-800°C for 4-6 h followed by sintering at 1200-1300°C for 2-4 h in order to achieve optimum sintered density. The specimens were lapped, electroded (silvered), and poled to achieve optimum piezoelectric properties. The samples were tested for electrical and mechanical properties.

The binders were tested for their solubility by preparing their 5% solutions in water. Viscosity measurement of the binder solutions was carried out using Brookfeld Viscometer, model RVT (supplied by M/s. Brookfeld Engineering Lab.Linc., USA) at 25°C. The pH of the binder solutions (5% conc.) was measured using pH meter (Philips India) at 25°C.

Netzsch Simultaneous Thermal Analyzer (STA) (Model 409) was used to obtain TG and DTA simultaneously. The instrument was provided with cylindrical platinum cups, Pt/Rh-Pt (10%) thermocouple and an electric thermal programmer to sense temperature over the range 20-1600°C at different heating rates. 10 mg of sample was heated linearly at a heating rate of 10°C/min against equal amount of reference sample (calcined alumina).

The ash content of various binders was measured after heating 10 g of sample at 600°C for 3 h in muffle furnace.

Testing of PZT ceramics

The specimens, processed with various binders having 20 mm dia and major faces electroded were used to study the various properties as per standard methods.

Density of test specimens was measured geometrically after green and sintered stages. The diameter and thickness were measured by micrometer, and density was calculated.

The sintered and lapped specimens (cylinder) having standard L/D ratio (length ~10 mm and diameter ~5 mm) were used for compressive strength measurement on Universal Tensile Testing Machine. The specimens were kept on a flat surface and load was gradually applied. The maximum load where the specimen (cylinder) got chipped off was noted down. Ten specimens with each binder were taken for testing and their average was reported as compressive strength.

The microphotographs of samples in green stage and sintered stage were obtained by using Scanning Electron Microscope (JOEL, JSM, Type-200 Kevex, Japan) at 5000x magnification and 40 Å resolution. The working distance was 20 mm and accelerating voltage was 25 kV.

The properties such as capacitance, dissipation loss factor, frequency, impedance, piezo electric charge constant (d33×10^-12 C/N), and Curie temperature, were measured experimentally, while properties such as dielectric constant (K_T), planar coupling coefficient...
piezoelectric voltage constant ($g_{33} \times 10^{-3}$ V/m/N), mechanical quality factor ($Q_m$), and frequency constant ($N_3 t$ -Hz-m) were calculated.

Results and Discussion

Solubility, pH and viscosity

Solubility, viscosity and pH values of various binders are given in Table 1. It is seen that PVA, starch, HEC and gum-arabic are soluble in hot water while PVP, PEG and methocel are soluble in cold water. Binders such as methyl cellulose (MC) and HPMC possess unusual properties of solubility, i.e., soluble in cold water and insoluble in hot water. Starch is a natural binder and is insoluble in cold water. The gum-arabic is an unrefined substance derived from plants and has very complex branched structure. It is ionic in nature and therefore, more sensitive to electrolytes. The pH data shows that pH is highest (6.77) in case of methocel, while lowest (4.24) for PVP. The pH values show the state of particulate dispersion in powder-liquid suspensions. As reported, flow behaviour of suspension indicates extensive flocculation at pH ~3, whereas well dispersed suspension at pH ~10. This is true for methocel, HPMC, and starch showing pH ~6.20 to 6.77 where well dispersed suspensions are obtained as compared to other binders. In case of PVP, pH is on lower side (4.24) indicating its sensitivity to the rate of polymerization. HEC has a pH ~4.84 indicating largest hydration time. Gum-arabic has pH of 4.51 and indicates low range of viscosity, while maximum viscosity is in the pH range 6 to 7.

The viscosity of binder solution in ceramic processing affects green strength which mainly depends on the suspension of binder with fine particulates. In general, if viscosity is on a higher side, it leads to non-uniform mixing of binder during granulation process. On the other hand, if viscosity is on a lower side, flow rate is very fast which reduces granulation time but this generally increases the grain size distribution and porosity. If viscosity is in a medium range, it results in proper binding and controlled granule size.

Viscosity of solution also affects settling rate which is less in the high viscosity liquids and becomes zero when viscosity is sufficiently high. The presence of binder solution or gel between particles greatly alters flow properties of systems.

