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Indirect solid freeform fabrication by binder assisted slip casting

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Abstract

A method has been developed for the consolidation of ceramic bodies in molds prepared by solid freeform fabrication. The method is based on slip casting with an added latex binder. The latex binder makes it possible to create internal structures, such as pore channels, without the cracking that usually takes place when shrinkage is obstructed by internal mold structures. The latex binder adds plasticity to the consolidating body in the wet state. This was observed by rheological measurements during slip casting. Measurements of mechanical properties showed that the latex binder also adds plasticity and strength in the dry state.

Keywords: Slip casting; Porosity; Plasticity; Solid freeform fabrication; Al_2O_3

1. Introduction

The possibilities to create complex shapes have been greatly enhanced with the development of 3D-CAD programs and solid freeform fabrication (SFF) processes. Common to all SFF processes is the fact that the object to be shaped is defined with a computer description and built layer-by-layer with computer-controlled equipment. The technique to build an object from a computer-designed model with high precision can be used to build molds. Indirect solid freeform fabrication of ceramics is based on the infiltration of a mold with a ceramic suspension. The suspension is consolidated and dried, and the mold is removed by melting and/or pyrolysis. With this method it is possible to obtain very complex geometries and objects with internal cavities and pores, as no mold partitioning is necessary. To build complex shapes with indirect SFF, it is necessary to be able to use mold inserts that can form internal cavities, pores or holes. In traditional ceramic forming there is a problem to remove the mold without damaging the complex-shaped component. With indirect SFF this is not a problem as the mold is melted, pyrolyzed or dissolved. The mold inserts generate geometrical constraints during consolidation of the ceramic body. This usually requires that the dimensional changes during consolidation and drying are very small to avoid formation of cracks.

There are several direct consolidation techniques that could be suitable for indirect SFF such as direct coagulation casting,[1] starch consolidation,[2] protein forming[3] or gel casting.[4] Other techniques possible are reviewed by Rak.[5] Several of the techniques mentioned above include shrinkage during drying. In a mold that constrains shrinkage, this can lead to cracking of the green body in a state in which the green body is very weak. A high green density can increase the green strength, minimize the shrinkage and probably compensate for some of the stresses developed by geometrical restraints. Schönholzer and Gauckler[6] showed that crack-free patterns with μm-sized features could be cast and dried in a mold on non-porous substrates. Suspensions with high solids loading were necessary to avoid cracks due to lateral shrinkage stresses. The strength of the green body can also be increased by addition of binders. Cross-linking of Na-alginate has been reported to strengthen the green bodies obtained by direct coagulation casting (DCC).[7] In gel casting a monomer is polymerized to consolidate and strengthen the green body of the ceramic. Gel casting has been reported

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to result in green bodies with very high strength that can be green machined.[8,9] The polymerized monomer forms a gel together with the liquid that is used as a casting medium. When this gel dries it results in potential shrinkage problems and drying must be performed in a controlled humidity chamber.[10] The gel-casting system was used by Chu et al.[11] for making objects by indirect SFF.

Slip casting is a well-known forming method for ceramics. Very high green densities are easily obtained with well-dispersed slips but slip-cast green bodies are very brittle. Constrained shrinkage often causes cracking during drying of the slip-cast bodies.[12] Organic binders can be added to increase the green strength but they tend to cause other processing problems. Addition of a water-soluble binder such as sodium carboxymethylcellulose (Na-CMC)[13] or specially developed additives[14] has been reported. Most water-soluble additives negatively affect the viscosity (long chains of dissolved molecules increase the viscosity of the water phase) and the addition has to be minimized. Migration is another common problem as the soluble molecules follow the water that is transported from the consolidated body into the plaster mold.

Emulsions of polymeric particles, i.e., latexes, have been used for several years in ceramic processing as binder in, for example, tape casting and pressing.[15,16] Systems of alumina, polyacrylic acid and latex binders have been thoroughly studied by Kristoffersson and coworkers.[17,18] Latex has been used as a binder in slips for infiltration of porous polymer structures built by a fused deposition process, which is a solid freeform fabrication technique.[19] In these experiments, the samples had to dry for 3–4 days, as there was no dewatering by plaster but only evaporation from the open surfaces of the mold. The results indicate the usefulness of latex as a binder, and sintered dense samples were obtained after evaporation of the mold and binder. Latex as a binder for slip casting has been used to obtain blanks for green machining.[20] The results showed an increase in green strength for samples containing latex when compared with cold isostatically pressed samples containing conventional pressing additives. Addition of small particles, i.e., addition of latex to a slurry, is known to affect the casting rate, which is dependent on the specific porous medium resistances of the consolidated layer and the mold.[21] The resistance of the consolidated layer is dependent on the particle packing, which is influenced by the stability of the slip and the particle size distribution. During consolidation, when the water is removed from the suspension and a solid network of particles is built, the latex particles can form a film that influences the mechanical properties of the consolidated body. The latex can then act as a binder and increase the strength and plasticity of the green body.

