Ceramics International 30 (2004) 503–507

CERAMICS INTERNATIONAL

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A novel gel tape casting process based on gelation of sodium alginate

Zhiyong Yu [a,*], Yong Huang [a], Chang-an Wang [a], Shixi Ouyang [b]

[a] *State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, PR China*
[b] *China Building Materials Academy, Beijing 100024, PR China*

Received 16 December 2002; received in revised form 5 July 2003; accepted 25 August 2003

Abstract

A novel gel tape casting process by sodium alginate is described. Sequestrant and calcium salts are added into ceramic suspension simultaneously, thus the gelation between calcium salts and sodium alginate is avoided because a stable complex was formed from sequestrant and calcium salts. By adding adipic acid, calcium ions are released from the complex and react with sodium alginate to form a three-dimensional (3D) network. Therefore, ceramic particles are held in this network thus resulting in a green tape. The effect of dispersant and binders on the rheological behavior of suspensions was investigated. The optimal amount of dispersant was found to be ∼0.3 wt.%. The addition of styrene-acrylic latex changed the rheological behavior of the suspensions and improved the flexibility of green tapes. Gelation rate suitable for tape casting could be easily controlled by the amounts of adipic acid and sequestrant. Green tapes with homogeneous microstructure have been fabricated by this process.

Keywords: A. Tape casting; A. Suspensions; D. Al_2O_3; Gelation

1. Introduction

The tape casting process can be divided into non-aqueous and aqueous systems according to the solvents used [1]. Non-aqueous solvents typically have lower boiling points and can avoid the hydration of some ceramic powders, but require special precaution concerning toxicity and inflammability. In recent years, the environmental and health aspects of the tape casting process have drawn more attention. Therefore, aqueous solvents, which have the advantages of incombustibility, non-toxicity and low cost, are considered as a substitute for non-aqueous solvents. However, the aqueous suspension has a smaller tolerance to minor changes in drying conditions and also the drying rate of the aqueous suspension is invariably much slower than that of the non-aqueous systems [1,2]. Therefore, non-homogeneous microstructure and cracks usually occur in green tapes. To overcome these comebacks, Xiang developed a gel tape casting process as an alternative route to the process, in which a monomer solution was used as a substitute for organic solvents and binders to coagulate ceramic suspensions [3]. However, the monomer used is acrylamide with neural toxicity. In this paper, a natural innoxious polymer, sodium alginate, was used to consolidate ceramic suspensions.

Sodium alginate is a type of gelling polysaccharide most commonly isolated from brown kelp. Sodium alginate can be dissolved in water at room temperature and undergo chemical gelation to form a three-dimensional (3D) network in the presence of multivalent cations, particularly calcium [4]. The alginates are usually used as processing aids in many traditional ceramic-forming processes, including dry molding, extrusion, slip casting, where they impart plasticity, workability, suspension stability, and suitable wet and dry strength. In fact, the chemical gelation of sodium alginate has also been used in gel-casting and solid free form fabrication techniques to produce ceramics [5,6]. In this paper, sodium alginate was used to fabricate green tapes by using a sequestrant to control gelation behavior.

2. Experimental procedure

2.1. Starting materials

The starting ceramic powder used here was α-Al_2O_3 (>99.7 wt.% purity, Henna Xinyuan Aluminum Corporation,

* Corresponding author. Tel.: +86-10-62785488; fax: +86-10-62771160.
E-mail address: yuzhiyong99@mails.tsinghua.edu.cn (Z. Yu).

0272-8842/$30.00
doi:10.1016/j.ceramint.2003.08.003

Table 1
Additives of gel tape casting suspensions

Binders	Sodium alginate
	Styrene-acrylic latex[a]
Dispersant	Ammonium citrate tribasic, $C_6H_{17}N_3O_7$
Calcium salt	Calcium phosphate tribasic, $Ca_3(PO_4)_2$
Sequestrant	Sodium hexameta phosphate, $(NaPO_3)_6$
Acid	Adipic acid, $C_6H_{10}O_4$
Plasticizer	Glycerol

[a] 50 wt.% polymer, glass-transition temperature (T_g), 5 °C.

