Chapter 4

Sucrose: An Alternate Binder in Dry Processing of Ceramics

4.1. Introduction

Fabrication of ceramic compacts requires use of various additives in order to achieve proper flow and cohesion of particles. Binder is the most important additive which is added during processing of ceramic powders in order to enhance mechanical properties of green products during and after forming operation.[69-71] For instance, mechanical strength must be high enough to maintain integrity of the green body during ejection from mold, subsequent handling and sometimes machining. Thus, binder addition is essential during shape forming of ceramic compacts. Its type and amount varies depending on the type of fabrication process. Essential requirements of binder are proper mixing ability with ceramic powder, adequate glass transition temperature, low ash content, easy burnout etc.[72-77]

Binder content should be such that it will give adequate strength and at the same time should not create microstructural defects in the green body during binder burnout step.[78-80] Hence selection and optimization of binder plays an important role in shape forming of ceramic compacts. A wide variety of binders are being used in traditional as well as advanced ceramic fabrication processes which include natural products like cellulose, or clays and synthetic products like polyacrylates or poly vinyl alcohol. Binders can be categorized into inorganic type such as sodium silicate, bentonite and organic type such as PVA, starch, carboxy methyl cellulose (CMC), dextrin, wax emulsion, poly ethylene glycol, lignosulfonate, methyl cellulose, paraffin, polyacrylate etc.

Poly vinyl alcohol (PVA) is largely used as a binder during dry pressing of ceramic powder. Several articles have reported the influence of PVA binder on mechanical properties of dry pressed green alumina products.[82-85] A search for an alternative binder revealed use of sucrose as binder and rheology modifier during plastic forming and slurry processing of ceramic mixture.[86-89] Sucrose has also been used as a pore forming additive during fabrication of porous ceramics.[90-91] Though sucrose has been used successfully as a binder in wet processing of ceramics, its

suitability and effectiveness as binder in dry powder processing has not been reported earlier. Thus, it was thought to examine the binding ability of sucrose during dry pressing of ceramics. Sucrose was also preferred due to its low cost, room temperature solubility in aqueous solvent, low viscosity binder solution, easy processing and non-toxic nature.

Based on the results of some preliminary study, systematic experiments were designed and performed to study the mechanical properties such as density and strength of dry pressed green samples as a function of sucrose content in the ceramic mixture. Observed results have been co-related with the microstructure of green samples. Machinability of the dry pressed green compacts was evaluated through a drilling experiment. Sucrose binder-ceramic interaction has been explained by IR study. The thermal analysis of sucrose binder has also been evaluated and discussed. Effect of sucrose content on porosity of sintered samples was studied. Finally, based on the experimental results, the optimum sucrose content to be used as binder during dry pressing of alumina compacts, have been standardized.

4.2. Experimental Procedure

4.2.1. Sample preparation

In the present study, two different grades of alumina powder such as coarse (Hindalco Pvt. Ltd. HIM 30, Avg. particle size 5 μm) and fine (ALCOA Acc, CT3000SG, Avg. particle size 0.7 μm) were used. Sucrose (Merck Specialities Pvt. Limited, Mumbai, $C_{12}H_{22}O_{11}$, molecular weight= 342.30)[92] was used as a binder in the form of aqueous solution for preparation of ceramic mixture. Table 4.1 illustrates the manufacturer-specified specifications of sucrose.

Based on maximum solubility of sucrose in distilled water, 60 wt% concentration solution, was considered and selected as binder in the present study. Alumina mixture compositions (Table 4.2) having sucrose solution (SS) in the range 1-18 wt% (equivalent to 0.6-10.8 wt% sucrose on dry weight basis) were prepared independently through dry mixing for 30 minutes manually using mortar and pestle. Depending on the binder content, the moisture content in the ceramic

mixture varied between 0.4 and 7.2 wt%. Rectangular samples (60 mm x 20 mm x 20 mm) were fabricated by uniaxial pressing in a small capacity hydraulic press at 100 MPa for each composition.