It is seen that viscosity of PVP and PEG is 8 cPs and 10 cPs, respectively (low range), PVA and methocel belong to medium range of viscosity (85-98 cPs) while starch, HPMC and HEC have viscosity 160-691 cPs (high range).

During processing, it is seen that samples consolidated from suspensions having medium range of dispersions tend to have high density and homogeneous compacts while samples consolidated from the flocculated suspensions show improper consolidation leading to tightly packed particle clusters (flocs) with large amount of intercluster (inter floc) porosity. Further, ceramic specimens prepared from flocculated suspensions remain highly porous after sintering leading to low sintered density and poor electrical properties.

Thermal behaviour of binders

The organic binders are added to ceramic formulations in order to compact the ceramic powder

<table>
<thead>
<tr>
<th>Binder</th>
<th>Solubility in water</th>
<th>Viscosity (cPs) at 25°C</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (vinyl alcohol)</td>
<td>Boiling water</td>
<td>85</td>
<td>5.28</td>
</tr>
<tr>
<td>Methocel</td>
<td>Room temperature water</td>
<td>98</td>
<td>6.77</td>
</tr>
<tr>
<td>Starch</td>
<td>Boiling water</td>
<td>300</td>
<td>6.20</td>
</tr>
<tr>
<td>Hydroxy propyl methyl cellulose</td>
<td>Warm water</td>
<td>160</td>
<td>6.41</td>
</tr>
<tr>
<td>Hydroxy (ethyl cellulose)</td>
<td>Boiling water</td>
<td>691</td>
<td>4.85</td>
</tr>
<tr>
<td>Poly (vinyl pyrrolidone)</td>
<td>Room temperature water</td>
<td>08</td>
<td>4.24</td>
</tr>
<tr>
<td>Gum-arabic</td>
<td>Boiling Water</td>
<td>12</td>
<td>4.51</td>
</tr>
<tr>
<td>Poly (ethylene glycol)</td>
<td>Room temperature water</td>
<td>10</td>
<td>4.95</td>
</tr>
</tbody>
</table>
without formation of voids, cracks, porosity and distortion. The presence/absence of such defects is largely indicated by their thermal behaviour. Several investigators studied various binders for different applications and emphasized their importance in the ceramic processing.\(^{10-19}\) The data derived from DTA curves of various binders is are in Table 2 as well as in the following text.

**Poly (vinyl alcohol)** — The DTA curve shows a broad exotherm with five shoulder peaks, peak maxima \((T_m)\) at 342°C and only one endotherm at 441°C. The TGA curve shows no weight loss up to 235°C, but the weight loss is rapid beyond 235°C with a total loss of 92% up to 600°C.

**Methocel** — The DTA curve shows three exotherms from 288°C to 558°C. The TG curve shows 70% weight loss over a temperature range of 250°C to 350°C due to oxidative degradation of binder. Subsequently, weight loss continues beyond 350°C resulting in total loss of binder of 88% at 600°C.

**Starch** — The DTA curve shows two exotherms in the temperature range 363-543°C. The TG shows sudden weight loss of 58% from 265°C to 360°C. Subsequently, the weight loss increases slowly and becomes 80% at 600°C.

**Hydroxy propyl methyl cellulose (HPMC)** — The DTA curve shows four exotherms ranging from 232°C to 480°C and two endothermic peaks at 309°C and 357°C, respectively. The TG shows weight loss of 78% over a temperature range of 230°C to 375°C and finally, weight loss becomes 85% at 600°C.

**Hydroxy (ethyl cellulose)** — The DTA curve shows four exotherms ranging from 249°C to 675°C. TG shows 60% weight loss over a temperature range of 225°C to 365°C, 10% over a temperature range of 365°C to 610°C, and 17% over a temperature of 610°C to 690°C, totalling a weight loss of 87% over a temperature range of 225-690°C.

**Poly (vinyl pyrrolidone)** — There are two broad exotherms in the DTA curve over a temperature range 180-600°C. Also, there is an endothermic peak at 467°C. The TG shows a weight loss of 73% from 270°C to 465°C and 19% over a temperature range of 465°C to 655°C.

**Gum-arabic** — The DTA curve indicates three exotherms from 300°C to 500°C. In TG, weight loss occurs in three stages: 57% over a temperature range 220°C to 330°C, 12% over a temperature range of 330°C to 435°C and 12% over a temperature range of 435°C to 600°C.

