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Agar-Based Aqueous Gel Casting of Barium Titanate Ceramics

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Agar was used for gel casting barium titanate ($BaTiO_3$) ceramics. Aqueous suspensions of bimodal $BaTiO_3$ powders, with 500 and 100 nm nominal particle sizes, were prepared with a 85:15 coarse:fine ratio. $BaTiO_3$ suspensions were mixed with agar solutions from 2 to 8 wt%, with 0.5 or 1.0 wt% agar (as a function of $BaTiO_3$ solids content) in the final gel-casting suspension. $BaTiO_3$ green densities up to ~53.2% of theoretical were obtained. Gel casting of high aspect ratio features (up to 7:1) could be routinely performed. Cast bodies were also amenable to computer-numerical-controlled based green machining.

Introduction

Barium titanate ($BaTiO_3$) is a ferroelectric ceramic widely used in discrete or multilayer ceramic capacitor production. Colloidal processing of this material has proven useful in yielding solids of superior homogeneity and reduced porosity, whether formed via slip casting,[1,2] tape casting,[3] or electrophoretic deposition.[4] Recently, gel casting has also been applied to process nano-$BaTiO_3$ ceramics.[5,6]

The process of gel casting is especially attractive as it is a near-net shape forming technique, capable of producing a variety of complex structures. However, the more traditional gel-casting systems are not without their drawbacks, as they are generally based on acrylamides, which are potent neurotoxins.[7] Consequently, attempts have been made to utilize less-hazardous gelling agents, such as those used in the food industry. Polysaccharides[8–14] (e.g., agar, agarose, carrageenan, locust bean gum, xanthan gum, starches, etc.) and pro-

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teins[15–17] (e.g., gelatin, bovine serum albumin, albumen, whey protein concentrate, etc.) have all been explored as alternative gelling agents for aqueous ceramic suspensions. The least expensive of these processing aids are proteins (e.g., egg albumen, whey protein concentrate, etc.) and starches. However, proteins are required in a relatively large concentration to impart sufficient gel strength, thus necessitating an organic burn-out stage before sintering. In addition, starches are used primarily in the formation of porous ceramics, as these agents are particulate in nature and invariably swell on hydration.

Conversely, the majority of polysaccharides (starches excluded) offer high gel strength at low concentration, are not as prone to foaming as protein solutions, and can be used to form nonporous bodies. Of these substances, agar presents an attractive combination of cost effectiveness and wide availability, while it is also a "food-grade" material, and consequently presents negligible safety issues in use. The gelation temperature and gel strength, among other characteristics, are dependent upon the agar source species, habitat, season of harvest, and the extraction and processing techniques used; the molecular size resulting from these variables has been shown to be of particular importance to agar properties.[18] The diversity of typical literature values for agar gelation temperature (solutions of 1.5 wt% concentration), as determined via oscillatory rheometry, is highlighted in Table I. [18–20]

In the present work, agar is used as a gelling aid for the preparation of $BaTiO_3$ ceramics. In particular, a nominally bimodal powder mixture of $BaTiO_3$ is used to increase cast densities, in combination with an agar concentration method previously outlined by Santacruz *et al.*[21,22] The rheological behavior of agar/$BaTiO_3$ suspensions has been assessed, paying particular attention to the dynamic viscoelastic response during cooling, which to date has received minimal attention in gel-casting literature.[23] Preliminary shape-forming capability trials have been performed, including producing a 1–3 architecture component (e.g., as used in sonar applications),[24,25] while successful green machining of gel-cast billets is also demonstrated.

Experimental Procedure

Materials

Two $BaTiO_3$ powders, with an advertised average particle size of 500 nm (Lot# IAM6068BTO5) and 100 nm (Lot# IAM3286BTO1), were obtained from a commercial supplier (Inframat Advanced Materials, Farmington, CT). These powders were characterized in detail for particle size, surface area, morphology, and zeta potential; these data are available in a prior publication.[26] All suspensions were prepared using an 85:15 volume ratio of the 500 and 100 nm $BaTiO_3$, as this mixture offered the lowest viscosity, and thus highest possible solids loading in suspension (55 vol%).[26] A polyelectrolyte surfactant was used, an ammonium salt of poly(methacrylate) ($PMA\text{-}NH_4$; Darvan C, R.T. Vanderbilt Co., Norwalk, CT), present at a concentration of 0.13 wt% of solids. The gelling agent was a general-purpose-grade agar, provided as a powder (Lot# 17543A; Stock #A10752, Alfa Aesar, Ward Hill, MA), with double-distilled water used as the suspension medium throughout the present study.

Table I. Selected Literature Values for Agar Gelation Temperature Determined by Oscillatory Rheological Analysis (1.5 wt% Agar Content)

Agar source	Gelation temperature (°C)	Cooling rate (°C/min)
Gracilaria changii[16]	38.4–43.8	2
Pterocladia capillacea[15]	30–34	1
Various[17]	37–38	0.5

Agar Rheological Testing

Rotational and oscillatory rheometry (Model AR-2000 Advanced Rheometer, TA Instruments, New Castle, DE) were applied to agar solutions in order to fully characterize the viscoelastic behavior of the gelling agent. Rotational rheometry was performed using a Peltier cooled/heated concentric cylinder test geometry, with a 28 mm diameter inner cylinder and a 1 mm annular gap (sample volume ~19.6 mL). Dry agar was mixed with double-distilled water and deposited into the equipment geometry and a thin layer of low-viscosity mineral oil was applied to the sample surface to prevent excessive evaporation. After equilibrating at 20°C, the suspension temperature was raised to 92°C at a rate of 1°C/min while sampling the apparent viscosity at a constant shear rate of $100\,s^{-1}$. The temperature was then reduced back to 20°C at the same ramp rate. No conclusions regarding gel strength were drawn from these experiments as the gel structure was continuously disrupted by the constant shear.