Table 4.1 Manufacturer –specified specifications of sucrose

Specification	Value (%)
Acidity or alkalinity	< 0.2 ml N%
Lead (Pb)	< 0.0004 %
Reducing sugars	< 0.02%
Sulfated ash	< 0.02%

Table 4.2 List of compositions used in the present study

Sucrose solution in the mixture (wt%)	Mixture composition (100%)		
	Alumina	Distilled water (wt%)	Sucrose (dry wt. basis) (wt%)
1	99	0.4	0.6
2	98	0.8	1.2
3	97	1.2	1.8
4	96	1.6	2.4
5	95	2	3
6	94	2.4	3.6
7	93	2.8	4.2
8	92	3.2	4.8
9	91	3.6	5.6
10	90	4	6
11	89	4.4	6.6
12	88	4.8	7.2
13	87	5.2	7.8
14	86	5.6	8.4
15	85	6	9
16	84	6.4	9.6
17	83	6.8	10.2
18	82	7.2	10.8

In order to determine the effect of moisture content on density and mechanical strength two series of samples were tested:

(i) Samples immediately after pressing (moisture content 0.4-7.2%) and

(ii) Samples after drying at 100˚C for 24 h (no moisture) for both coarse and fine alumina mixture.

Binder burnout of dried samples was carried out, as per the thermal analysis of sucrose, by heating the sample at 1 ˚C/min with 1h dwell time at each of 195˚C, 220˚C, and 400˚C followed by bisque firing at 1000˚C for 2h. Sintering was done in a separate furnace at 1700˚C for 2h.

4.2.2. Sample characterization

The green density was calculated from the ratio of weight and volume of a minimum of five samples. The dimensions were measured with a digital caliper having accuracy 0.01 mm. The sample weight was measured with an accuracy 0.0001 g and was corrected for binder and moisture content of the sample. Mechanical strength of dry pressed green compacts was evaluated using a three point bending fixture with a span length of 30 mm in a Universal Testing Machine (AGS-5KND, P/N 340-33309, Shimadzu Corporation, Japan). The crosshead speed was 0.5 mm/min for all the samples. The flexural strength of dry pressed regular samples (60 mm x 20 mm x 20 mm) was calculated using the following expression:

$$\sigma = \frac{3F_{max}L}{2bd^2} \quad \text{.....(4.1)}$$

where, L is the span length, b and d are the width and thickness of the rectangular samples. The reported strengths are the average result of at least five samples.

Microstructural analysis of fractured surface of green samples was carried out using a Scanning Electron Microscope (SEM Inspect S50, Sweden) to examine the packing and distribution of particles with binder content. Dried samples were tested for machinability in the green stage through drilling operation using a radial drilling machine (Vijay Electronics, India, HP ¼, volt 220/230, Sl. No. VE0011,

Single Phase) with a high speed steel drill bit (size 3/32 and 9/64) operating at 1440 rpm.

Thermal decomposition of sucrose binder was studied by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA). TGA and DTA measurements were conducted in air at a heating rate of 10 ˚C/min. Loss on ignition and burnout residue study was carried out by thermolysis of bulk amount of binder in air in a separate chamber furnace. The binder to ceramics interactions were studied by IR spectroscopy (Varian Scimitar 1000 FT-IR).

Percentage porosity (A.P %) of sintered samples was calculated using Archimedes principle through the water immersion method.

4.3. Results

4.3.1. Density and strength of green compacts

Variation in density of green alumina compacts with incremental sucrose addition in the range 0.6-10.8 wt% is shown in Fig. 4.1. The green density gradually increased with increase in binder content up to a maximum value and then started decreasing rapidly. The sucrose content that resulted in maximum green density was referred to as optimum composition. The optimum sucrose content was 7.2 wt% and 8.4 wt% for fine alumina and coarse alumina compacts respectively irrespective of the moisture content.