**Poly (ethylene glycol)** — The DTA curve shows three exotherms over a temperature range of 67°C to 437°C. TG shows no change in weight up to 178°C. The weight loss of 90% is observed over a temperature range 179°C to 353°C indicating a maximum weight loss at the lowest temperature and 9% loss is observed over a temperature range of 353°C to 437°C.

Thermal behaviour of binders indicates the temperature conditions for binder removal from ceramic compacts which is beneficial during processing to avoid cracks, porosity, deformation in ceramics. A maximum weight loss at a low temperature indicates low working temperature. As seen in case of PVA and PEG, 90% loss is seen up to 250°C, while methocel, HPMC, starch show 70-80% weight loss up to 400°C. In other words, it means requirement of higher temperatures for complete binder removal in case of methocel, HPMC and starch.

It has been reported in the literature\(^{20-25}\) that many physico-chemical processes occur during binder removal and therefore, optimization of processing conditions is considered essential to achieve reproducible data.

The DTA/TG data (Table 2) show that 90% weight loss is observed in case of PVA at temperature as low as (240°C) which is indicative of short thermal cycle for binder removal. On the other hand, HEC binder requires higher temperature, which is not desirable, for its complete removal in processing of piezoelectric ceramics.

**Ash content, green density, sintered density and shrinkage characteristics**

Zero level of ash content imparts excellent properties to ceramic materials, while its higher level affects their microstructures and hence performance. Therefore, ash content of polymers is very important in order to judge their suitability as binders for piezoelectric materials. It is seen from the ash content data on various binders (Table 3) that ash content varies from 0 to 4% which suggests a significant variation in the oxidative thermal behaviour of these binders. PVA, PEG and PVP show complete loss at 600°C with zero level of ash content while starch, HPMC and methocel have less ash content (max. 0.5%). Gum-arabic and HEC show ash content of 2.90% and 3.87%, respectively which suggests presence of carbon residue in the end.
Table 2 — DTA and TGA data for various binders

<table>
<thead>
<tr>
<th>Binder</th>
<th>Maximum weight loss (%) at 600°C</th>
<th>Exothermic peak maxima (°C)</th>
<th>Endothermic peak maxima (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (vinyl alcohol)</td>
<td>92.00</td>
<td>342.0</td>
<td>441.0</td>
</tr>
<tr>
<td>Methocel</td>
<td>88.00</td>
<td>355.0</td>
<td>No endothermic peak</td>
</tr>
<tr>
<td>Starch</td>
<td>80.00</td>
<td>363.0</td>
<td>No endothermic peak</td>
</tr>
<tr>
<td>Hydroxy propyl methyl cellulose</td>
<td>85.00</td>
<td>254.0</td>
<td>357.0</td>
</tr>
<tr>
<td>Hydroxy (ethyl cellulose)</td>
<td>87.00</td>
<td>293.0</td>
<td>No endothermic peak</td>
</tr>
<tr>
<td>Poly (vinyl pyrolidone)</td>
<td>92.00</td>
<td>578.0</td>
<td>467.0</td>
</tr>
<tr>
<td>Gum-arabic</td>
<td>81.00</td>
<td>460.0</td>
<td>421.0</td>
</tr>
<tr>
<td>Poly (ethylene glycol)</td>
<td>95.00</td>
<td>237.0</td>
<td>368.0</td>
</tr>
</tbody>
</table>

Table 3 — Ash content, green and sintered density and shrinkage characteristics of PZT ceramics

<table>
<thead>
<tr>
<th>Binder</th>
<th>Ash content (%)</th>
<th>Green density (g/ml)</th>
<th>Sintered density (g/ml)</th>
<th>Shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (vinyl alcohol)</td>
<td>0.00</td>
<td>5.00</td>
<td>7.60</td>
<td>15.00</td>
</tr>
<tr>
<td>Methocel</td>
<td>0.25</td>
<td>4.98</td>
<td>7.57</td>
<td>15.70</td>
</tr>
<tr>
<td>Starch</td>
<td>0.50</td>
<td>4.96</td>
<td>7.65</td>
<td>15.60</td>
</tr>
<tr>
<td>Hydroxy propyl methyl cellulose</td>
<td>0.30</td>
<td>4.95</td>
<td>7.60</td>
<td>15.50</td>
</tr>
<tr>
<td>Hydroxy (ethyl cellulose)</td>
<td>3.87</td>
<td>5.00</td>
<td>7.66</td>
<td>15.50</td>
</tr>
<tr>
<td>Poly (vinyl pyrolidone)</td>
<td>0.00</td>
<td>4.94</td>
<td>7.66</td>
<td>16.30</td>
</tr>
<tr>
<td>Gum-arabic</td>
<td>2.90</td>
<td>5.03</td>
<td>7.65</td>
<td>15.00</td>
</tr>
<tr>
<td>Poly (ethylene glycol)</td>
<td>0.00</td>
<td>4.75</td>
<td>7.69</td>
<td>16.50</td>
</tr>
</tbody>
</table>