The aim of this work was to create a structure with designed pore channels with indirect solid freeform fabrication. Slip casting in SSF molds on a plaster plate was evaluated to obtain such a structure. The influence of latex on the properties of the ceramic material in the wet state (in a slip), during casting and in the dry state (in green bodies) were studied in order to optimize the process. The influence on the slip was studied by rheological measurements and the influence on the green body was studied by measuring the mechanical properties of the green body.

2. Experimental procedure

2.1. Materials

An alumina powder (AKP 30, Sumitomo Chemicals, Japan) with an average particle size of 0.4 μm and a specific surface area of 7.7 $m^2\ g^{-1}$ was used for all experiments. For dispersion, 0.3 wt.% on alumina powder of an ammonium salt of a polyacrylic acid, Dispex A40 (Ciba Specialty Chemicals Ltd., England) was used. A water-based latex, i.e., a copolymer of styrene and an ester of acrylic acid (Mowilith DM 7651S, Celanese Emulsions Norden AB, Sweden) with a particle size around 150 nm, was used as a binder for slip casting. The latex is stable at neutral and high pH and was therefore compatible with the stable alumina slip, which had a pH around 9.

2.2. Characterization of slips and consolidation

Slips for rheological measurements and for slip casting were prepared by dispersing the alumina in water with the dispersing agent in a planetary mill (PM 400, Retsch, Germany) using silicon nitride containers and silicon nitride balls at 200 rpm for 30 min. The latex was added after milling using a magnetic stirrer. The slips were stirred for 24 h before characterization. All slips had a solid content of 50 vol% calculated on the amount of alumina and latex. The rheological properties of the slips were characterized with a controlled stress rheometer (StressTech, RheoLogica AB, Sweden). The viscosity of the slips was measured using a bob and cup (CC25) in the shear rate range 1–700 s^{-1} with a pre-shear at 400 s^{-1} for 60 s and an equilibrium time of 60 s. The rheological properties of the wet green bodies, i.e., the cast layers, were characterized by an oscillation measurement using a plate on a cast layer during dewatering on a plaster plate. A schematic of the measurement cell is shown in Fig. 1. The oscillation measurement was performed at a frequency of 1 Hz applying a constant stress of 1500 Pa on the cast layer, which was

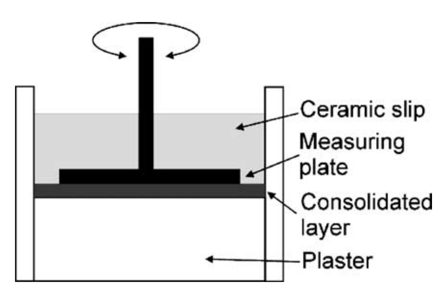

Fig. 1. Measurement cell for oscillation measurement of cast layer.

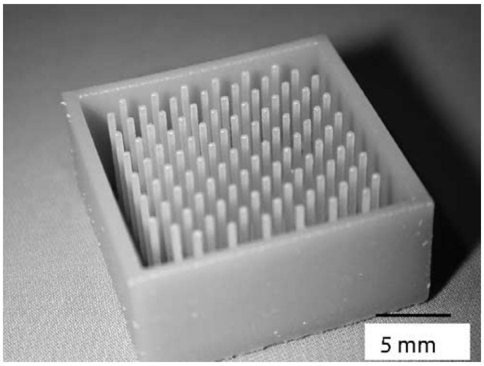

Fig. 2. Solid freeform fabricated mold for slip casting.

around 3 mm thick. The plate was applied on the cast layer at a normal force set to 8 N. The casting continued during the measurement. It would have been preferable to perform the measurements with a normal force-measuring cell that allows the plate to move upwards as the consolidated layer increases its thickness.[22] This was however not possible on the rheometer used in this study.