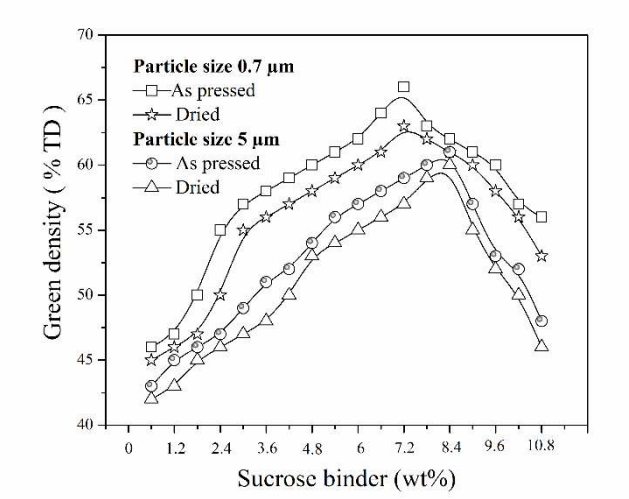

Fig. 4.1 Effect of sucrose binder content on green density of as pressed and dried alumina compacts

The above observation can be attributed to comparatively higher surface area of fine particles that helped in better wetting of particle surface and hence higher inter-particle bridging. However, the density of fine alumina compacts was always higher than that of coarse alumina compacts for all compositions. This can be related to better packing and compaction of fine particles for the same applied pressing pressure.[74] Maximum density achieved for fine alumina compacts was 66% and 63% of theoretical density (T.D. 3.99 g/cc) for as pressed and dried samples respectively. Similarly green density reached 61% and 60% of theoretical value for the as pressed and dried coarse alumina compacts respectively. Increase in density with incremental addition of sucrose up to the optimum can be attributed to inter-particle bridging and cohesion of particles in the presence of binder and the sharp decrease in density beyond optimum, can be related to excess binder phase which can be treated as replacement of ceramic particle with equal volume of binder causing separation of particles in the green compact.

Also, the density of as pressed compacts was always higher in comparison to that of dried samples for all compositions irrespective of the particle size of alumina powder. This can be related to the plasticizing effect of moisture which helped in better compaction. Depending on sucrose content, green density of dried samples was in the range 45-63% T.D. and 42-60% T.D for fine alumina and coarse alumina respectively.[72, 87-88,93]

Fig. 4.2 illustrates dependence of green flexural strength as a function of binder content for as pressed and dried samples. It was seen that the flexural strength trend was similar to that obtained for density of green samples. Maximum strength achieved for fine alumina compacts was 5.5 MPa and 12.5 MPa for as pressed and dried samples respectively. Similarly, maximum strength was 4.4 MPa and 7.52 MPa for as pressed and dried coarse alumina compacts, respectively.

Increase in strength with incremental addition of sucrose up to the optimum can be attributed to the interaction between the binder molecules and between ceramic particles and binder. Beyond the optimum, the decrease in strength can be linked to the excess binder in the inter-particle spaces leading to reduction in particle packing and compactness, resulting in sharp fall in strength. However,

depending on binder concentration, flexural strength of dried samples was in the range 12.5-0.6 MPa and 7.52-0.3 MPa for fine and coarse alumina compacts respectively.

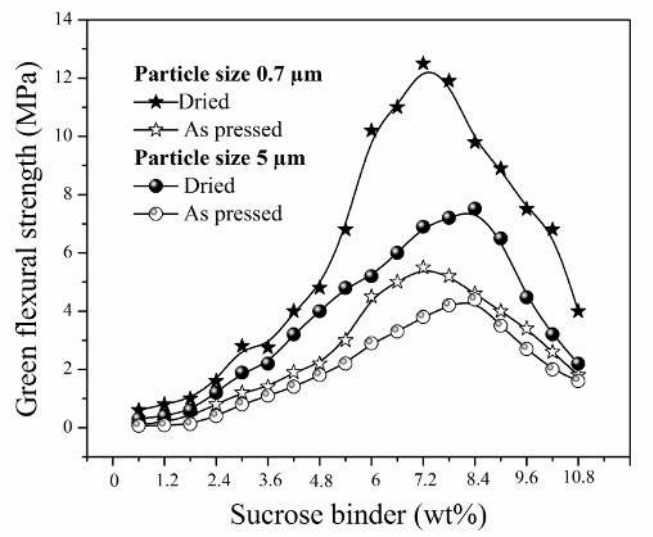

Fig. 4.2 Variation in flexural strength of as pressed and dried alumina compacts as a function of sucrose binder content.