This data infers that PVA and PEG are expected to be useful binders for processing PZT ceramics because of negligible ash content. The binder such as starch, HPMC and methocel have less ash content. Gum arabic and HEC are not used because of their high ash content which affects the piezoelectric properties.

The density and shrinkage data of ceramics with different binders are also given in Table 3. The density of specimens indicates degree of compaction (formation) and shrinkage during sintering and therefore, PVA based PZTs have maximum green density (5.0 g/ml) while HEC and gum-arabic based PZTs have green density equal to PVA. On the other hand, HPMC, methocel, PVP and PEG based PZTs have green density on lower side (4.75 g/ml).

The green density also indicates the distribution of binder, wettability of the particulates during processing, adhesion after drying, packing ability of the powder and intrinsic strength of the binder. The samples showing less green density may require higher pressures for compaction so that agglomerates are deformed and bond ceramic particles together. The shrinkage data indicate direct relation with green density.
density, and samples with low green density have higher shrinkage (varies from 15% to 16.5%) (Table 3). In case of PVP and PEG, shrinkage is 16.30% and 16.50%, respectively suggesting low green density. The shrinkage in gum arabic is minimum (15.00%) indicating high green density. If shrinkage is of high order, it promotes rapid grain growth and thus high porosity.

It is also observed that all specimens incorporated with the binders under study show maximum theoretical density (90%) with different extent of shrinkage. The rate of grain growth during sintering depends upon the rate of shrinkage and inhibition of grain growth plays an important role to reduce porosity in the compact. Interestingly, the specimens with PEG, PVP, starch have low green density, but high rate of shrinkage to achieve required theoretical density. The scanning electron micrographs of the samples clearly show variation in the grain size and porosity for the same density.

**Scanning electron micrographs**

The microphotographs of ceramics reveal particles packing in green as well as sintered bodies. The data on green samples are given in Table 4 and microphotographs of these binders recorded by scanning electron microscope are presented in Figs 1-4. The data indicate the extent of porosity in the specimens. It is observed that the specimens compacted with PVA (Fig. 1), and PVP (Fig. 2) show less pore diameter ~1.2 μm and therefore, impart maximum green density. In contrast, gum arabic

<table>
<thead>
<tr>
<th>Binder</th>
<th>Green average pore dia (μm)</th>
<th>Sintered average grain size (μm)</th>
<th>Sintered average pore dia (μm)</th>
<th>Compressive strength of sintered PZT (kg/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (vinyl alcohol)</td>
<td>1.00</td>
<td>1.56</td>
<td>1.13</td>
<td>32.15</td>
</tr>
<tr>
<td>Methocel</td>
<td>1.74</td>
<td>1.98</td>
<td>2.19</td>
<td>16.79</td>
</tr>
<tr>
<td>Starch</td>
<td>—</td>
<td>1.62</td>
<td>1.51</td>
<td>36.21</td>
</tr>
<tr>
<td>Hydroxy propyl methyl cellulose</td>
<td>1.10</td>
<td>1.98</td>
<td>1.61</td>
<td>18.45</td>
</tr>
<tr>
<td>Hydroxy (ethyl cellulose)</td>
<td>1.18</td>
<td>2.56</td>
<td>1.71</td>
<td>21.29</td>
</tr>
<tr>
<td>Poly (vinyl pyrolidone)</td>
<td>1.21</td>
<td>—</td>
<td>—</td>
<td>27.09</td>
</tr>
<tr>
<td>Gum-arabic</td>
<td>1.73</td>
<td>2.53</td>
<td>2.26</td>
<td>25.27</td>
</tr>
<tr>
<td>Poly (ethylene glycol)</td>
<td>1.12</td>
<td>3.07</td>
<td>2.17</td>
<td>17.30</td>
</tr>
</tbody>
</table>

![Fig. 1 — SEM of piezoelectric ceramic green compact formed with poly (vinyl alcohol) as a binder (magnification 5000 x)](image1)