The casting rate was measured by drain casting slips with 0, 1, 3 and 5 wt.% latex in cylinders on a plaster plate for 1, 5, 15, 30 and 120 min in order to measure the cast thickness.

Slip casting was performed in molds prepared by solid freeform fabrication. The molds were prepared with an ink-jet printing method (Thermojet (3D Systems, USA)). The molds, shown in Fig. 2, consisted of an outer box with one open side (20 mm × 20 mm × 10 mm). Small rods were built inside the molds (diameter 0.5 mm, spacing 1.77 mm center-to-center of rods). These rods were built to form straight-through pore channels through the ceramic body. The rods were attached to the mold at one end and obstructed the shrinkage during drying. The mold was placed on a plaster plate with the open side towards the plate and slip was poured into the mold through an opening at the top. After drying in the mold (room temperature, 24 h), the compact was heated to 600 °C at a heating rate of 1 °C/min to melt and pyrolyze the mold leaving the ceramic green body.

2.3. Characterization of green and sintered bodies

The possible migration of binder was studied by slip casting bodies of at least 10 mm height, dividing them in an upper and a lower half, and comparing weight loss after heating all samples to 1000 °C. Cross-sections of the samples that were slip cast for 120 min were studied by scanning electron microscopy (SEM) to detect possible density gradients due to migration of the latex during casting. Cylinders with a diameter of 12 mm and a height of 5 mm were slip cast to test the green strength by diametral compression[23] on 10 samples of each concentration of latex. The test was performed in a universal test machine (Zwick GmbH and Co., Germany) at a loading speed of 0.5 mm/min. The applied force versus ram movement was registered. The green strength and the deformation were calculated and the fracture behavior was studied. The density was measured by water-intrusion according to Archimedes' principle on the samples heated up to 1000 °C and on sintered samples. Sintering was performed in air at 1600 °C for 1 h.

3. Results and discussion

The results of the viscosity measurements are shown in Fig. 3. The viscosity decreases slightly with the addition of 1% latex to the slip and shows an increase upon further addition. The moderate increase is caused by the change in the particle size distribution that takes place when latex is added to the slip. The shear thinning remains relatively constant when the viscosity changes. This is an indication that the stability remains unchanged by the latex addition. If any destabilization occurred the viscosity would increase dramatically at low shear rates.

Fig. 4a and b shows the storage modulus and phase angle versus time obtained from the oscillation measurement on the wet consolidated body during casting. The rapid increase of the storage modulus for 0 and 1% of latex is an indication that the casting rate is higher for these slips (a solid body forms rapidly). This is also verified in the direct measurements of casting rate (see below). The slower increase in storage modulus for slips with 3 and 5% latex indicates that the casting rates are lower for these slips. The storage modulus reflects the stiffness of the wet green body and the obtained plateau value is lower the higher the addition of latex. The phase angle is a measure of the relationship between the storage and the loss modulus in the material. A material with a phase angle of 0° is completely elastic. The higher the phase angle the more viscous is the material. A completely viscous material, like water, has a phase angle of 90°. Fig. 4b shows that the phase angle is increased with increasing amounts of added latex. This shows that the plasticity of the wet body is increased by the latex addition. This is believed to be due to the inherent properties of the latex particles and will be discussed further. The phase angle indicates the viscous response of the wet green body and increases with increasing

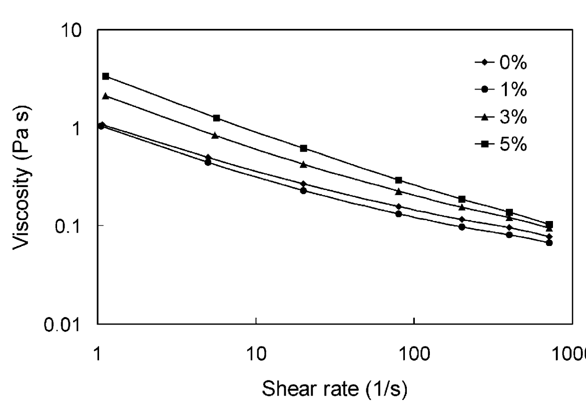

Fig. 3. Viscosity vs. shear rate for slips with addition of latex.