Unlike density, flexural strength of as pressed samples was always less in comparison to that of dried samples. Presence of water in the as pressed sample reduces the mechanical strength. Linear drying shrinkage of sucrose based green alumina samples was in the range 0.1-1%, which is almost negligible

4.3.2. Microstructure of green samples

A remarkable variation in microstructure of green alumina compacts was observed as a function of sucrose content. SEM micrograph of fractured surfaces of green sample prepared using 6 wt% (below optimum), 7.2 wt% (optimum) and 9.6 wt% (above optimum) sucrose binder, respectively is shown in the Fig. 4.3. Microstructure of samples with optimum sucrose content showed homogeneous distribution of binder and uniform particle packing.

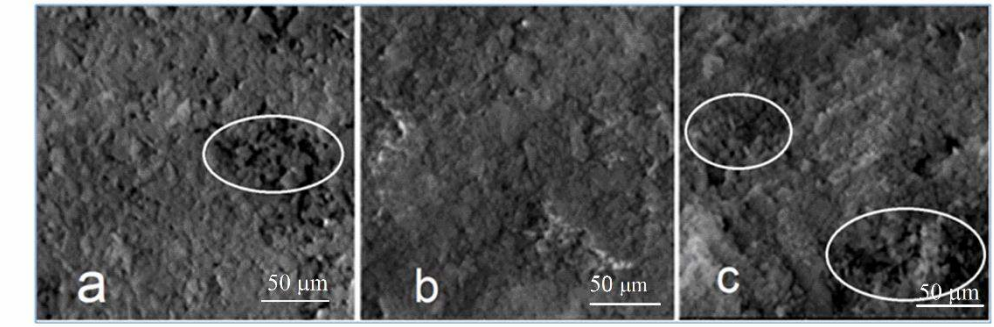

Fig. 4.3 Fractured surface of fine alumina samples with 4.8, 7.2 (optimum) and 9.6 wt% sucrose binder

In contrast, samples with 6 and 9.6 wt% sucrose resulted in microstructures with loose packed regions (highlighted area in micrographs a and c), which confirms non-homogeneous microstructure. Thus, it is clear that, optimum binder addition is just sufficient for uniform distribution of sucrose solution throughout the ceramic matrix and hence resulted in uniformity in particle distribution and optimum particle packing during compaction. The homogeneous and uniform packing of particles in samples with optimum binder is reflected in terms of maximum density and strength of green compacts.

4.3.3. Green machining

Machinability of sucrose based green compacts was studied in terms of ability of samples to withstand drilling operation without formation of cracks and defects. Green machining helps to introduce additional features such as holes, rounded corners, surface features etc., and to achieve green products with near net shape compacts immediately after shape forming, which were otherwise difficult to introduce during pressing. Various machining operations can be drilling, grinding, polishing, finishing etc. to achieve customer specified requirements.

It is interesting to note that green alumina samples with sucrose content in the range 3.6-10 wt% were strong enough for machining. These samples not only survived the drilling operation but also yielded a drilled hole with perfect edges and no associated cracks. Fig. 4.4 shows samples with sucrose content 1.8, 2.4, 3 wt%

which were broken during drilling and samples with 3.6, 4.8, 7.2, 9.6 wt% sucrose (survived machining) after drilling.

Fig. 4.4 Drilled green alumina samples prepared with sucrose content 1.8, 2.4, 3 , wt% (left) and 3.6, 4.8, 6, 7.2 wt% (right)

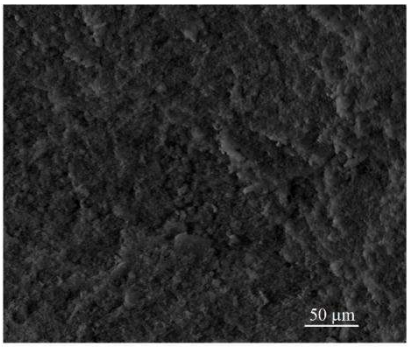

Fig. 4.5 SEM micrograph of the drilled surface of green alumina sample fabricated with 7.2 wt% (optimum) sucrose content

SEM micrograph of the drilled surface of a fine alumina compact with 7.2 wt% sucrose binder, revealed good surface finish with homogeniety in particle packing without any visible defects (Fig. 4.5). Drilling experiment proved that sucrose based green samples are strong enough for green machining.