China) with a mean particle size 2.9 μm, and specific surface area 0.434 m^2/g. All additives of the suspensions used in this work are listed in Table 1.

2.2. Suspension preparation and tape casting

The process flowchart is presented in Fig. 1. Sodium alginate was dissolved in the deionized water to form a solution, and then the styrene-acrylic latex was added into the solution and stirred for 30 min. After alumina powders, dispersant, plasticizer, sequestrant and calcium salts were added into the mixture of binders, the suspension was ball milled for 24 h. Before casting, the resulting suspension was deaired under vacuum (0.02 atm) for 10–15 min and then adipic acid was added into. The prepared suspension was cast at room temperature, subsequently consolidated to form a green tape.

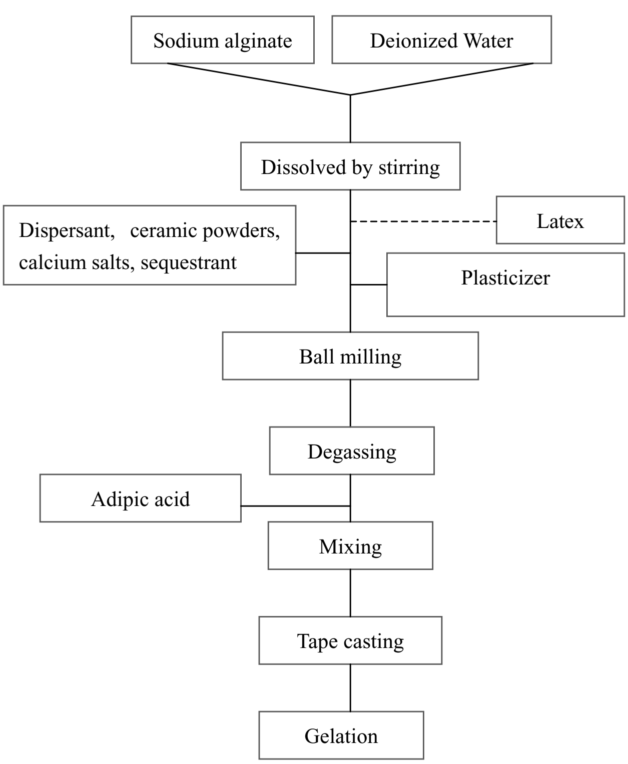


Fig. 1. Flowchart of gel tape casting process.

2.3. Characterization

The rheological properties of suspensions were measured using a rheometer MCR300 (Physica Corp., Germany). The microstructure of green tape was observed by scanning electron microscope (SEM, CSM950). Mercury porosimetry was used to characterize the density of green tapes.

3. Results and discussion

3.1. Suspensions preparation

Suspensions with 52 vol.% solids loading (50 vol.% alumina and 2 vol.% calcium phosphate tribasic) and 1 wt.% sodium alginate (based on water) were prepared. The effect of the amount of dispersant (based on ceramic powders) on the viscosity of the suspensions is shown in Fig. 2. It is obvious that the viscosity of the suspensions decreases with the increases of dispersant amount. The minimum of viscosity, corresponding to the best dispersion of alumina particles in the suspensions, is observed when ∼0.3 wt.% dispersant is added. While the amount of dispersant increases beyond 0.3 wt.%, the viscosity increases again, which implies that there exists an optimum concentrations at which just enough dispersant is present to provide maximized coverage of the ceramic particles and any excess dispersant may be harmful in decreasing viscosity. This dispersant content was used for the preparation of all the suspensions in the following experiments.