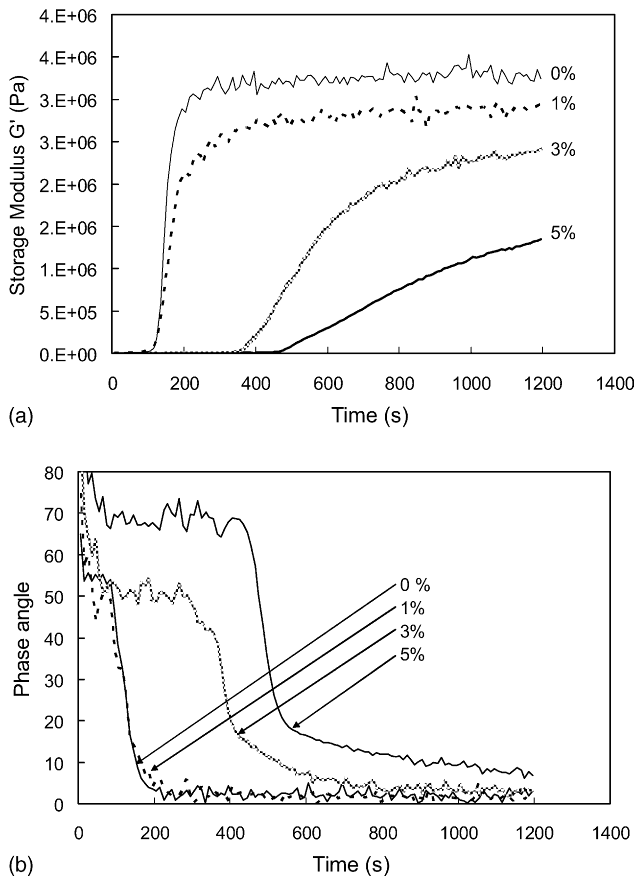

Fig. 4. (a) Storage modulus vs. time during oscillation measurement of cast layers with latex added to the slips. (b) Phase angle vs. time during oscillation measurement of cast layers with latex added to the slips.

amounts of latex at and above 3% in the slip. The phase lag is about the same for 0 and 1% latex. This is due to the particle size distribution at an addition of 1% latex, which allows the smaller latex particles to fit into the interstices of the alumina particles. The more viscous response of the bodies with 3 and 5 wt.% latex also affects the behavior of the body during drying. The viscous response to an applied stress will relax with time, which means that the stresses that occur during drying will be relaxed. This is a time-dependent behavior and earlier studies have indicated a longer relaxation time for systems with latex added than for systems without binder.[17] Longer relaxation times mean that the body continues to relax during drying. This is thought to be one of the factors that explain why bodies with latex do not crack during constrained drying.

The casting of a slip with latex particles added obeys the slip casting equation suggested by Aksay and Schilling.[21] This is shown in Fig. 5 where straight lines are obtained when the casting height is plotted against the square root of time. The filtration resistance of the consolidated layer increases with increased additions of latex due to a larger fraction of small particles in the slip, thereby decreasing the casting rate. However, the straight lines obtained show that the filtration resistance is constant during the entire casting process of a certain slip, thus indicating the absence of latex migration. To

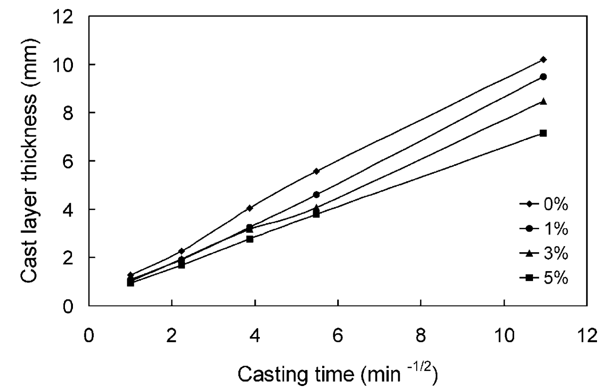

Fig. 5. Cast layer thickness vs. casting time for slips with addition of latex.

verify this, green bodies were cut in an upper and a lower part and heated to 1000 °C in order to evaporate the binder. No difference in weight loss was observed which also indicates the absence of migration. SEM studies of the bodies sintered to 1450 °C revealed an apparently homogeneous distribution of the porosity.

