INVESTIGATIONS ON ALUMINA CERAMIC FORMING USING NATURAL RUBBER LATEX AS A BINDER

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by

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Abstract

Ceramics are the major category of materials that have attractive mechanical, thermal, and electrical properties, resistance to high temperature, chemical inertness, and biocompatibility. Therefore, these materials have been employed in various advanced applications in the automotive, aerospace, defense, nuclear, and bio-medical sectors. The fabrication of high-quality complex-shaped ceramic components is particularly needed for achieving specific functions. The machining of sintered ceramics to make complex shapes is an energy-intensive, costly, and slow process. In this respect, the near-net shaping strategy is an essential part of ceramic fabrication. Ceramic fabrication techniques such as powder pressing, slip casting, tape casting, gel casting, injection molding, extrusion, and additive manufacturing are extensively used to produce ceramic components of various shapes and dimensions. Various processing additives such as solvents, dispersants, binders, plasticizers, lubricants, and antifoams are generally utilized in these processes to achieve specific processing requirements. Currently, most of the additives used are petroleum-based organic compounds that create environmental impacts and global warming. One of the approaches to avoid these problems is to replace toxic organic solvents with water and other synthetic additives with naturally renewable molecules. In the present work, natural rubber latex (**NRL**), a naturally renewable bio-polymer, has been utilized as a binder in the processing of alumina ceramic by powder pressing, slip casting, tape casting, and gel casting.

NRL is used as a binder in powder pressing of alumina. The ammonium poly(acrylate) dispersed alumina slurry and **NRL** form well-dispersed co-dispersions easily using magnetic stirring due to their high negative surface potentials in the pH range of 9.6 to 10. The granulated feedstock for powder pressing is prepared through co-coagulation of the co-dispersions using a formic acid solution followed by centrifugation, drying, and grinding. The average particle size of the coagulated co-dispersions increases from 0.34 to 12.30 μm when the concentration of **NR** increases from 0 to 10 wt.%. The feedstock granules prepared using 6 and 8 wt.% **NR** concentrations have superior flow properties as evidenced by the flow time and Hausner ratio measurements. The powder-pressed compacts achieve a maximum green density of 67.7 %T.D. at a relatively low compaction pressure of 20 MPa due to the highly flexible **NRL** binder. The green compacts exhibit uniform microstructure. The green compacts prepared at 2 wt.% **NR** shows severe end capping due to poor mechanical strength. The green strength increases from 0.55-1.91 MPa when the **NR** concentration increases from 4 to 10 wt.%. A remarkable increase in green strength in the range of 2.30-9.39 MPa (almost 2.3 to 6 times) is achieved on annealing

the pressed compacts at 200℃ due to the cross-linking of **NR** chains through the carbon-carbon double bonds induced by the Lewis acid character of alumina. The annealed green compact is amenable to machining by milling, drilling, and lathing using conventional machines and tools. The cross-linked **NRL** binder shows a near-steady state of burn-out without creating any crack in the green body. The powder-pressed bodies sintered at 1550 ℃ show 18% linear shrinkage, 97% T.D., and 1.8 μm average grain size.

NRL is studied as a binder in the slip casting of alumina and the results are compared with that of slip casting using a conventional polyvinyl alcohol (PVA) binder. The polyacrylate dispersed aqueous alumina slurry and **NRL** form co-dispersions easily due to their high negative surface potentials. The slip casting slurries prepared using the **NRL** binder achieves a high alumina loading in the range of 40 to 55 vol.% compared to the 41.1 vol.% achieved with 2 wt.% PVA binder. The alumina-**NRL** co-dispersions show shear thinning flow behavior with viscosity and yield stress values suitable for slip-casting. The cast layer thickness formed in one hour decreases from 8.5 to 4.2 mm when the **NR** concentration increases from 0 to 8 wt.% due to the gelation of **NR** binder at the mold-cast layer interface. The cast layer thickness formed in one hour at 4 wt.% **NR** concentration increases from 4.13 to 6.5 mm when the alumina slurry concentration increases from 40 to 55 vol.%. The cast layer thickness formed from alumina slurry containing **NRL** binder is nearly 3 times higher than that formed from an aqueous slurry of the same alumina concentration containing 2 wt.% PVA binder. The slip-cast alumina bodies produced using **NRL** binder exhibit higher green density in the range of 53.4 to 62.5 % T.D. compared to 52.1% T.D. achieved from alumina slurry containing 2 wt.% PVA binder. The binder migration normally noticed in slip casting using water-soluble PVA binder is not observed in **NRL** binder-based alumina slip casting. The green strength increases from 0.45 - 1MPa by increasing the **NR** concentration from 0 to 8 wt.%. The strength increases to 0.45 - 9.68 MPa on annealing the green bodies at 200℃ due to the cross-linking of **NR**. The annealed slip-cast green bodies are amenable to machining by milling and drilling using conventional machines and tools. The slip-cast alumina bodies sintered at 1550℃ show 97%T.D. with a homogeneous microstructure and 1.82 μm average grain size. The slip casting using **NRL** binder is capable of producing crucibles of wall thickness as low as 1.2 mm.