4.3.4. IR analysis of sucrose binders

For explanation of high density and strength of sucrose based green samples, IR study was performed to detect the functional groups present in sucrose, which are responsible for providing high strength and density.[74,94] The IR spectrum (Fig. 4.6) shows vibration modes of sucrose. The presence of sucrose was confermed from the peak for the adsorption bonds in the range 3600 cm^{-1} to 3200 cm^{-1} (Intermoecular hydrogen bond and free hydroxyl groups) The presence of sucrose was also confirmed from the peaks in the range 950-1300 $cm^{-1,}$ as

described to stretching[96-97] vibration mode of C-O-H and C-O-C vibration. Sucrose has the capability of holding water molecules through hydrogen bonding.[94] It is expected that the associated sucrose-water molecules adsorb onto the alumina particle surface through hydrogen bonding.

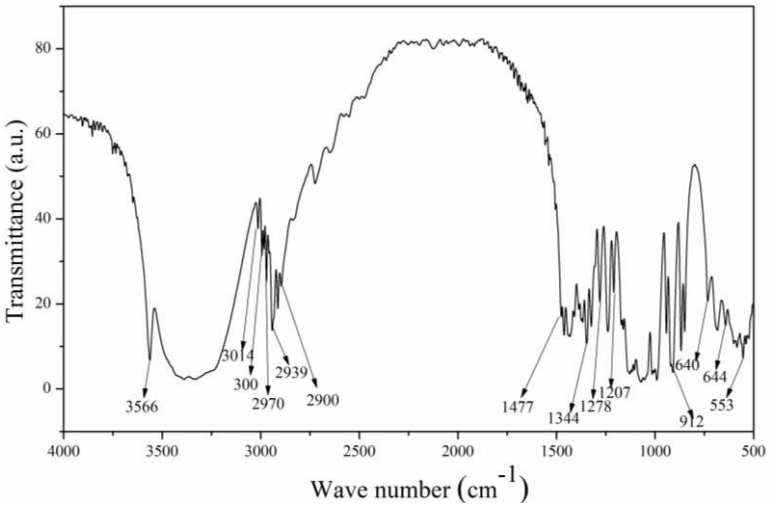

Fig. 4.6 IR spectrum of sucrose binder

4.3.5. Binder burnout characteristics of sucrose

In order to establish the binder burnout schedule of sucrose based green alumina samples, the thermal decomposition and burnout behavior of sucrose was studied independently through TGA, DTA and thermal pyrolysis of bulk sample. Fig. 4.7 (a) and (b) represents the TGA and DTA experimental results carried out in air.

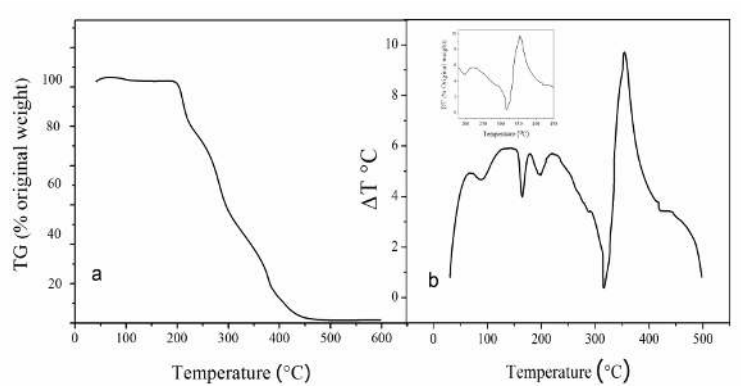

Fig. 4.7 (a) Thermogravimetric analysis and (b) Differential thermal analysis of sucrose binder in air

