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Egg White as an Environmentally Friendly Low-Cost Binder for Gelcasting of Ceramics

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Slurries with different solids loading (34–50 vol%) of alumina were made with egg white (ovalbumin)–water premix. The ovalbumin content in the premix was decreased with increase in solids loading to lower slurry viscosity. The slurries were cast into bulk shapes and heated to 80°C, resulting in denaturation of ovalbumin forming a gel. The gelled samples were dried under controlled humidity and sintered in air to densities 94%–97% of theoretical. Alumina slurries formed with egg white (no water) were used to form tapes as thin as 60 μm in the sintered state.

I. Introduction

There has been a drive toward use of environmentally friendly additives in ceramic processing, such as the development of water-based injection molding[1] and tape casting.[2] Gelcasting[3] a recently invented near net shape ceramic forming process capable of forming small to large size ceramic components also uses aqueous ceramic slurries containing water-soluble binders.

Binder is one of the most important additives in slurries or mixes used in advanced ceramic forming. The nature and amount of organic binder influence the surface charge on particles, foaming and foam stability, highest attainable solids loading, green strength, dimensional control, and defect formation during binder burnout. Processes that use a small amount of organic binder(s) and yet yield components with high green density and strength are most desirable for ceramic forming.

One of the recently reported gelcasting systems[4] uses water-soluble monomer (methacrylamide (MAM)) and cross-linker (methylenebisacrylamide (MBAM)) in amounts that result in high solids loading, yet low viscosity and very low binder amount (4–5 wt%) in dried green parts.

There are a number of environment friendly natural binders that undergo gelation with changes in temperature and which have been used for injection molding and gelcasting of ceramics. The most common natural binders that have been used in ceramic forming are gelatin,[5] agarose,[6] and polysaccharide.[7] The present study is motivated by the common observation of the physical change caused to the liquid contents of an egg by boiling it in water. The present authors built on the above observation and studied the use of egg white in forming water-based ceramic loaded slurries and its use in shape forming of ceramics.[8] Ovalbumin is the major protein in egg white and henceforth egg white is referred to as ovalbumin in this article. The use of ovalbumin in shape forming of ceramics as described here was additionally motivated by the idea of gelcasting where a water-based slurry containing a monomer and cross-linker is polymerized *in situ*, causing the slurry to take the shape of the mold by simply heating to temperatures below 100°C.

The use of proteins in shaping of ceramics has been reported recently.[9,10] Lyckfeldt *et al.*[9] have proposed the use of bovine serum albumin (BSA), whey protein concentrate (WPC), and albumin, respectively, as gelling agents in aqueous ceramic slurries. Although the process is similar to gelcasting, no comparisons have been drawn with the gelcasting process.[3,4] The use of albumin in ceramic slurries was restricted to around 5–8 wt%, even when it was known that such a low amount of binder results in weaker gels, as higher amounts result in shear thickening behavior. Lyckfeldt *et al.*[9] have reported rheological behavior of alumina slurries based on a premix of albumin and water but different slurry compositions with varying binder amounts were not investigated and the slurry stability over a longer period was not studied. The applicability of protein forming was demonstrated only for bulk shapes.[9]

As found from the present study the use of egg white ovalbumin in ceramic slurries can have many advantages over comparable systems such as the MAM/MBAM used in aqueous gelcasting.[4] With the use of ovalbumin the net binder content in the dried green body can be kept to levels lower or comparable (0.6–4.0%) to that in gelcasting. Ovalbumin-based slurries do not need any chemical additives to initiate and complete gelation, which is in contrast to MAM/MBAM-based gelcasting slurries, which not only require an initiator and catalyst, but have to be cast soon after the initiator and catalyst are added. Also, ovalbumin is nontoxic, biodegradable, cheap, and widely available.

In the present study, alumina slurries were made using premixes with different ratios of water to liquid ovalbumin. Measurements were made to study the relative influence of ceramic solids loading and ovalbumin content on slurry rheology. The slurry stability was evaluated via relative suspension height (RSH) measurements. Besides forming bulk shapes with the above slurries, tape casting was demonstrated with slurries formed solely with liquid ovalbumin.

II. Experimental Method

(1) Preparation of Ceramic Slurry

1-Octanol (5 mL per 100 mL of egg white) was added to egg white and stirred using a magnetic stirrer for 2 h. Stirring of egg white is typically accompanied by froth generation, which was significantly restricted here by the addition of 1-octanol. The froth was removed and the ovalbumin was mixed with distilled water (premix) in different ratios (Table I). This premix was used to prepare the ceramic slurries. Slurries were then prepared by mixing/milling the egg white–water premix with alumina powder (Alcoa CT 3000 SG, d_{50} = 0.7 μm and surface area 7 m^2/g) and the dispersant Darvan 821 A in polypropylene containers using 3 mm diameter zirconia milling media for 24 h; 1 mL of 40 wt% Darvan solution per 100 g of alumina powder was used for all slurries.