Fig. 6a–c shows cross-sections of samples slip cast in the mold fabricated by solid freeform fabrication. Samples without latex exhibited extensive cracking. The samples with 1% latex exhibited a reduced amount of cracking. No cracks were observed in the samples with 3 and 5% latex.

The fracture behavior of samples without latex or with 1% latex is solely brittle. It is obvious that addition of latex above 1% gives a transition from elastic to plastic fracture behavior. This can be seen in Fig. 7, which shows the green strength and the deformation at failure versus the addition of latex (average of at least five samples). The green strength has a steep increase up to an addition of 3% latex. The deformation at failure increases constantly with increased additions of latex from 1 to 5%. These results clearly show that the properties of the green bodies can be altered towards a more plastic behavior. This means that stresses induced from drying will be reduced due to the increased plasticity. This is confirmed by results obtained by Martinez and Lewis.[24] They measured the stress evolution in silica films, latex films and composite films during drying. The results showed that the maximum stress that the film experienced during drying was decreased by 1/3 when 10 vol% of latex was added to the silica system. The reduction of stresses in films with latex added is stated to be due to the deformation of latex particles during drying. Table 1 shows the additions of latex expressed in weight percent and volume percent in our study. The addition of 3 wt.% latex corresponds to 10.7 vol% in our case. This addition is obviously enough to reduce the stresses that develop during restrained drying in the SFF molds. The addition of only 1 wt.% latex (3.8 vol%) was however too low which is seen in Fig. 6b. It is also obvious that a deformation of the latex particles takes place during drying. The addition of latex to the ceramic slip causes an additional porosity in the green bodies compared to the system without addition of latex. The green density decreases with about half of the volume of latex

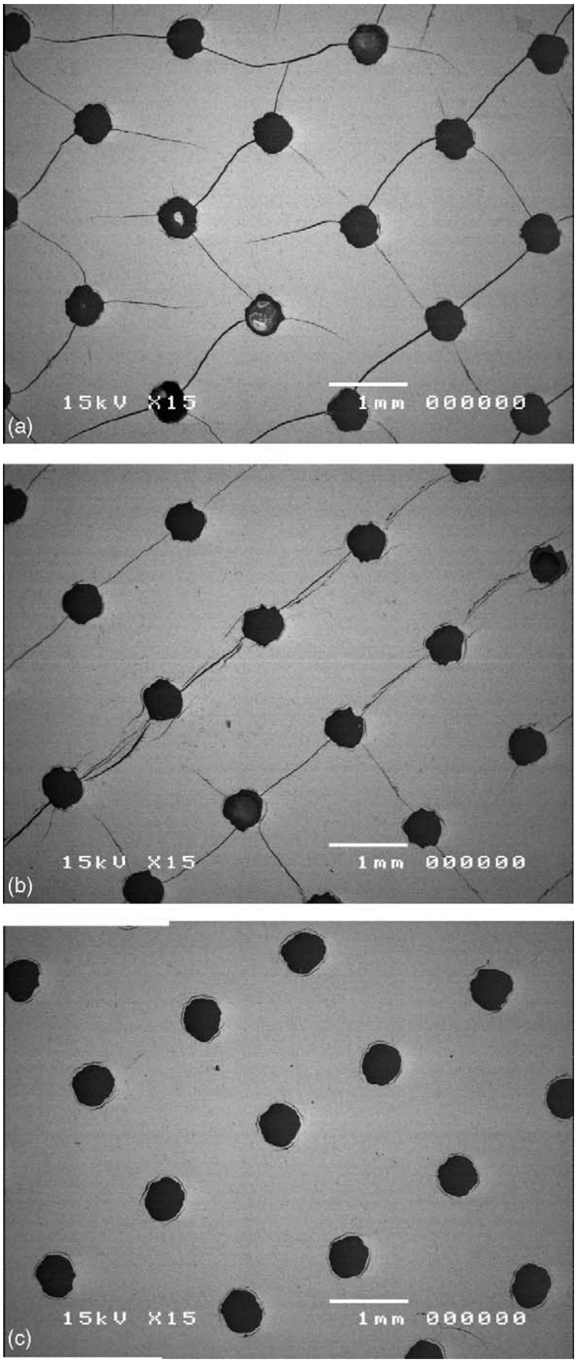

Fig. 6. SEM photos of cross-sections of sintered bodies slip cast in solid freeform fabricated moulds with (a) 0%, (b) 1% and (c) 3% latex added to the slip.

added to the slip, which means that the latex particles spread in the dried state so that they occupy half of the volume in the wet state. The deformation of the latex particles is a key property that explains the possibility of these systems to be slip cast in molds designed to give pore channels by cores that constrain the shrinkage. The glass transition temperature T_g of the latex must be lower than the ambient temperature when casting and drying so that the latex will be in a viscous liquid like state during drying of the samples.