A slow and stepwise weight loss in air can be observed during the heating process in the temperature range 195-450˚C, it reaches a plateau, with almost no residue (Fig. 4.7 (a)). The slow weight loss up to about 100˚C was attributed to detachment of adsorbed water molecules from the sucrose surface.[97,99] The DTA curve (Fig. 4.7 (b)) has three endothermic peaks, at around 195˚C, 225˚C and at around 400˚C respectively resulting from heat induced decomposition. The thermal decomposition of sucrose was considered to start at temperature higher than 195˚C. Sucrose decomposes as

$$C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.2)$$

As per the thermal profile/binder burnout characteristics of sucrose in air, the organic burnout schedule of green samples was established, which has already been mentioned in the experimental procedure.

4.3.6. Porosity of sintered compacts

Fig. 4.8 shows the porosity of sintered fine and coarse alumina samples as a function of sucrose content in the green compact.

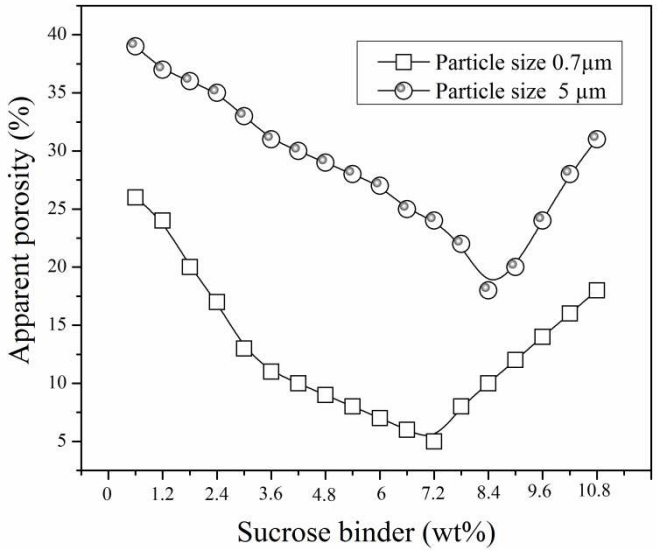

Fig. 4.8 Variation of porosity of sintered alumina compacts prepared with fine and coarse alumina powder as a function of sucrose binder content

It is interesting to note that incremental sucrose addition in green samples resulted in lowering of porosity in respective sintered samples, till the optimum, beyond which a rapid increase in porosity was observed. A minimum in porosity

(5% and 18% for fine and coarse alumina compacts, respectively) was observed for sintered samples with optimum sucrose content corresponding to maximum density and strength of green compacts. This observation can be related to maximum particle packing of samples at the optimum sucrose content. Comparatively higher porosity was observed for samples corresponding to sucrose content below optimum. This can be attributed to low packing density. Similarly, increase in porosity of sintered samples with incremental sucrose addition in green samples, above optimum, can be linked to additional pores created due to burning out of excess sucrose. Optimum sucrose content is just sufficient to obtain maximum packing density. Depending on the sucrose content in green samples, porosity of sintered compacts varied in the range 5 to 26% and 18 to 39% for fine alumina and coarse alumina compacts respectively.

4.4. Discussion

The glass transition temperature T_g of organic binders is one of the most important parameter which not only controls the performance of binder during dry pressing but also affects the green properties such as density and strength of dry pressed compacts.[100] T_g of sucrose is 60˚C. Because the T_g of sucrose was several degrees higher than the dry pressing temperature (25-30˚C), it required plasticization for obtaining a good compaction.[101] Thus, we have taken the advantage of plasticizing effect of water by using aqueous sucrose solution as binder. Addition of sucrose binder in the form of aqueous solution helped providing plasticity and workability to the alumina mixture. This can be attributed to the ability of sucrose to hold water molecules through hydrogen bonding. Also, sucrose solution helped uniform mixing and homogeneous distribution of binder in the pressed compact.