![Fig. 2 — SEM of piezoelectric ceramic green compact formed with poly (vinyl pyrolidone) as a binder (magnification 5000 x)](image2)
(Fig. 3) and methocel (Fig. 4) show pore diameter ~1.73 μm and 1.74 μm respectively suggesting porous material. It is also clear that the distribution is uniform in PVA, PVP, methocel, whereas samples with other binders show non-uniform binder distribution. Kingrey et al.⁹³ and Sproson et al.⁹⁴ studied the morphology of binder packing and internal pore distribution and reported that binder must adhere to ceramic powder particles and also it should be present in the pores interstices to impart strength to compacts.

The data on microstructure of sintered samples is given in Table 4 and Scanning Electron Microphotographs are represented in Figs 5-8. It is clear from the data that specimens with gum-arabic (Fig. 7) and HEC (Fig. 8) show higher grain size i.e. ~2.53 μm and 2.56 μm, respectively, indicating rapid grain growth without inhibition. On the contrary, samples with PVA (Fig. 5), and HPMC (Fig. 6), show controlled rate of grain growth with low grain size.

**Compressive strength of piezoelectric compacts**

The compressive strength for compacts with different binders is given in Table 4. It is clear that the specimens with PVA and starch show higher compressive strengths, i.e., 32.15 and 36.21 kg/mm², respectively, whereas methocel, HPMC, PEG show low compressive strengths, i.e., 16.79, 18.45, 17.30 kg/mm², respectively. Further, the specimens with PVP, gum-arabic and HEC are found to be in the

![](image1)

*Fig. 3 — SEM of piezoelectric ceramic green compact formed with gum arabic as a binder (magnification 5000 x)*

![](image2)

*Fig. 4 — SEM of piezoelectric ceramic green compact formed with methocel as a binder (magnification 5000 x)*

![](image3)

*Fig. 5 — SEM of sintered piezoelectric ceramic formed with poly (vinyl alcohol) as a binder (magnification 5000 x)*

![](image4)

*Fig. 6 — SEM of sintered piezoelectric ceramic formed with hydroxy propyl methyl cellulose as a binder (magnification 5000 x)*
medium range, i.e. 27.09, 25.27 and 21.29 kg/mm², respectively.

The compressive strength is supported by green density, sintered density and microstructure of the formulations. A comparison of these properties shows that the specimens with low green density have more shrinkage, rapid grain growth and considerable porosity resulting in low compressive strength. It is also seen that even if final sintered density is maximum (90%), microstructure data point out presence of porosity indicating low compressive strength. In other words, specimens with PVA, starch, PVP and gum-arabic show encouraging results for compressive strength.

Curie temperature of poled ceramics

Okazaki and Mure et al.35-39 have reported the importance of grain size on the electrical or piezoelectric properties of PZT ceramics and their effect on microstructural parameters. The curie temperature, defined as operating temperature where dielectric constant is maximum, is derived from the variation of capacitance with temperature and is given in Table 5. It is evident that the specimens processed with PVP possess highest Curie temperature (280°C) implying highest working temperature, while PZT with gum-arabic shows lowest Curie temperature (252°C). The data also reveals that the specimens with PVA and PVP show high Curie temperature relating to low pore size observed in their scanning electron microphotographs. This is supported by the SEM data of the sintered ceramics. The specimens with PVA, starch and PVP as binders have high Curie temperatures and, therefore, are more suitable for working at high operational temperatures, i.e., production of ultrasonics for cleaning, drilling, etc. On the other hand, specimens with gum-arabic, show low Curie temperature and are not favoured because of loss of piezoelectric properties.

Comparison of electro-mechanical properties of piezoelectric ceramics

The data on capacitance (C), resonance frequency (f₀), anti-resonance frequency (fₐ), piezoelectric charge constant (d₃₃), piezoelectric voltage constant (g₃₃), planar coupling coefficient (Kₚ), mechanical quality factor (Qₘₐ) and dielectric constant (KT₃) of the PZTs with different binders is given in Table 6.
Table 6 — Comparison of electrical properties of PZTs with different binders