To study the evolution of viscoelastic properties upon gelation, oscillatory rheometry was performed on agar solutions prepared under atmospheric conditions on a hotplate at 92 ± 2°C, using a parallel-plate test geometry (40 mm diameter stainless-steel plate, along with a temperature-controlled Peltier base plate). Both plate surfaces were covered with adhesive-backed, 600 grit silicon carbide paper in order to reduce slippage at the interface, and a plate gap of 1 mm was used for all experiments (sample volume ~1.3 mL). A solvent trap and geometry cover were used to limit evaporation and a variety of preprogrammed cooling rates were investigated (5–30°C/min); this system has a maximum manufacturer-quoted heating/cooling rate of 50°C/min, although most tests were conducted at 10°C/min to minimize potential thermal lag. An oscillation frequency of 1 Hz and a maximum applied strain of 0.5% were used for all experiments, which is well within the nominal elastic region for agar-type gels.[27,28]

Combined Agar/Suspension Rheological Testing

Agar solutions for combined rheological testing were prepared in a pressure cooker using overpressure conditions (15 psi) to reach higher temperatures, and thus afford higher agar concentrations, based on the approach of Santacruz *et al.*[21,22] Before mixing with hot agar solutions, the $BaTiO_3$ suspensions were heated in a water bath to 60 ± 2°C. Mixing of the two components was performed by hand, as well as ultrasonically (80 W for ~1 min; Model 500 Sonic Dismembrator, Fisher Scientific, Ottawa, ON, Canada). In all cases, the agar content represented 0.5 wt% of the total solids content. Oscillatory rheometry was performed on the gel-casting slips in a similar manner as for agar solutions. The suspensions were cooled from 60°C to 5°C at a rate of 10°C/min, at an oscillation frequency of 1 Hz, and a maximum strain of 0.5%.

Gel casting and Green Machining

Gel-casting suspensions were cast into discs, with diameters of either 22 or 50 mm and respective thicknesses of either 5 or 10 mm, as well as into a variety of shaped Teflon/PVC molds. Disc molds were maintained at room temperature during casting, while complex molds were preheated in an oven, set at 65 ± 5°C, for 30 min before casting to facilitate mold filling. After casting, the molds were placed in a refrigerator for roughly 1 h to accelerate gel setting. Gel-cast samples were demolded before being allowed to dry at room temperature. They were then covered with glass or plastic vessels (with openings providing limited air exchange) to encourage even, slow drying. The machining of dried gel-cast green bodies was investigated using a desktop computer-numerical-controlled (CNC) milling machine (Model MDX-15, Roland DG, Irvine, CA). The unit utilizes a 10 W dc motor running at 6500 rpm for cutting. Tungsten carbide bits of either 1/8″ or 1/16″ diameter, with ball or mill ends, were used with a variety of material feed rates.

Results and Discussion

Agar Rheological Testing

In preparing agar solutions in a beaker on a hotplate, it was found that formulations up to 5 wt% could be readily fabricated. The elevated viscosity of solutions with higher agar concentrations led to the accumulation of difficult-to-remove vapor bubbles during heating and stirring. These bubbles, along with the high viscosity, made it extremely hard to sample the solution using a syringe or otherwise. Consequently, a practical limit of 5 wt% existed for the preparation of agar suspensions under atmospheric pressure. Higher concentration suspensions were easily prepared using the overpressure conditions afforded when using an electric pressure cooker.[21,22] As the solutions were maintained in nominally sealed autoclavable jars and cooled to <90°C before opening, solution bubbling was not an issue. Concentrations up to 10 wt% were possible using this latter approach, although in practice, these still proved quite viscous during subsequent handling. Ultimately, 8 wt% agar solutions prepared by the overpressure method were considered the maximum practical concentration for gel casting purposes.

Through the use of rotational rheometry, it is possible to qualitatively observe the viscosity changes associated with agar dissolution and gelation. The development of viscosity on heating agar suspensions is demonstrated in Fig. 1. Solutions with 3 wt% agar, or less, show an initial decline in viscosity on heating, which is most likely driven by the relationship between solvent viscosity and temperature. At modest temperatures, 35–50°C, the apparent viscosity begins to increase as a result of agar dissolution into solution. The temperature at which agar dissolution is initiated appears to

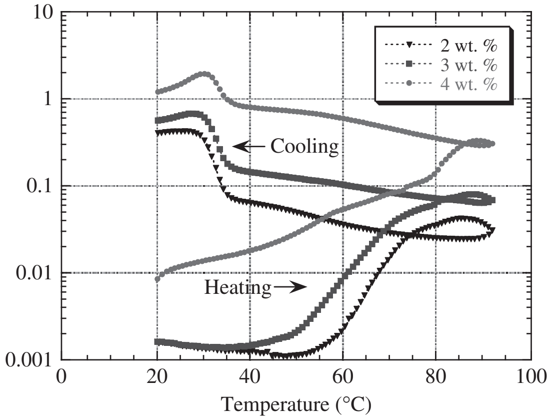

Fig. 1. Evolution of the viscosity on heating/cooling agar suspensions as a function of temperature (heating and cooling rate of 10°C/min).

be related to the agar content, with the higher agar concentrations dissolving at lower temperatures. In fact, 3.5 wt% (not shown) and 4 wt% agar suspensions display only an increase in viscosity on heating from room temperature. The observations for lower agar concentrations shown in Fig. 1 are generally in accord with those of Millán *et al.*,[8] while there is a small deviation in the response for the higher agar concentrations.

From Fig. 1, it can be seen that agar dissolution is completed at temperatures <90°C, as shown by the peaks in the viscosity traces on heating. Higher agar concentration suspensions, though beginning dissolution at lower temperatures, require slightly higher temperatures for this process to be completed. This feature highlights the existence of a practical limit to the preparation of more concentrated agar solutions under normal atmospheric conditions, as eventually the temperature required for complete dissolution approaches the solvent boiling point. Upon cooling fully dissolved agar solutions, a gradual viscosity increase is apparent. The rate of increase is similar for the given agar concentrations. At roughly 35°C, gelation begins, as shown by an abrupt increase in viscosity. Gelation is complete at approximately 30°C, after which the apparent viscosity begins to decrease again, as either the gel structure that is formed is disrupted by the constant applied shear or wall slippage occurs.

