



Aluminium acetate as alternative cross-linker for temperature controlled gel-casting and joining of ceramics



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ABSTRACT

In an earlier established gel-casting process, the biopolymer alginate is cross-linked with Ca^{2+} -ions released through the temperature controlled dissolution of calcium iodate-particles ($\text{Ca}(\text{IO}_3)_2$). In this study, aluminum acetate (AlAc) is compared to $\text{Ca}(\text{IO}_3)_2$ as an alternative temperature controlled cross-linker for an alginate–alumina slurry. Both cross-linkers are characterized regarding gel-forming properties, resulting microstructure, impurities, mechanics of sintered parts and the ability of joining ceramic blocks in the green state via connecting gelation with and without adding slurry. Rheological measurements show that both cross-linker have a similar gelling behavior and lead to gelled blocks of high quality. AlAc-particle create a denser and more homogenous microstructure, while $\text{Ca}(\text{IO}_3)_2$ -particles induce pores, abnormal grain growth and lower mechanical values. Nevertheless $\text{Ca}(\text{IO}_3)_2$ shows excellent joining properties which makes it a suitable alternative to pressure joining. In summary, AlAc is an excellent alternative cross-linker but $\text{Ca}(\text{IO}_3)_2$ remains the method of choice for joining gelled bodies.

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1. Introduction

Various types of gel-casting processes have been studied over the last decade and they are more and more frequently used for fabricating complex ceramic parts because of their advantages regarding processing time and shape complexity [1–4]. One of the most outstanding gel-casting processes is based on the ionotropic gelation of the biopolymer alginate. Ionotropic gelation of alginate-ceramics bases on the cross-linking between the guluronic acid-blocks of the heteropolymer alginate with multivalent cations (typically Ca^{2+}) [5,6]. This method is highly versatile and a wide range of shaping routes can be used. Among the calcium release methods, the temperature controlled release of Ca^{2+} from calcium iodate ($\text{Ca}(\text{IO}_3)_2$) is considered the best applicable. This method uses the rapidly increasing solubility of $\text{Ca}(\text{IO}_3)_2$ and the corresponding release of Ca^{2+} -ions with temperature [7].

Gelation of an alginate slurry with $\text{Ca}(\text{IO}_3)_2$ has been successfully used for casting complex shaped ceramics [8], extruded ceramic membranes [9]. Additionally, calcium-induced alginate gelation was successfully used for oxide ceramics (e.g., alumina,

zirconia) [10–12] and non-oxide ceramics (e.g., ZrB_2 –SiC, WC) [13,14]. These examples show that $\text{Ca}(\text{IO}_3)_2$ is an ideal choice for cross-linking complex shaped ceramics with almost no limitations regarding processability and sample geometry. The main disadvantage of all calcium-triggered ionotropic gelation techniques is the presence of other elements/ions from the cross-linking source besides calcium. For instance, additional elements such as phosphorus, sulphur and iodine which derive from $\text{Ca}(\text{PO}_4)$ [10], CaSO_4 [15] and $\text{Ca}(\text{IO}_3)_2$ [16] respectively, have an impact on the final performance of the fabricated ceramics. The presence of such impurities typically negatively influences the properties of most ceramics, e.g. inhomogeneities, uncontrolled grain growth, sintering behavior and mechanical properties [17–20]. Therefore, it is necessary for a wider range of applications to find an alternative cross-linking source without the presence of additional elements or impurities. However, the alternative cross-linking source must feature the same good gel-forming quality and processability of $\text{Ca}(\text{IO}_3)_2$.

In general, the choice of a cross-linker is mainly dictated by the composition of the envisaged ceramic. For instance for aluminum compounds (e.g., alumina, zirconia toughened alumina, mullite, spinel, aluminum carbide) a promising, optional cross-linker is aluminum acetate (AlAc). Al^{3+} -ions serve a cross-linker and the acetate-ions as an organic compound are easily removed by

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thermal treatment which avoids undesired impurities. Previous works have shown that Al^{3+} can bind alginate chains almost as good as Ca^{2+} [21,22]. This suggests that AlAc is an ideal gelling agent for ionotropic gelation in ceramic process technology. However, the solidification of alginate ceramic slurries at room temperature (RT) with AlAc takes up to 11 h [23] and temperature induced gelation with AlAc has not been investigated so far, although the advantages for fast temperature controlled gelation are obvious. This can be seen for $\text{Ca}(\text{IO}_3)_2$, where the gelation time can be adjusted via temperature control from only a few minutes to several hours [24].

In this study two cross-linkers for alginate-based ionotropic gelation, $\text{Ca}(\text{IO}_3)_2$ and AlAc, are used to produce alumina parts by a temperature controlled route. The influence of both cross-linkers on the gelation behavior of the slurries and resulting microstructure and mechanical properties of the finally sintered parts is investigated in detail. Temperature ramp controlled oscillation rheology is used to compare the gelation behavior of the two cross-linkers during slurry fabrication, while ceramography and four-point bending tests (4-PB) are used for investigation of morphology, microstructure and mechanics. Additional to the processing and mechanical properties, the possibility to apply this process for joining green bodies is also investigated. By exploiting the more rapid binding of Ca^{2+} -ions to the alginate chains, individual parts are joined by bringing in contact gelled blocks. The possibility to use this method for rapidly fabricating more complex ceramic parts without additional pressure is considered. The quality of joining is assessed by characterizing the failure behavior and the characteristic strength of joined ceramics with 4-PB and compared to single block References.