<table>
<thead>
<tr>
<th>Binder</th>
<th>Cap (nF)</th>
<th>Tan Delta</th>
<th>$d_{33}$ (C/N)</th>
<th>$f_c$ (KHz)</th>
<th>$f_p$ (KHz)</th>
<th>$Z_m$ (Ohms)</th>
<th>$Q_m$</th>
<th>$K_T$</th>
<th>$g_{33}$</th>
<th>$K_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (vinyl alcohol)</td>
<td>3.04</td>
<td>0.016</td>
<td>431</td>
<td>101.70</td>
<td>121.63</td>
<td>21</td>
<td>78.46</td>
<td>2563</td>
<td>16.85</td>
<td>0.62</td>
</tr>
<tr>
<td>Methocel</td>
<td>2.84</td>
<td>0.014</td>
<td>420</td>
<td>101.46</td>
<td>120.70</td>
<td>23</td>
<td>81.33</td>
<td>2400</td>
<td>17.51</td>
<td>0.61</td>
</tr>
<tr>
<td>Starch</td>
<td>3.21</td>
<td>0.015</td>
<td>425</td>
<td>101.54</td>
<td>122.66</td>
<td>20</td>
<td>75.46</td>
<td>2707</td>
<td>15.70</td>
<td>0.64</td>
</tr>
<tr>
<td>Hydroxy propyl methyl cellulose</td>
<td>3.10</td>
<td>0.015</td>
<td>435</td>
<td>100.71</td>
<td>122.30</td>
<td>21</td>
<td>77.03</td>
<td>2534</td>
<td>17.14</td>
<td>0.65</td>
</tr>
<tr>
<td>Hydroxy (ethyl cellulose)</td>
<td>3.00</td>
<td>0.016</td>
<td>459</td>
<td>100.77</td>
<td>123.46</td>
<td>20</td>
<td>73.54</td>
<td>2613</td>
<td>17.58</td>
<td>0.66</td>
</tr>
<tr>
<td>Poly (vinyl pyroldione)</td>
<td>2.98</td>
<td>0.017</td>
<td>469</td>
<td>101.11</td>
<td>123.65</td>
<td>22</td>
<td>71.48</td>
<td>2515</td>
<td>18.64</td>
<td>0.66</td>
</tr>
<tr>
<td>Gum-arabic</td>
<td>3.01</td>
<td>0.017</td>
<td>430</td>
<td>101.45</td>
<td>122.24</td>
<td>23</td>
<td>71.78</td>
<td>2540</td>
<td>16.95</td>
<td>0.63</td>
</tr>
<tr>
<td>Poly (ethylene glycol)</td>
<td>2.97</td>
<td>0.016</td>
<td>440</td>
<td>102.79</td>
<td>125.16</td>
<td>21</td>
<td>74.27</td>
<td>2510</td>
<td>17.55</td>
<td>0.64</td>
</tr>
</tbody>
</table>

It is seen that the specimens with PVP as binder exhibit maximum piezoelectric charge constant $d_{33}$ (469) suggesting better performance in the transmittance applications. The specimens with low $d_{33}$ have better properties in respect of capacitance, $Q_m$ and impedance. In contrast, the specimens with PVP have highest piezoelectric voltage constant $g_{33}$ (18.64) and may therefore, perform better for underwater detection applications which comprise of listening approach (hydrophone) and active method of emitting sound pulses. The specimens formed with Methocel, PVA and HPMC have high mechanical quality factor ($Q_m$) (81.33) and suggest suitability of these materials for applications such as wave filters, accelerometers, gas lighters, etc.

The most important aspect of piezoelectric ceramics is the coupling coefficient ($K_p$) which signifies strength of the electrical energy that is converted into mechanical energy when electric field is applied or vice-versa. It is seen that specimens with PVP, HEC and HPMC as binders have high coupling coefficient ($K_p$) ~0.66 and conversion capacity of electrical energy to mechanical energy is maximum and therefore, favourable for applications such as phonograph pick-ups and delay line transducers.

Conclusions

A critical analysis of the data generated suggests that PVA with medium viscosity (85 cPs), possesses better flow to achieve homogenous compacts, maximum green density (5 g/ml), minimum porosity (1 μm) and maximum weight loss 91% at 237°C. The ash content in case of ceramics with PVA as a binder is approximately zero which is beneficial for their processing without any detrimental effect on their piezoelectric properties. The compressive strength data is also better for PVA based PZTs and, therefore, gives better performance. The electrical properties are also observed to be stable with very low ageing, and thus PVA appears to possess better performance characteristics. PVA, therefore, holds a bright potential as a binder for piezoelectric ceramics as compared to other binders reported in this investigation.

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