In the range of shear rate tested, the suspension with 52 vol.% solids loading and 1 wt.% sodium alginate shows an initial shear thinning behavior at low shear rates followed by a shear thickening behavior (shown in Fig. 3). Such behavior is unfavorable for tape casting because of the high shear stress generated under the blade (∼50 s^{-1} in our conditions). The shear thickening behavior usually occurs in a high concentrated suspension. Indeed, the structure of the suspension is determined by the interaction forces between particles [7,8]. At low shear rates, the agitation action can

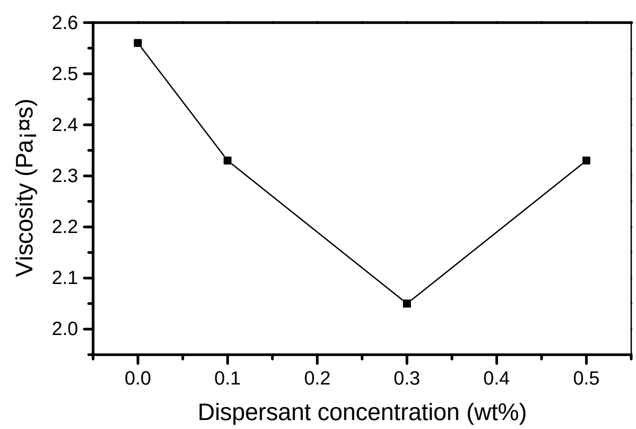


Fig. 2. Effects of dispersant content on the viscosity of Al_2O_3 suspensions (shear rate: 50 s^{-1}).

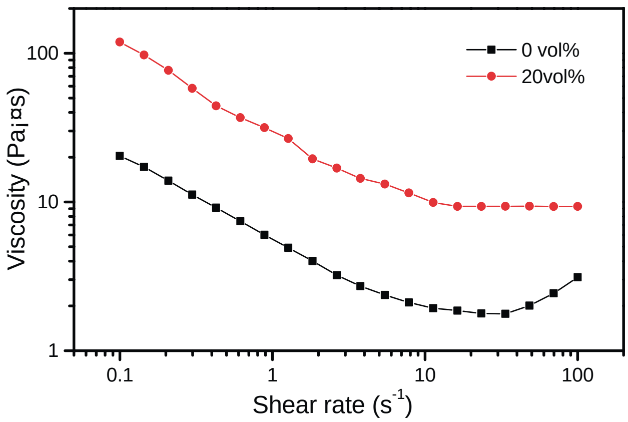


Fig. 3. Viscosity curves of Al_2O_3 suspensions with different latex concentration.

gradually break down the structure in suspension by overcoming the attractive energy and the viscosity of the suspension decrease. At high shear rates, the hydrodynamic forces between particles become dominant. This will lead to the formation of clusters in suspensions and the viscosity of the suspension increased.

The green tapes obtained using above suspensions were easily removed from the carrier and no obvious cracks were observed but tapes were not flexible enough for handling. The plasticizer (glycerol) could not effectively improve the flexibility of green tapes. In our previous work, alumina suspensions with 20 vol.% styrene-acrylic latex and 1 vol.% glycerol have been shown suitable for tape casting [9]. Therefore, 20 vol.% styrene-acrylic latex (based on sodium alginate solution) was simultaneously added into suspensions to improve the flexibility of the tapes here. As shown in Fig. 3, the addition of latex has a great effect on the viscosity of the suspensions and the type of their rheological behavior. The shear thickening behavior observed earlier disappears, and the suspensions containing latex exhibit a shear thinning behavior more suitable for tape casting now.