2. Experimental procedure

2.1. Materials

For the slurry preparation α -alumina powder was purchased from Krahn Chemie GmbH, Germany (TM-DAR, particle size ~ 200 nm, purity 99.99%, Lot.: 9105). Ammonium hydroxide (NH_4OH , Product No: 30501, Lot.: SZBB0250) and 5-sulfosalicylic acid dihydrate (SSA, Product No: 52130, Lot: BCBK0642V) obtained from Sigma–Aldrich Chemie GmbH, Germany, are used as pH adjuster and dispersing agents. The cross-linkers calcium iodate ($\text{Ca}(\text{IO}_3)_2$, Product No: 30501, Lot.: MKBC8376V) and aluminum acetate dibasic (AlAc Product No.: 289825, Lot.: BCBN0146V) as well as the alginic sodium salt from brown algae acting as gelling agent (alginate medium viscosity, Product No.: 2033, Lot.: 051M0054V) were purchased from Sigma–Aldrich Chemie GmbH, Germany, while Protanal LFR 5/60 sodium alginate (Lot.: H10673) was obtained from FMC Biopolymer USA. Double deionized water (ddH_2O) with an electrical resistance of $18 \text{ M}\Omega$ (Synergy[®], Millipore, Germany) was used for all experiments. All chemical were used as received.

2.2. Particle characterization of used cross-linkers

Scanning electron microscopy (SEM Supra 40 Zeiss, Field emission, Germany) was applied to analyze the particle size and morphology of $\text{Ca}(\text{IO}_3)_2$ - and AlAc-particles. SEM analysis was carried out without any conductive coating.

2.3. Slurry preparation

The slurry was prepared using a protocol adapted from Brandes et al., [9]. In short, 1.2 g alginate (0.6 g of each alginate type) were dissolved in 50 ml ddH_2O (solvent) at RT and mixed for 30 min at 300 rpm (IKA Rw20.n, Staufen, Germany). The pH was set at pH 9

adding dropwise NH_4OH . To ensure a better viscosity the Al_2O_3 -particles (180 g) were premixed with SSA (0.6 wt%) and slowly added to the alginate solution under continuous stirring for 1.5 h at 1900 rpm and RT for obtaining agglomerate-free alumina slurries. To reduce frictional heating and water evaporation, the slurry was kept in a cooling bath ($\sim 4^\circ\text{C}$). Afterwards, the slurry (~ 48 vol.% solid content) was cooled in a fridge until its temperature was below 10°C .

2.4. Casting and gelation

The cooled slurry was degassed (60 mbar) in a temperature controlled (10°C) vacuum dispersion system (Dispermat LC2, VMA-Getzman, Germany) at 4000 rpm for 10 min. In the following step, 5.5 mmol of the cross-linker (~ 2 g $\text{Ca}(\text{IO}_3)_2$ or ~ 0.9 g AlAc) was admixed at the same pressure and stirring velocity. As shown in Fig. 1A, the slurry was casted into rectangular block molds made of LEGO[®] basic bricks (brick type 2×4 , width and depth: ≈ 25 mm; height: small mold composed of 4 bricks ≈ 36 mm, large mold composed of 8 bricks ≈ 64 mm). The molds were sealed with polytetrafluorethylene (PTFE) to prevent drying of the samples during the subsequent heating process. After filling and sealing, the molds were placed in a temperature controlled humidity chamber for 15 min at 45°C and 80% relative humidity (KBF, Binder, Tuttingen, Germany). For the two applied joining processes (Fig. 1B), namely slurry joining and contact joining, two small gelled blocks were used. In the slurry joining process, slurry and cross-linker were mixed as previously described for the sample block fabrication. Here, approximately 0.2 ml of slurry was spread on each contact surface of the small blocks with a spatula before placing the blocks on top of each other. For the contact joining process the small gelled blocks were directly placed on top of each other. Both types of joined blocks were stored in the climate chamber (45°C , 80% relative humidity) for further 15 min until demolding. Afterwards, all samples were dried for two days at 25°C and 90% relative humidity followed by final drying for two days at 20°C and 50% relative humidity.

Each prepared block was cut with a wire saw (Well[™] 6234, Mannheim, Germany) to obtain 9 bending specimens (Fig. 1C). The specimens were ground and finally sintered at 1500°C for 2 h (Nabertherm HT0817, Lilienthal, Germany), using a heating rate of $500^\circ\text{C}/\text{h}$. Due to the low amount of alginate (0.6 wt.%), no extra debinding step was necessary.

2.5. Small deformation oscillation rheology

To analyze the samples' viscoelastic properties during gelation, small deformation oscillatory measurements of storage modulus (G') and loss modulus (G'') were conducted (Discovery Series Hybrid Rheometer HR3, TA Instruments) with a plate–plate geometry ($\phi = 40$ mm). The gap distance, strain and frequency were set to 1 mm, 0.2% and 1 Hz, respectively. Prior to each measurement, the cooled slurry (10°C) and the cross-linker were directly mixed and 1.1 ml of slurry was placed between the plates with a syringe. To simulate the warming of the slurry during handling and temperature controlled gelation a heating rate of $1^\circ\text{C}/\text{min}$ and a starting temperature of 10°C were selected. This is in conformity with the measured warming inside a sample during the manufacturing and gelation process. The dissipation factor $\tan(\delta)$ was calculated from loss modulus (G'') and storage modulus (G') to determine the degree of cross-linking on the ideal elastic behavior.

2.6. Surface analysis of the gelled green bodies

Surface roughness (R_a) of gelled blocks derived from each type of cross-linker ($\text{Ca}(\text{IO}_3)_2$ versus AlAc) was determined using

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