As noted above, the type of basic constant shear rate, controlled cooling rate curve shown in Fig. 1 provides some qualitative information on gelation behavior, and has been used extensively in a number of prior gel-casting studies.[5,6,8,9,21,22] However, for a more quantitative evaluation of rheological response, dynamic oscillatory measurements of the viscoelastic properties need to be made, including the storage and loss moduli (G' and G'', respectively), ideally under conditions that do not disrupt the gelling structure (i.e., low strain). To date, there has been very little study of these properties in gel-casting systems,[23] and none where G', G'', and the phase angle, δ, have been directly compared during cooling and gelation. In the present work, a variety of cooling rates, agar loadings, and solution pH levels were studied, in order to present a more comprehensive evaluation of the gel-casting process when using agar. In each case, as the rheometer could not analyze excessively strong gels, agar solutions were prepared at lower concentrations (i.e., ≤5 wt%) under atmospheric conditions.

Figure 2 demonstrates the evolution of storage modulus (G'), loss modulus (G''), and phase angle (δ), as well as the normal force on the Peltier plate, upon cooling a 4 wt% agar solution at 10°C/min. Several fea-

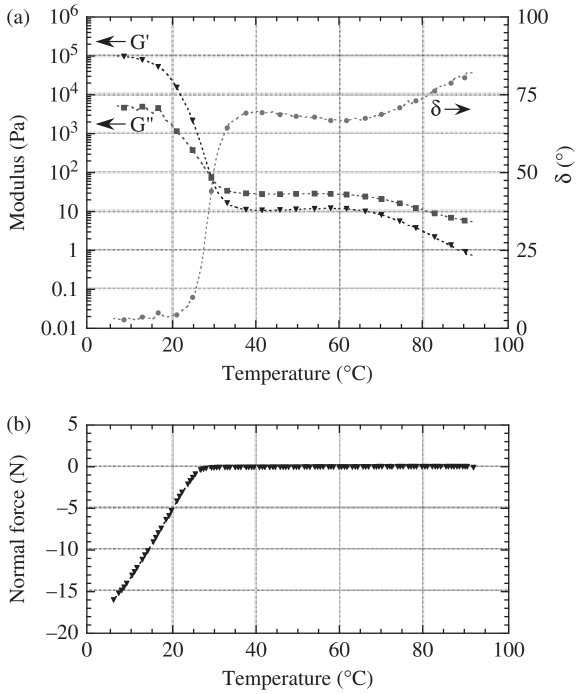

Fig. 2. (a) Evolution of the storage modulus (G'), loss modulus (G''), and phase angle (δ) during cooling of a 4 wt% agar solution at 10°C/min. (b) Evolution of the normal force upon cooling of the same agar solution.

tures visible in Fig. 2a are common to all the agar solutions studied. As expected, at high temperatures, G'' is greater than G' (and accordingly $\delta > 45°$), and the solutions are seen to behave more as liquids than solids. After a plateau region, during which both moduli remain roughly constant, gelation begins to occur. This is apparent from the crossover of G' and G'', combined with the dramatic decrease in δ, and indicates the formation of a gelled structure with more "solid-like" or elastic characteristics. The change in normal force on the Peltier plate (Fig. 2b) also provides useful information regarding the gelation process. Here, a *positive* normal force indicates a push down on the Peltier (or correspondingly, an expansion of the sample), while a *negative* force indicates a pull upwards (or sample contraction). For each sample, two distinct regions on the normal force curve are visible. The first, possessing a very small gradient (not apparent on the full scale shown in Fig. 2b), is associated with solvent evaporation and indicates that the setup used to prevent volatilization was effective. The second region has a considerable slope, and begins at a temperature just below the crossover of the G' and G'' moduli curves (shown in Fig. 2a). This rapid decrease in normal force results from contraction of the gelled solid adhering to the upper and lower plate during cooling. This feature validated the use of SiC paper on each contacting surface to prevent slippage; indeed, gels were seen to be well adhered to the geometry during sample removal.

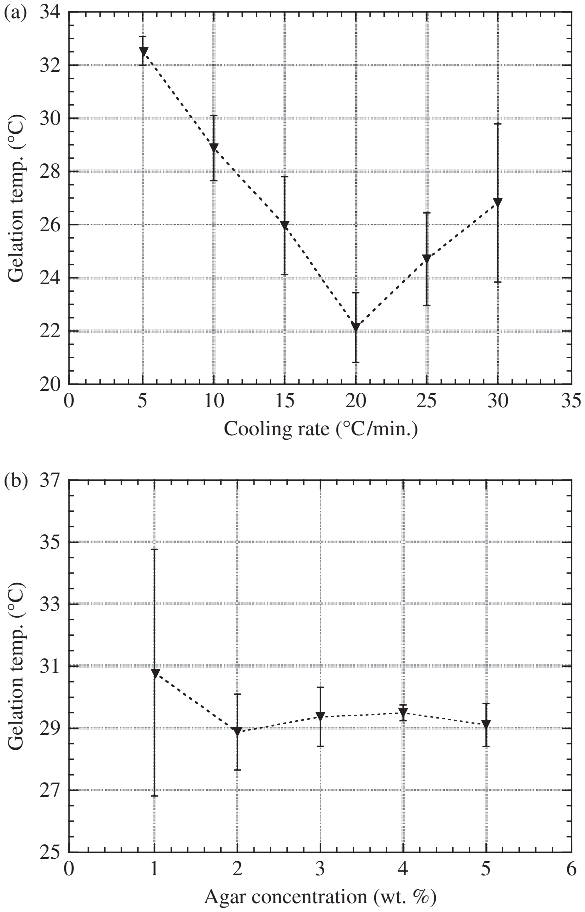

Fig. 3. (a) Gelation temperature of 2 wt% agar solutions for various cooling rates. (b) Gelation temperature of agar suspensions as a function of agar concentration at a cooling rate of 10°C/min.