Unlike slurries A1–A4 (Table I) the slurry for tape casting was prepared using only ovalbumin (no water) with 32 vol% alumina

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Table I. Slurry Formulations and Ovalbumin Content in Dried Green Body

Slurry	Egg white in premix (vol %)	Alumina solids loading (vol %)	Egg white in dried green body (%)	
			Theoretical[†]	Experimental
A1	82	34	4.9	4.9
A2	67	35	3.9	3.3
A3	50	40	2.3	2.7
A4	20	50	0.6	1.5

[†]Based on the typical water content in egg white.

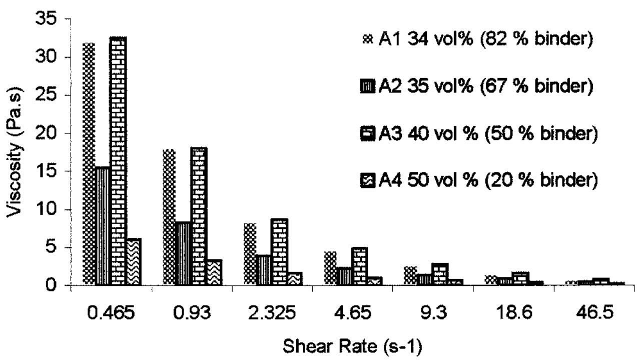

Fig. 1. Rheological behavior of slurries with different alumina loading and ovalbumin content.

particle loading with 1.5 g of Darvan per 100 g of alumina powder and 1-octanol.

(2) Characterization

Thermal degradation of binder was studied by carrying out TGA to 1000°C. Dispersion of alumina particles in the slurry was evaluated by RSH measurements of 1 vol% alumina slurries with powder-to-dispersant and powder-to-binder ratios maintained the same as for slurry A3.

Rheological measurements were conducted for all slurry compositions shown in Table I. A manually controlled coaxial cylinder viscometer (Brookfield, Model RVT/73232) with shear rates varying from 0 to 47 s^{-1} was used for these measurements. Initially, the slurry was subjected to a shear at 50 rpm for 1 min. Viscosity measurements were then made in an upward sweep with increasing shear rates and in continuation followed by the same measurements during the downward sweep.

(3) Casting and Postprocessing

The as-prepared slurries were deaired under low vacuum for 1 h and cast into petroleum jelly coated rectangular molds. The molds were placed in a preheated oven at 80°C for 1 h. The molds were then cooled to room temperature; the parts were removed from the mold and then dried under controlled humidity conditions.

Tapes were cast on thin PET sheets using a laboratory-scale doctor blade and were placed under high humidity (95%) at 60°C. The humidity level was gradually decreased to 50% over a period of 6 h. Both the rectangular bars and tapes were subjected to binder burnout and sintering as follows: 0.5 h dwell time at each of 120°, 350°, and 550°C followed by bisque firing to 900°C for 2 h. Sintering was done in a separate furnace at 1600°C for 2 h.

III. Results and Discussion

TGA analysis of ovalbumin directly extracted from fresh eggs indicated an ash content of 8.8%, which is mostly due to the metal ions present in ovalbumin. This ash content, for example, corresponded to an impurity content of 0.48% for ceramic samples made with slurry A3. Also since one of the main objectives of the present study was to examine the feasibility of the use of ovalbumin in ceramic processing, ovalbumin as extracted from eggs was used directly without any purification steps. It is notable that even with the use of this unpurified form of ovalbumin, the calculated individual metal oxide (such as Na_2O, CaO, Fe_2O_3, MgO) impurity levels were significantly lower than that present in the as-received powder.

RSH data indicated that the ovalbumin-based slurries (pH 8.9) were highly stable over the typical time period required for the steps—deairing, casting, and gelation—following milling. After 8 days the RSH was 0.94 and complete settling of alumina particles took more than 25 days.

A comparison of the rheological data of slurries A1 and A2 (Fig. 1) shows the lowering of slurry viscosity as a result of a decrease in the amount of ovalbumin in the premix. The difference in viscosity of slurries A1 and A2 was reduced at higher shear rates because of shearing of the long-chain molecular structure of ovalbumin. Comparison of slurries A1 and A4 indicates that in comparison to ceramic solids loading, the ovalbumin amount in the premix plays a dominant role in affecting slurry viscosity at all shear rates. This is expected considering the high molecular weight of ovalbumin.