3.2. Control of the gelation of sodium alginate

In order to complete casting processing under control, a controllable reaction of calcium salts with sodium alginate must be considered. Generally, it is difficult to control the gelation rate between calcium salts (such as $CaCl_2$, CaC_2O_4) and alginate, which makes it impossible to complete casting processing at suitable period. In this work, the reaction rate was adjusted by sequestrant ($(NaPO_3)_6$) and adipic acid ($C_6H_{10}O_4$). Generally, if adding $Ca_3(PO_4)_2$ and $(NaPO_3)_6$ into the ceramic suspensions simultaneously, the gelation reaction between calcium salts and sodium alginate will be avoided because a stable complex was formed from the reaction between $(NaPO_3)_6$ and $Ca_3(PO_4)_2$. After $C_6H_{10}O_4$ is added into the ceramic suspensions, the complex would decompose and calcium ions are released slowly, thus leading to gelation.

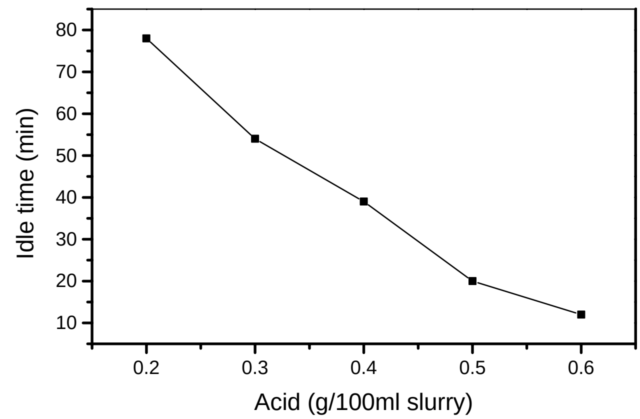


Fig. 4. Relationship between amount of acid and idle time.

The gelation rate of suspension with 52 vol.% solids loading was investigated. The beginning of gelation in ceramic suspensions was determined by changes in suspensions temperature, since the gelation is an exothermic reaction. The process was monitored in terms of idle time, t_{idle}, the time between the addition of the acid and the commencement of gelation, which is equivalent to the time available for casting the suspensions during processing. Figs. 4 and 5 show the variation of idle time with the amount of acid and with sequestrant, respectively. These data show clearly idle time is reduced by an increase of acid content and increased by an increase of sequestrant content. The idle time, i.e. the release rate of calcium ions, can be easily adjusted by the concentration of the reagents, thus the process can be easily completed under control.

3.3. Characterization of green tapes

The green densities and the flexibility of green tapes using three formulations of binders are summarized in Table 2. Although the tapes with only sodium alginate showed poor flexibility, the tapes with alginate and latex show good flexibility, which is similar to the tapes with only latex. The relative density of the green tapes with latex is higher than

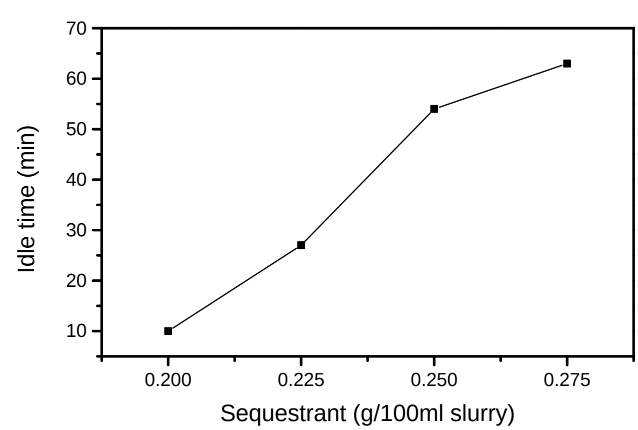


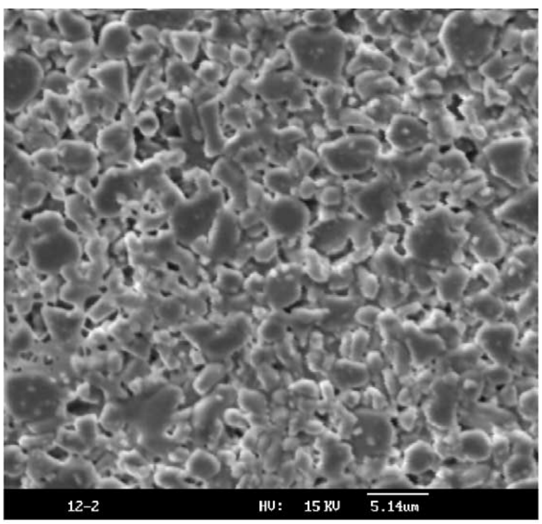
Fig. 5. Relationship between amount of sequestrant and idle time.