From the curves produced for each individual sample (as represented by Fig. 2), two features were of interest, namely the gelation temperature and the gel strength. Although there are many methods used to quantify gelation temperature,[29] here the gelation point was taken as the temperature at which $G' = G''$. This exact temperature was calculated using linear interpolation of the two curves. Fig. 3a compares the gelation temperatures noted for different cooling rates of 2 wt% agar solutions, while Fig. 3b compares the gelation temperatures determined for different agar loadings. Two trends are clearly visible in Fig. 3a. For cooling rates up to 20°C, an increase in cooling rate corresponds to a decrease in gelation temperature. However, at more excessive cooling rates, gelation temperature begins to increase with cooling rate. This effect could be useful, as gels setting at a higher temperature generally exhibit higher strength.[30] Obviously, still higher cooling rates than those used in this study would be necessary to exploit this effect, as the highest gelation temperatures here were noted for the slowest cooling rate. It has been documented elsewhere that slower cooling rates lead to higher gelation temperatures when cooling rates up to 20°C/min are used.[31] However, to the best of the authors knowledge, the effect of cooling rates > 20°C/min has not been reported elsewhere. Investigation into the effect of agar loading on gelation temperature provided less distinct results (Fig. 3b). Within experimental error, the gelation temperature is essentially independent of agar concentration. In contrast to these results, gelation temperatures have been shown to increase by as much as ~5°C when varying agar concentrations from 1 to 3 wt%.[31] Other studies have also shown an increase in gelation temperature with agar content.[18–20] It is notable that these studies consistently utilized slow cooling rates, as shown in Table I, and this behavior may, therefore, arise simply from solvent evaporation and consequent agar concentration, which is effectively eliminated at the higher cooling rates.

The gel strength was quantified by taking the magnitude of the storage modulus, G', in the gelled state. Gel strengths as a function of agar loading and as a function of pH, after cooling to both 20 and 10°C, are provided in Fig. 4. In analyzing the strength of gelled agar solutions, the expected trend of enhanced strength with agar loading was noted, as shown in Fig. 4a. Storage moduli increase in a steady fashion up to 5 wt% agar; at 10°C, a strength increase approaching one order of magnitude is observed when raising agar content from 2 to 5 wt%. Perhaps more surprising is the correlation between gel strength and pH for 2 wt% agar solutions, provided in Fig. 4b. There is a clear benefit to adjusting the suspension pH to ~ 10, while neutral pH and excessively basic conditions are detrimental. In fact, preparation at pH ≥ 11 results in a change in color of the agar suspension to a brown or black shade. This same discoloration has been noted previously, and has been attributed to a reaction between the solvent and a sulfuric ester present on the polysaccharide.[32] In that same prior study, pH levels of 9.8 were shown to encourage swelling of agar gels over other pH levels. Thus, it would seem that pH levels of ~ 10 encourage agar/water solubility and increase the resultant gel strength. Raising the solution pH from 8 to 10 offers a 15% increase in storage modulus by the time the agar has cooled to 10°C. This presents a simple means of strengthening agar gels, and thus gel cast samples, without increasing the agar content.

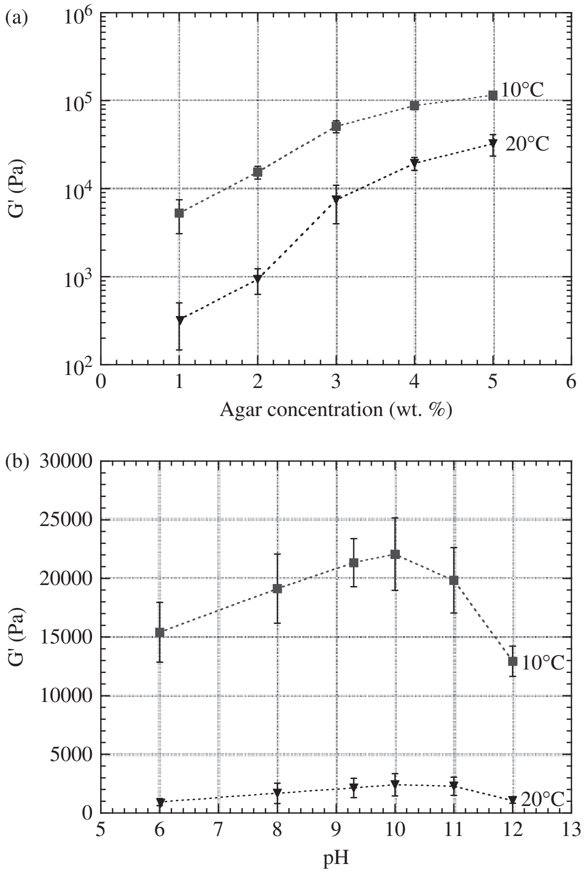

Fig. 4. (a) The effect of agar content on the gel storage moduli (10°C/min cooling rate). (b) The effect of pH on the storage moduli of 2 wt% agar gels (10°C/min cooling rate).

As previously stated, all data concerning agar gelation temperature and gel strength were obtained using agar solutions prepared under atmospheric conditions. However, agar solutions of low agar content (i.e., ≤ 5 wt%), prepared in the pressure cooker, were also analyzed in a similar manner and yielded results that consistently fell within the range of error marked on the figures shown previously. Assuming complete dissolution of the agar in both environments, such an observation should be anticipated, as there is no evidence for a change in the agar gelation mechanism (i.e., a coil-to-helix transition) due to a change in the preparation method. As a consequence, there is a notable benefit to preparing agar using overpressure conditions, as higher agar concentrations are possible, although this alternate preparation route provides no differences in gelation temperature or gel strength. Conversely, Santacruz *et al.*,[22] found that agarose gels prepared using a pressure cooker exhibited an approximately one order of magnitude *lower* viscosity than when prepared at atmospheric pressure. This response was attributed to incomplete dissolution of the agar for higher agar concentrations when prepared more conventionally using a hot plate. However, this observation is perhaps a little surprising based on the results of Fig. 1, as it can be seen that the viscosity of what is initially an agar suspension actually *increases* as the agar is dissolved into solution. Consequently, a partially dissolved agar solution may be anticipated to possess a lower viscosity than one that is fully dissolved. Alternate reasons for this apparent discrepancy might be solvent loss (i.e., water evaporation), when preparing gels on a hot plate, or even possible solvent increase when using a pressure cooker if the gels are not prepared in a nominally sealed container. It is notable that the viscosity observed for a 5.6 wt% agarose gel prepared in a pressure cooker by Santacruz *et al.*,[22] is almost identical to a 1 wt% agarose gel prepared on a hot plate by Millán *et al.*,[8] which should be readily dissolved at such a low concentration.