The **NRL** is proposed as an eco-friendly binder in the aqueous tape casting of alumina. The tape casting slurries prepared by mixing 58.2 vol.% alumina slurry dispersed using the ammonium poly(acrylate) dispersant and **NRL** show shear thinning flow behavior and adequate viscosity and yield stress values. Tape casting slurries of high total solids loading in the range of 60.57 to 60.88 vol.% is achieved at **NR** concentrations in the range of 14.2 to 18.1 wt.%. The high solid content of the tape casting slurry formulations enables the fast drying of the cast tape within a reasonable time of 15 minutes at 70℃. The strength, modulus, and % elongation at break of the green alumina tape are in the ranges of 1.62 to 1.85 MPa, 267.5 to 50.8 MPa, and 41 to 254 %, respectively, at **NR** concentrations in the range of 14.2 to 18.1 wt.%. Annealing in between two glass plates transforms the flexible green tape to a rigid and brittle one due to the self-cross-linking of **NR** which avoids its curling at the edges during the binder removal. Roll pressing of the green tapes produces a remarkable improvement in microstructure and density at a thickness reduction of 20%. The roll-pressed green tape achieves a density of 98.5% T.D by sintering at 1600ºC. The sintered tapes show a uniform microstructure with an average grain size of 3.2 µm.

NRL is employed as gelling agent and binder in the freeze-gel casting of alumina. The alumina-**NRL** co-dispersions prepared by mixing ammonium poly(acrylate) dispersed 58.2 vol.% aqueous alumina slurry and concentrated **NRL** show low viscosity and yield stress values required for gel casting. The gelation of the co-dispersions is achieved by freezing in a mold and subsequent mold removal and thawing in an acetone medium. The growing ice crystals disrupt the protein layer on the latex particles leading to their coagulation. The exchange of water with acetone during thawing in an acetone medium strengthens the alumina-**NR** particle network by further coagulation. The minimum concentration of **NR** required to percolate and form a stable alumina-**NR** gel is 8 wt.% by weight of the alumina powder. The strength and modulus wet gel achieved are 60 kPa and 640 kPa, respectively, which are sufficient for handling during further processing. The frozen body passes through a semi-fluid state during thawing which enables the gel to flow and fill the space created by the melting of ice crystals leading to dense ceramics. The acetone exchange enables faster drying of the gel bodies at room temperature without creating any deformation or crack. The diametrical compressive strength and modulus of the dried green body are 0.34 MPa and 18 MPa, respectively. The diametrical compressive strength and modulus improve to 2.14 MPa and 150 MPa, respectively, on annealing at 200 ℃ due to cross-linking of **NR** chains. The green bodies on debinding and sintering at 1550℃ produce alumina ceramics of uniform microstructure with ~96% T.D and 1.3 µm average grain size. The freeze-gel casting using **NRL** binder has the capability to fabricate near-net shape alumina ceramics.

NRL functions as a pores stabilizer and binder for the preparation of macroporous alumina ceramics by freeze-gel casting without freeze drying. The gels prepared by freezing and thawing the alumina powder-**NRL** co-dispersions achieve shape stability at a minimum **NR** concentration of 20 wt.%. A 20 wt.% **NR** is required to stabilize the pores in gels prepared at alumina slurry concentrations in the range of 42.72 - 25.44 vol.% whereas 30 wt.% **NR** is required to prevent pore collapse in gels prepared from a slurry of alumina concentration up to 15 vol.%. Two-times acetone exchange removes ~ 96.5 % of the water present in the gels which results in fast drying, low drying shrinkage, and a smooth green body surface. The diametrical drying shrinkage varies from 2.1 to 10.32 % when the alumina slurry concentration varies from 42.74 to 15 vol.%. The cross-linking of **NR** chains by annealing at 200 °C prevents the melting of **NR** and thereby avoids pores collapse during binder removal. The achieved porosity (44.5 to 71.12 % at alumina slurry concentration in the range of 42.74 to 15 vol.%) by acetone exchange followed by air drying is lower by 10-15 % of the porosity obtained by freeze-drying of the corresponding frozen bodies. Macroporous ceramics produced from the frozen bodies by both the acetone exchange followed by air drying and freeze-drying methods exhibit a similar lamellar pore structure. The lamellar pore width in ceramic obtained by the acetone exchange followed by the air drying route is lower by nearly 42 % than that obtained by freeze-drying due to the pore shrinkage during air drying of the acetone exchanged bodies. The macroporous ceramics show a compressive strength and Young's modulus in the ranges of 3.8 to 35.3 MPa and 306.2 to 1486.5, respectively, at an alumina slurry concentration in the range of 15 to 42.74 vol.%.