Table 2
Green densities and flexibility of green tapes

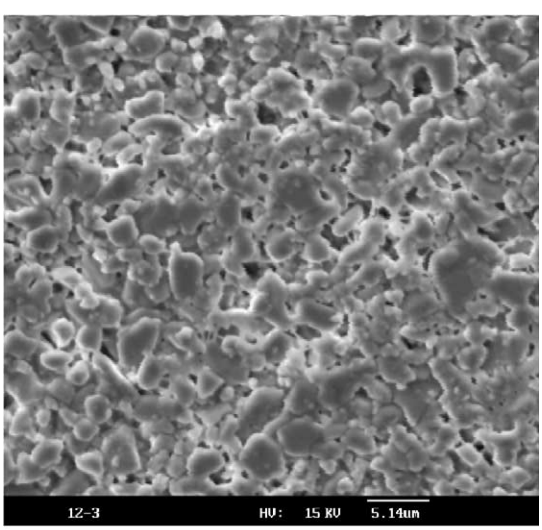
Binders	Green density (% TD)	Observation
Alginate	~56	Poor flexibility
Latex	~58	Good flexibility
Alginate + latex	~58	Good flexibility

with only alginate. However, the addition of alginate to the suspensions with latex shows no obvious influence on the density of green tapes.

In conventional aqueous tape casting process, the drying procedure is a critical stage. Usually, the drying of green tapes is inhomogenous. During drying, both the anisotropic migration of the solvent and the differential shrinkage will generate stresses in the green tapes and usually lead to cracking. Obvious difference in microstructures of upper and bottom layers is usually observed [10–12]. In this process, the ceramic powders and organic additives are solidified in the 3D network due to the in situ gelation of sodium alginate simultaneously in whole tape. Therefore, there is no need for a special drying procedure in which temperature and humidity are controlled carefully in order to avoid crack and inhomogeneity due to migration of solvent carrying binders, plasticizers and fine powders. Fig. 6 shows the microstructures of upper surface, bottom surface of a green tape containing 20 vol.% latex and 1 wt.% sodium alginate. It can be seen no obvious difference was observed between the upper surface and bottom surface. This shows more homogenous microstructure could be obtained by addition of sodium alginate.



(A)



(B)

Fig. 6. SEM micrograph of Al_2O_3 green tapes (A: upper surface; B: bottom surface).

4. Conclusions

A novel gel tape casting has been described. Sodium alginate has been used to consolidate alumina tapes from aqueous suspensions. However, because of low flexibility of resulting tapes, styrene-acrylic latex was also added to enhance the flexibility. Special drying procedure, which is critical stages in conventional tape casting, is avoided.

The use of dispersant can effectively improve fluidity of the suspension. The optimal amount of dispersant is ~0.3 wt.%. The styrene-acrylic latex strongly affects the rheological behavior of the suspensions. Suspensions containing styrene-acrylic latex exhibit a typical shear thinning behavior suitable for this process.

The time available for casting (idle time) can be controlled by varying the concentration of adipic acid and sequestrant. The idle time is reduced by an increase of acid content or increased by an increase of sequestrant content. The processing can be easily controlled by changing the addition amounts of adipic acid and sequestrant.

Green tapes with homogeneous microstructure were fabricated by this novel forming process.

Acknowledgements

This work was supported by the National Key Basic Research Development Program of China (Grant No. G2000067204).

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