Combined Agar/Suspension Rheological Testing

Oscillatory rheological tests were performed on 55 vol% $BaTiO_3$ suspensions, combined with a variety of different agar solutions. The results contrast those of agar solutions alone, as the storage modulus, G', is greater than the loss modulus, G'', over the entire range of temperatures studied (Fig. 5). Correspondingly, the value of the phase angle, δ, does not exceed 45°, indicating that the combined suspensions behave in a more elastic manner than viscous. The lack of a G'/G'' crossover point made it impossible to ascertain the gelation temperature of the combined $BaTiO_3$ powder/agar suspensions, contrary to the case of agar solutions alone. However, the normal force curves, as exemplified in Fig. 5b, could be used to approximate the gelation temperatures, and they consistently fell within 28 ± 2°C, corroborating the gelation temperature measured for agar solutions noted in Fig. 3b.

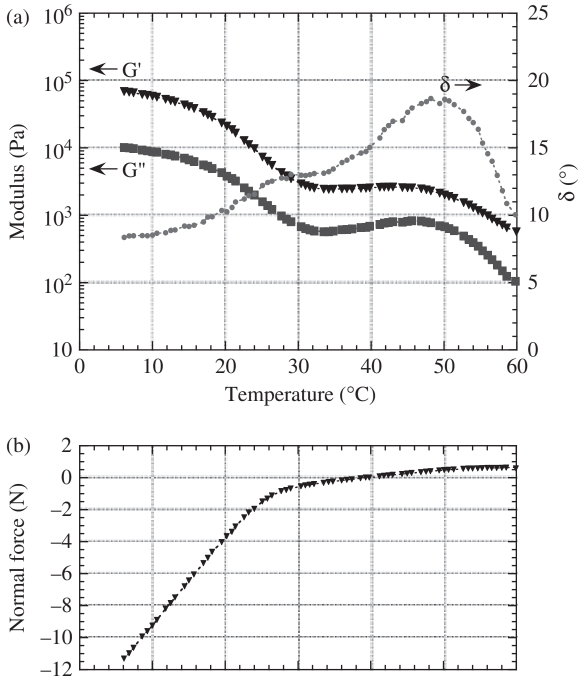

Fig. 5. (a) Evolution of the storage modulus (G′), loss modulus (G″), and phase angle (δ) upon cooling a gel-cast suspension (55 vol% bimodal $BaTiO_3$ with 4 wt% agar solution) at 10°C/min. (b) Evolution of the normal force upon cooling of the same gel-cast suspension.

Interestingly, curves display a plateau, sometimes even a peak, in storage and loss moduli, beginning at approximately 45–50°C. This behavior was also seen in agar solution oscillatory tests, though its cause and consequences were not clear. It is possible that the lead-in to this plateau is related to the thermal history of the sample and indicates the occurrence of a stabilization process. If that were the case, a well-stabilized sample would display relatively constant properties above its gelation temperature. Further investigation is required to more fully understand this feature of the oscillatory measurements.

Similarities exist in both Figs. 5b and 2b concerning the evolution of normal force on cooling of samples. The normal force measurement, during rheological tests of agar solutions and of combined suspensions, is seen to be relatively constant before gelation. The slope of the curve in this initial region is greater for combined suspensions than for agar alone. This indicates no enhanced weight loss due to evaporation, as the same equipment setup was used, but an increased tendency to contract before gelation. This feature essentially corroborates the more elastic nature of the combined suspensions compared with the agar alone, and highlights a resistance to viscous deformation that must be overcome during gel casting of such suspensions.

From the individual plots of storage moduli, G', the gel strengths were noted, again by linear interpolation, at temperatures of 20° and 10°C. The measured strengths, as a function of the agar precursor content, are shown in Fig. 6a. These values were taken when the samples cooled to the noted temperature, although some degree of strengthening continued to occur over time. Generally, the storage moduli were seen to increase by an average of 25% in the 10 min following the initial oscillatory tests. As expected, the use of higher concentration agar precursor solutions leads to higher gel strengths, when the overall agar content is held constant with respect to the $BaTiO_3$ solids content.

The drawback to using higher concentration precursors is, of course, the additional viscosity they impart

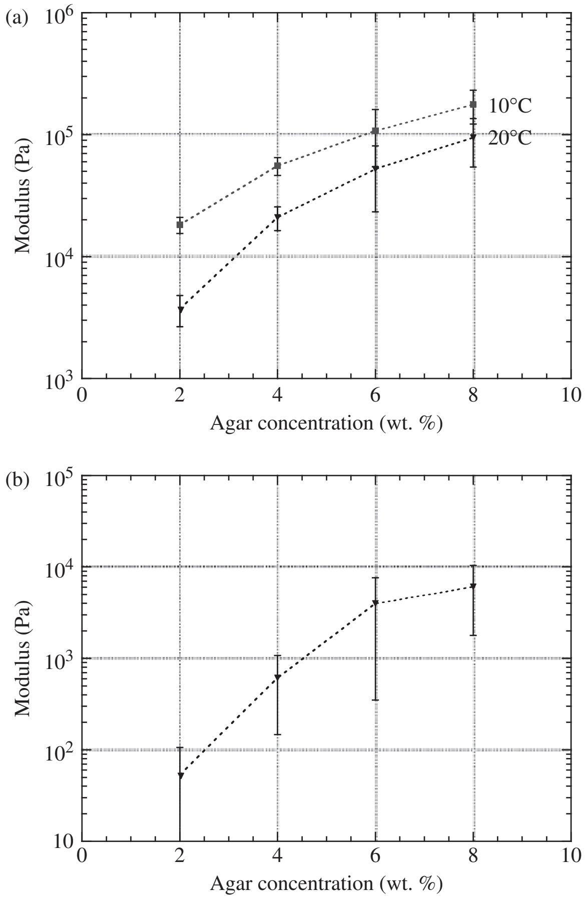

Fig. 6. (a) The effect of agar precursor concentration on the storage moduli (G′) of gel-casting suspensions (prepared with 55 vol% BaTiO$_3$ and a final agar content of 0.5 wt% as a function of the total solids content). (b) The effect of agar precursor concentration on the loss moduli (G″) of gel-cast suspensions at 55°C (prepared with 55 vol% BaTiO$_3$ and a final agar content of 0.5 wt% as a function of the total solids content).

on the resulting combined agar/ceramic slip. Qualitatively, combinations prepared using 2 wt% precursors were very thin with no noticeable difference in viscosity from concentrated BaTiO$_3$ suspensions alone, while those prepared from 8 wt% precursors were excessively viscous, bordering on a paste-like consistency. Taking the magnitude of the loss modulus, G'', to be a representation of the mixture viscosity, it is possible to quantitatively see the effect of increasing the agar precursor concentration. Fig. 6b compares G'' at 55°C as a function of agar precursor concentration, and illustrates an increase in loss modulus upon raising the agar precursor concentration from 2 to 8 wt% of more than two orders of magnitude.