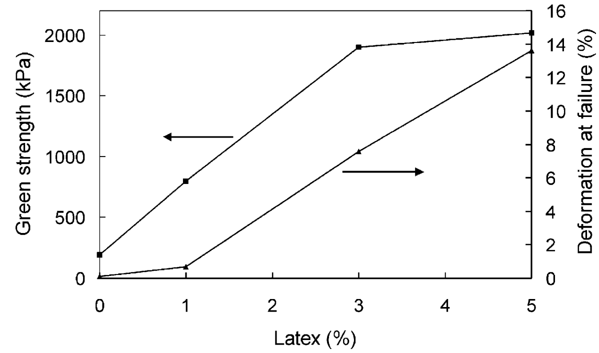

Fig. 7. Green strength and deformation at failure vs. latex added to the slip measured by diametral compression.

It could be argued that it is possible to obtain green bodies strong enough to endure the hindered shrinkage just by increasing the solid loading or by manipulating the interparticle forces so that a weakly flocculated system would be obtained. Weakly flocculated systems have been shown to exhibit plastic properties in the wet state[25,26] during compression and can be formed using isopressing. Interparticle forces have an influence as long as the solvent remains in the body and affects the particle packing behavior. However, the plasticity is completely lost during drying and in the dried state. The green strength obtained in a slip-cast body without organic additives is the result of the van der Waals forces between the particles. The van der Waals forces increase with the number of particle contacts. This means that a homogeneous and dense packing of the particle increases the bonding of the green body. It has also been shown that the green body without organic additive is brittle which means that any defects or critically large defects will lower the strength of the green body.[27] A homogeneously packed particulate body can be obtained from a stabilized well-dispersed slip. Dry green bodies obtained from weakly flocculated slips will be brittle, less dense and thus weaker. The green bodies prepared in this study without latex added had a green density of 64% which is to be regarded as optimal from a just about monosized powder. All green bodies without latex cracked when cast in restrained molds. It is therefore concluded that plasticity in the dry green body is necessary to obtain crack-free samples from molds that induce restraints.

Both slip casting and flocculated systems formed by isopressing have a common advantage compared with

Table 1
Amount of latex added expressed in weight and volume percent and densities of green and sintered samples

Addition of latex		Relative densities[a]	
By wt.% on Al_2O_3	By vol% on total amount of solid	Green samples (%)	Sintered samples (%)
0	0	64.1	99.3
1	3.8	62.2	98.5
3	10.7	58.9	98.5
5	16.6	56.1	98.5

[a] Obtained from drain casting.

direct consolidation methods (e.g. gel casting). Direct consolidation methods have to work with very concentrated slips because the green density corresponds directly to the powder concentration in the slip. Both slip casting and flocculated systems can be handled at lower powder volume concentrations prior to forming as the forming process involves removal of liquid. This makes it possible to use screening or sedimentation to remove large potential defects prior to forming the ceramic body.

One possible problem of slip casting with latex binder in indirect SFF is that the green density cannot increase freely by shrinkage during drying. It will increase from the powder concentration in the slip owing to the filtration and packing process during casting. Compared to an unconstrained component the green body will shrink somewhat due to plastic deformation but not so much as a green body slip cast in a mold without constraints. This can reduce the sintered density especially for a powder that is difficult to sinter dense such as alumina. The sintered component cast in the mold made by freeform fabrication had a sintered density of 96–97% relative density as compared to >99% which would be typical for the sintering of this powder after forming with a traditional method. Other ceramics that have a higher sintering activity, such as zirconia, are easier to sinter completely dense with this method.

4. Conclusions

It has been shown that slip casting with addition of latex is suitable for indirect SFF when objects with complex geometry or designed porosity are desired. The addition of latex gives a plastic contribution to the green body in the wet state and in the dry state. It is believed that the glass transition temperature of the latex should be low so that spreading on the powder particle surfaces is obtained. The suggested forming method is robust and versatile and can easily be applied to any ceramic material.

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