Though the range of sucrose (0.6 to 10.8 wt % on dry weight basis) considered in the present study is comparatively higher than the commonly used binder amount (1 to 5 wt %) for dry pressing of ceramic powder, the actual molecular mass of binder per g of powder is less for sucrose in comparison to other binders such as PVA. This is due to the fact that molecular weight of sucrose (Mw= 342.6) is approximately hundred times lower than that of the commonly used binder

PVA (Mw= 31,000 approximately).[69] Low molecular weight of sucrose is reflected in comparatively less viscosity of binder solution even for the highest (10.8 wt %) sucrose content. This is an additional advantage for dry processing of ceramics. Thus, the range of sucrose amount considered as binder in the present study for dry pressing of alumina powder is justified.

Green density and flexural strength results of sucrose based dry pressed green alumina samples are comparable or even better in comparison to those of PVA based samples.[69,102] Addition of optimum amount of sucrose (7.2 wt% and 8.4% for fine alumina and coarse alumina compacts respectively) resulted in 63% and 60% relative density for fine alumina and coarse alumina samples respectively. In comparison, typical values of green density of PVA (3 wt%) based alumina (0.4 μm size) samples is 56.8% and that for polyeurathane (3 wt%) based alumina (avg. size 0.7 μm) sample is 58%.[72]

Similarly, average green flexural strength of fine alumina samples with 7.2 wt% sucrose was 12.5 MPa in comparison to 12.7 MPa for polyeurathane based alumina sample.[72] Thus, green properties of sucrose based dry pressed samples are comparable with the properties of samples prepared using other binder. It has already been mentioned that sucrose based alumina samples with binder content near optimum are strong enough for green machining. Thus, on the basis of density and strength results, it is clear that sucrose provides adequate binding of particles in the dry pressed green compact.

Addition of sucrose binder in the optimum range can be preferred among the selected compositions, for successful fabrication of alumina compacts through dry pressing in order to obtain samples with maximum green density and strength but minimum porosity in the fired sample. It is suggested that for fabrication of porous compact, sucrose addition above optimum will serve dual role as both binder and pore former, depending on the porosity requirement.

4.5. Summary

Systematic experiments in the present study have shown a new possibility in terms of the use of sucrose (in the form of aqueous solution) as a binder in dry processing of ceramics. The following observations have conclusively shown that sucrose acts as a binder for dry pressing of ceramic compacts and also an optimized amount of sucrose binder leads to best packing of particles in the compact.

1. Sucrose binder in the form of aqueous solution (0.6-10.8 wt% on dry weight basis) provided high green density and strength to the dry pressed alumina compacts irrespective of the particle size of alumina powder and moisture content.
2. The high green strength was controlled by the plasticizing effect of binder solution resulting in better particle packing.
3. Optimum sucrose content (7.2 wt% and 8.4 wt% for coarse and fine alumina samples, respectively) was established in terms of achievement of maximum density (66% and 63% T.D for as pressed and dried fine alumina samples) and maximum strength (5.5 and 12.5 MPa for as pressed and dried fine alumina sample) in the green compact. Highest density and strength of compacts with optimum sucrose content was supported by the SEM micrograph showing homogeneous distribution of binder and uniform packing of particles in the green sample.
4. Depending on the binder content, green density of dried samples was in the 45-63% T.D and 42 to 60% T.D for fine and coarse alumina compacts, respectively. Similarly, flexural strength of dried samples was in the range 12.5 to 0.6 MPa and 7.52 to 0.3 MPa for fine and coarse alumina compacts, respectively.
5. Observed mechanical properties of sucrose-based green samples are either comparable or even better than those reported for other binders such as PVA.
6. Dry pressed samples with sucrose content 3.6 wt% and above are strong enough for green machining.

7. Sucrose binder shows gradual burnout characteristics with no residue in air atmosphere, which is an advantage for ceramic processing.
8. Samples with optimum sucrose content, exhibited minimum porosity (5% and 18 % for fine alumina and coarse alumina, respectively).
9. Low cost, room temperature solubility in aqueous solvent and comparatively less viscosity binder solution are the additional advantages associated with use of sucrose as alternative binder in dry pressing of the compacts.