Gel-Casting Behavior

Successful agar gel cast ceramics are those that exhibit the required strength during casting and demolding, fill the mold properly, and which dry without distortion or cracking to provide a homogenous green body. It has been shown in the previous section that the strength of gelled agar/ceramic suspensions can be enhanced through the use of increasingly concentrated agar precursor solutions. However, both the elastic and viscous rheological properties of such suspensions are negatively affected in terms of flowability as the water content decreases. It can, therefore, be seen that the strength and mold-filling capabilities are optimized under opposing conditions, and a balance between the two must be reached. It is also clear that drying shrinkage is to be expected with this system, as a large quantity of water is associated with the gelling agent. In order to limit shrinkage, water content in both the suspension and the agar precursor should be kept as low as possible.

Considering the suspension formulation of this study (55 vol% bimodal BaTiO$_3$), it is useful to summarize the effects of adding agar precursors of different concentration on the overall solids loading. In Fig. 7a, contour lines are plotted that highlight the total solids content of 55 vol% suspensions after a certain quantity of agar precursor solution is added. The marked diluting effect of adding agar solutions to ceramic suspensions is clear. For example, if only a weak agar precursor solution of 2 wt% is used, and the desired agar concentration in the gel-casting suspension is 1 wt%, the overall solids content of the suspension will be decreased from 55 to roughly 20 vol%. This would have a drastic impact on drying shrinkage, and could well result in cracking and warping. Even a very concentrated 10 wt% agar precursor would decrease the solids content from 55 to 42 vol% for the same agar requirement. Figure 7a effectively emphasizes a major issue associated with polysaccharide gel casting, and stresses the importance of using high-concentration precursor solutions and keeping the overall content of the gelling agent to a practical minimum.

However, there is an aspect of diminishing returns indicated by Fig. 7a. At high agar precursor concentrations, it is not as beneficial to further increase the concentration as it is at low agar concentrations. This is

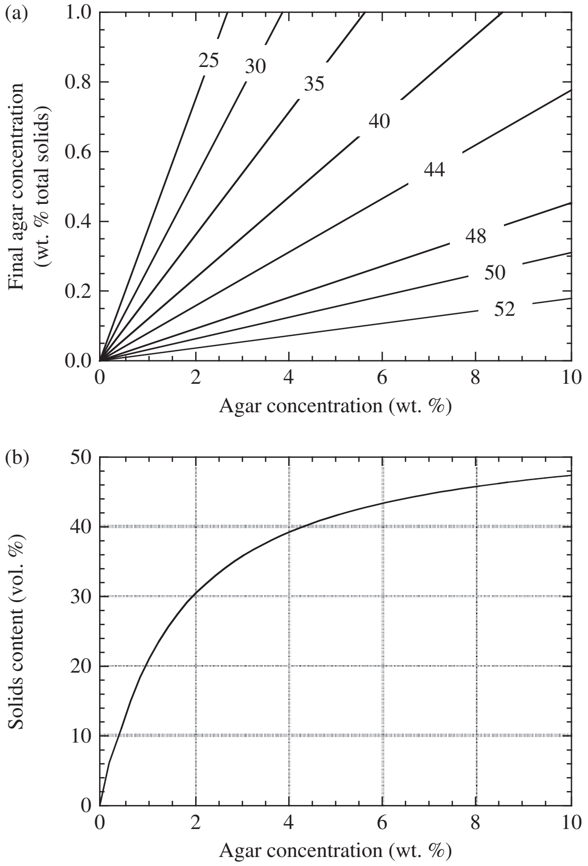

Fig. 7. (a) Contour map of theoretical solids loadings in combined agar/ceramic suspensions (with 55 vol% $BaTiO_3$ in the initial suspension). (b) Theoretical final solids content of 55 vol% suspension mixed with various agar precursor concentrations (with a final agar content of 0.5 wt% of the total $BaTiO_3$ solids content).

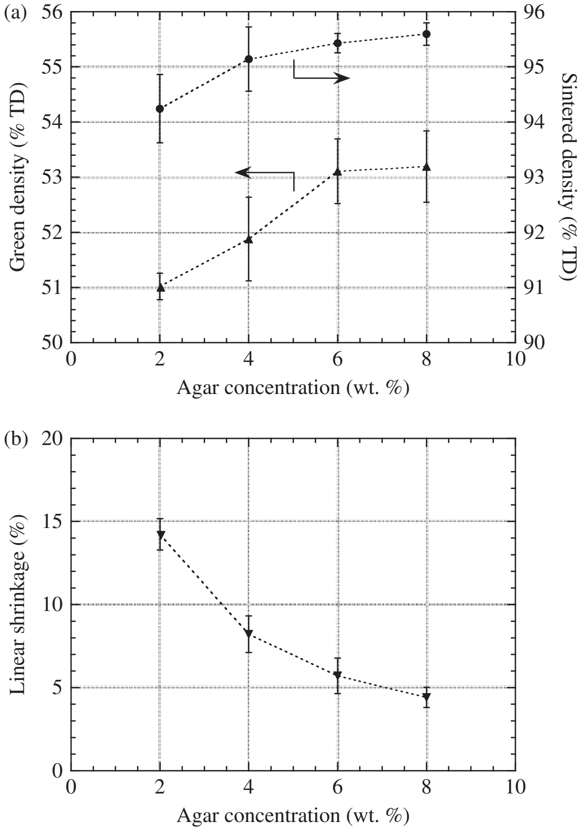

Fig. 8. (a) The measured green and sintered densities of dried, gel-cast solids as a function of initial agar concentration in suspension; samples sintered at 1300°C for 2 h. (b) The drying shrinkage of gel-cast solids as a function of initial agar concentration in suspension. All samples were prepared with 55 vol% $BaTiO_3$ and a final agar content of 0.5 wt% as a function of the total solids content

most easily illustrated by considering a range of suspensions in which agar is required at a final concentration of 0.5 wt% of total solids. Under this constraint, the correlation between agar precursor concentration and final solids loading is shown in Fig. 7b. Given that the curve asymptotically approaches 55 vol%, slight improvements of an already concentrated agar precursor provide only minimal advantages in counteracting dilution.