The tape casting slurry was also shear thinning in behavior and had viscosities of 30 and 9.2 Pa•s at shear rates of 0.5 and 4.7 s^{-1}, respectively. The slurry was used to make ceramic tapes of variable thickness. The green tapes had a uniform microstructure (Fig. 2) and the tapes were quite flexible. The minimum thickness achieved in the sintered tapes was around 60 μm (Fig. 2) and the sintered density was near 95%.

For forming bulk rectangular samples, as-prepared slurries A1–A4 were cast into aluminum molds and kept at 80°C in a preheated oven for 1 h and at 50°C and 95% relative humidity for 5 h. Heating the ovalbumin (protein) to near 80°C causes denaturation of the protein structure involving unfolding of the coiled protein structure or alteration in the nature of the folded structure.[11] As a result of this denaturation the fluid slurry turned into a gel with ceramic particles bound in the gel structure. The gelled

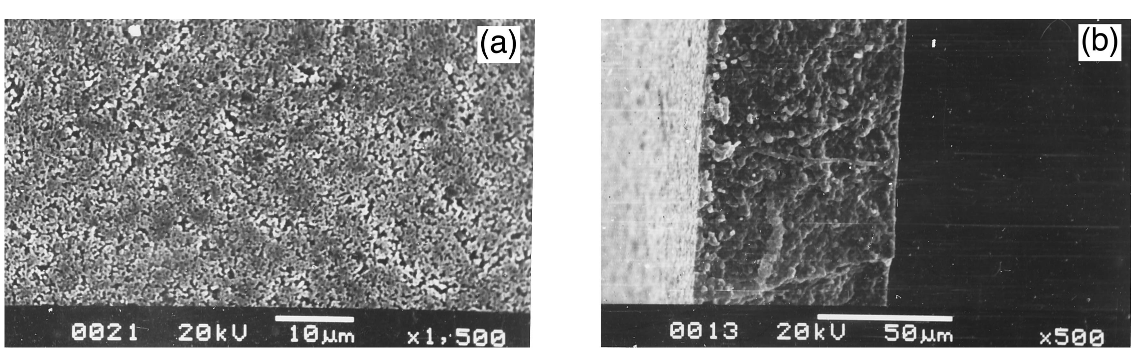

Fig. 2. (a) Surface of the green alumina tape and (b) view of the sintered alumina tape.

green ceramic body was rigid and strong and could be easily removed from the mold.

The green ceramic bodies once removed from the mold were dried slowly, initially under high humidity, and then the humidity was gradually decreased to lower levels. A few samples that were dried within the mold with only the top sample surface exposed exhibited appreciable migration of the binder to the exposed surface, resulting in separation of the top layer due to differential shrinkage during drying. SEM analysis of the green samples indicated homogeneous distribution of the binder (ovalbumin) and absence of agglomerates. Adsorption of binder on the alumina particle surfaces was expected because of the polar nature of the binder and the powder particles. SEM analysis also showed the presence of bubbles, which could not be removed because of inadequate deairing treatment of the slurries.

Although no strength measurements were performed for the green bodies, it could be seen qualitatively through wear against SiC polishing paper that the alumina samples made with ovalbumin were considerably stronger than the ones produced by MAM-MBAM for the same weight percent binder in the dried green body. Further, the samples could be easily drilled without causing any damage, even using a manually operated drill.

The alumina samples made with slurries A1–A4 were sintered to densities ranging between 94% and 97%. Regions devoid of bubbles appeared to have little porosity. The linear shrinkage from a dried state to a sintered state for samples made with slurries A1–A3 was around 19%, while for the sample made with slurry A4 it was around 16%.

IV. Conclusions

Egg white (ovalbumin) can be used to form highly loaded aqueous ceramic slurries that exhibit shear-thinning behavior. The viscosity of the slurries could be tailored by adjusting the amount of ovalbumin in the slurry for a specific volume percent of alumina particle loading. The ovalbumin-based slurries could be used in forming ceramic shapes by casting and forming a gel on heating, similar to other known gelcasting systems.

Although use of ovalbumin as a binder has many advantages, such as its low cost, biodegradable nature, nontoxicity, and easy availability, ovalbumin in the slurry encourages the formation of bubbles during mixing and milling and it adds metallic impurities to the ceramic components. Bubbles can be minimized through vacuum deairing of slurries and the use of appropriate antifoaming agents. Ovalbumin can be used in purified form with relatively less metallic impurities for forming ceramic components for electronic or high-temperature structural applications. Ovalbumin of slightly higher purity (3 wt% ash content) than that extracted from eggs is available at about 5 times the cost, which is still lower than the cost incurred with other gel-forming materials. This is notable in light of the fact that the contribution of unpurified ovalbumin toward metal oxide impurities is lesser than the level of the same metal oxide impurities already present in the commercial-grade high-purity powders.

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