Gel casting of discs with an overall agar content of 0.5 wt% of total solids corroborated the theoretical benefits of avoiding suspension dilution. Figure 8a compares the green and sintered densities of dried discs to the concentration of the agar precursor used; sintering was performed at 1300°C for 2 h. It is apparent that the achievable green densities increased with agar precursor concentration, but were much lower than the ~66% of theoretical density that can be achieved via slip casting of similar suspensions.[26] Conversely, the sintered densities were extremely close to those achieved for the same 85:15 coarse:fine particle size ratio mixture after slip casting and sintering.[26] This observation demonstrates that gel casting can be applied in a comparable manner to other forming techniques to obtain high-sintered densities. It should be noted that for slip-cast samples, higher sintered densities were achieved with a nominal 70:30 coarse:fine mixture under identical conditions, in spite of the higher viscosity when in the suspension state.[26] Consequently, it is expected that further density improvements could be achieved in the present work through modification of both the suspension formulation and the sintering conditions. Gel casting using higher concentration agar precursor solutions yielded not only higher density solids, but also limited drying shrinkage, as shown in Fig. 8b, which is favorable from the perspective of improved dimensional stability.

Casting into a variety of complex molds proved successful in creating difficult-to-form ceramic pieces. Based on the casting of simple discs, 6 wt% agar precursor suspensions were chosen for complex castings due to their combination of manageable viscosity and strength. A moderately thin-walled tube (4 mm wall thickness) with 0.5 wt% agar was found to be strong enough for demolding approximately 1 h after casting, and could be subsequently dried without cracking or warping (Fig. 9a). It is clear that during casting, the suspension flowed well and evenly, filling the heated Teflon mold entirely.

The ability of the gel-casting process to form pillars of ceramic on a common base was also investigated. This type of structure is often machined from a solid sintered piece in the forming of 1–3 piezoelectric composites, for example for sonar or ultrasound applications, resulting in significant material wastage and added expense. As a consequence, the direct casting of this component architecture is a potentially interesting process to significantly reduce production costs. Casting of this structure required a higher agar concentration to impart the necessary strength for demolding, namely 1 wt% of total solids. Such a casting is shown immediately after demolding in Fig. 9b. The successfully cast pillars ranged from 8.2 mm in diameter down to 1.9 mm, at the narrowest, and all pillars were 25.4 mm in height (i.e., a maximum achievable aspect ratio of $\sim$13.5:1). As shown, not all pillars were strong enough to support their own weight at the given agar concentration, and so the component needed to be inverted during drying.

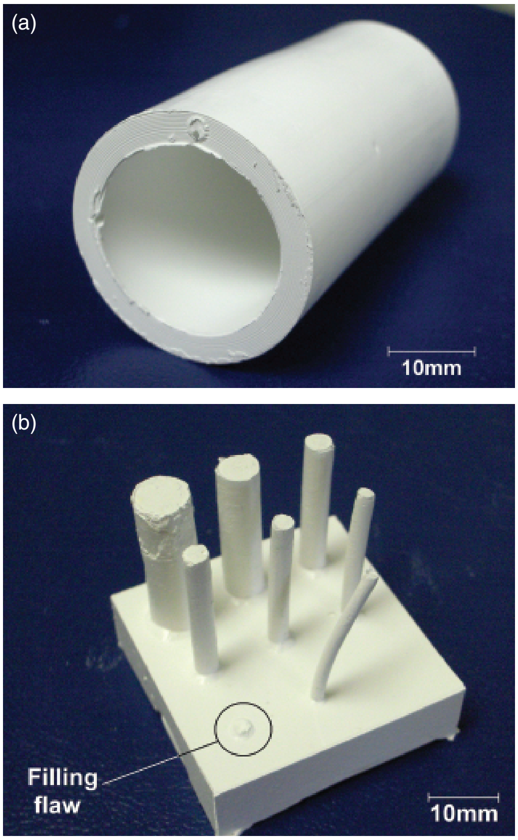

Fig. 9. (a) Gel-cast and dried tube (0.5 wt% agar from 6 wt% precursor). (b) Gel-cast "pillar" structure (1 wt% agar from 6 wt% precursor solution) immediately after demolding.

Green Machining

Dried, gel-cast solids were successfully CNC machined into a variety of shapes. Cutting speeds parallel to the upper surface (i.e., x and y directions) ranged from 10 to 12 mm/s, while those normal to the surface (i.e., z direction) were varied between 0.5 and 4.0 mm/s. In each case, the thickness of material removed per horizontal pass of the milling bit was constant at 0.5 mm. No differences in the quality of machining were noticed across these ranges of cutting speeds.

To investigate the capability of producing internal features, a 2-mm-thick disc was milled flat on both surfaces and a hexagonal array of 1.5875 mm (1/16th in.) diameter through-holes was then drilled into the surface using a ball-end milling bit. This type of pattern resembled that found on ceramic filters used industrially to sieve molten metal, highlighting a practical use for the process of gel casting. The agar concentration in the sample was 0.5 wt% of total solids, added as a 4 wt% precursor. Such a machined disc, after being sintered at 1300°C for 2 h, is pictured in Fig. 10a. As shown, the holes were clean and free from any chipping. Some isolated voids were left from bubbles in the suspension, which were exposed by milling, indicating the need for a deairing step before casting.

To examine the ability of the milling process to form external features, a series of 10 thin fan blades was machined. Each blade narrowed in thickness from $\sim$0.8 mm at the base to $\sim$0.35 mm at the tip, and

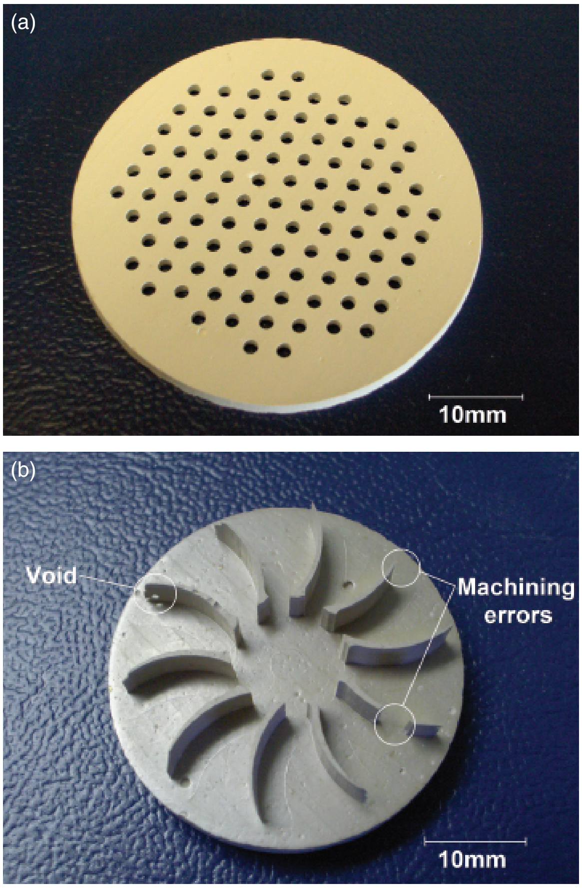

Fig. 10. (a) A simple "filter"-type disc machined from a gel-cast billet (0.5 wt% final agar content from an initial 4 wt% precursor solution) and subsequently sintered at 1300°C for 2 h. (b) Fan blades successfully machined from gel-cast puck (1 wt% final agar content from an initial 8 wt% precursor solution), and subsequently sintered at 1300°C for 2 h.

stood ~5.2 mm proud of the surface (i.e., a successfully machined tip aspect ratio of ~15:1). This example is shown, after sintering, in Fig. 10b. Because of the delicate nature of the fan blades, the agar requirement was higher than for the filter (1 wt% of total solids). As shown, all of the fan blades were fully formed with the exception of those containing air bubbles and those damaged due to a communication error between computer and milling machine. A few of the fan tips were broken during handling and inspection immediately after sintering, reflecting the brittle nature of this material, even in a densified state.

The difference in machinability between solids containing 0.5 and 1 wt% total agar clearly suggested that tailoring of the suspension formulation for each specific application would be desirable. Internal features were easily machined when only 0.5 wt% agar was present, and thus for certain simple forming processes, it may be possible to use a low-agar, low-viscosity suspension when gel casting. However, if a more complex geometry is necessary, a slip having a higher agar concentration, and thus higher viscosity, may be required to offer the mandatory strength during green machining.

Conclusions

In the present work, an environmentally benign and food-grade biopolymer, agar, has been used for gelcasting $BaTiO_3$-based suspensions. To achieve high solids content before casting, an 85:15 ratio mixture of two commercially available powders was used, with nominal particle sizes of 500 and 100 nm, respectively. Assessment of the rheological behavior of agar solutions was performed using both constant shear and oscillatory measurements. It was demonstrated that agar gels with concentrations varied between 1 and 5 wt% showed an essentially constant gelation temperature on cooling of ~30°C, contrary to some prior studies, which showed apparently decreasing gelation temperature with increasing agar concentration. The reason for this discrepancy is not clear; however, these previous studies invariably used very slow cooling rates (i.e., 0.5–2°C/min), such that drying artifacts cannot be discounted, which can be expected to be increased at higher agar concentrations. Assessment of the shear moduli of agar gels demonstrated that gel strength increases with agar concentration, and also with solution pH to a maximum at ~pH 10. Consequently, processing agar-based suspensions in this general pH range can be viewed as favorable from the perspective of preform green-strength; coincidentally, processing of $BaTiO_3$ suspensions was found to be optimally conducted at pH 9.3.[26] The preparation of agar solutions was limited to a practical concentration of 5 wt% under atmospheric conditions. This could be extended to 8 or even 10 wt% when gels were produced at elevated pressure and temperature. It was found that agar prepared under either condition showed a similar rheological response when the agar concentration was constant.

Gel-casting mixtures were prepared by blending a high-concentration $BaTiO_3$ suspension with an agar solution of known concentration. The constituent ratio was then controlled to yield a known final agar concentration in the mixture. The rheological behavior of $BaTiO_3$/agar suspensions showed generally similar behavior to agar alone, although the suspensions had an oscillatory response that was predominantly "solid-like," even above the gelation temperature. Gel casting of $BaTiO_3$ was conducted with 55 vol% solids suspensions, using agar solution concentrations varied between 2 and 8 wt%, with the final agar concentration adjusted to either 0.5 or 1.0 wt% of the total solids content. After drying, for a constant final agar concentration (i.e., 0.5 wt% of the total solids), the green density of the cast $BaTiO_3$ ceramics was found to increase with the agar content in the initial solution, while drying shrinkage decreased in a similar manner. This behavior can be anticipated based upon the total liquid content in the suspensions (i.e., double-distilled water), which decreases with increasing initial agar solution concentration. A dried green density of $\sim$53.2% of theoretical was achieved for an initial 55 vol% $BaTiO_3$ suspension, mixed with a 8 wt% agar solution, to give a final agar concentration of 0.5 wt% of the total solids in the final suspension.

Casting was performed using a variety of polymer-based molds, in order to make components such as ceramic tubes and pillar arrays (e.g., for the preparation of piezoelectric 1–3 composites). Anisotropic features such as pillars could be routinely cast to an aspect ratio of 7:1 without deformation, while pillars up to $\sim$13:1 could also be formed but required careful drying to minimize distortion. In addition to being able to cast moderately complex architectures directly, it has also been demonstrated that CNC-based green machining is readily achievable, including the production of thin, high aspect ratio features such as turbine blade tips, which have an aspect ratio exceeding 15:1.

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