Studies on Slurry Extrusion for Dental Restoration

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Abstract

This study investigates dental restoration via dental powder delivery by slurry extrusion, followed by laser densification of these extruded slurries. The entire process is fully controlled by a computer. The shape of the extrudate before laser densification depends strongly on the formulation of slurries. Slurries prepared in a stable pH range can disperse high volume of solids, but have low viscosities and spread uncontrollably when extruded. In contrast, slurries first prepared in a stable pH range and subsequently adjusted to an unstable pH range have exhibited pseudoplastic behavior. Such slurries have a low extrusion pressure to avoid phase separation, and at the same time their yield points are high enough to maintain the shape of extrudates.

Keywords: Slurry extrusion, dental porcelain, dental restoration, solid freeform fabrication

I. Introduction

There are currently more than 10,000 dental laboratories in the US and a majority of these laboratories use porcelain-fused-to-metal (PFM) restoration for permanent fixed prosthodontics. PFM restoration is a very time consuming and labor intensive work because PFM restoration requires a multi-stage process using multiple materials (both ceramics and metals) and each stage involves multiple processing steps [1]. For example, it normally takes 2-4 weeks to make a three-unit bridge and labor costs account for about 90% of the final cost. This study is part of an overall effort to develop a novel multi-materials laser densification (MMLD) process for dental restorations [1-3]. This process utilizes laser-assisted solid freeform fabrication (SFF) to fabricate artificial dental units layer-by-layer directly from a computer model without part-specific tooling and human intervention. As such, the labor cost will be substantially reduced, and better and faster dental restorations will be achieved.

One of the key issues in the MMLD process is to deliver dental alloy and porcelain powders to the desired locations precisely and accurately. Most of the techniques currently being developed for the freeform fabrication of dense structural ceramics and metals require the use of powder-loaded polymers or resins to maintain the shape of the components [4,5]. These polymers and resins are burned out in the subsequent heat treatment while contamination may remain in the preform. This is not desirable for dental restoration for which a clean and no contamination environment is needed in order to satisfy the requirement of the aesthetic appearance.

In this paper, aqueous dental porcelain slurries were prepared with no addition of polymers or resins. The aqueous porcelain slurry was deposited onto metal substrates by extrusion. The shape of extrudates depends strongly on the formulation of slurries. The zeta potential of the powder particle changes significantly with pH value. At the pH value for zeta potential close to zero, surface charges of the porcelain powder are almost neutral and particles are easy to contact with each other because the repulsive force between them is small. This leads to flocculation of the slurry and the slurry exhibits pseudoplastic behavior. When the zeta potential is positive or negative, surface charges of the powder particles become predominantly positive or negative respectively. The repulsive force between particles makes the slurry relatively stable. Slurries prepared in a stable pH range can disperse high volume of solids, but have low viscosities and spread uncontrollably when extruded. In contrast, slurries first prepared in a stable pH range and subsequently adjusted to an unstable pH range have exhibited pseudoplastic behavior [6,7]. Such slurries have a low extrusion pressure to avoid phase separation, and at the same time their yield points are high enough to maintain the shape of extrudates.

II. Experimental

The dental porcelain powder was provided by Degussa-Ney Dental Inc., Bloomfield, CT. The chemical composition of the porcelain is confidential; however, it is within 5% of the nominal composition of the Weinstein patent [8], which has the following composition (wt%): 63.40% SiO_2, 16.70% Al_2O_3, 1.50% CaO, 0.80% MgO, 3.41% Na_2O, and 14.19% K_2O. The as-received powder has angular shapes and their equivalent particle sizes range from 5 to 50 micrometers. To reduce the size of the porcelain powder, ball-milling process was conducted using a single axis mixer machine. The vial and balls for the ball milling process were all made of alumina. The weight ratio of the powder to alumina balls was between 5 and 10, and the duration of the milling process was 72 hours with de-ionized water as the medium.

Porcelain slurries were prepared using de-ionized water as the solvent with a solid loading of 50 – 60 vol.% of porcelain powder. Uniform and stable slurries were obtained by gently mixing the slurry for 24 hours using the mixer machine. The porcelain slurry was delivered using a Multi-Material Laser Densification (MMLD) machine designed and constructed at the University of Connecticut. The machine consists of four major components: (i) the process chamber that can have a vacuum down to 10^{-2} torr, (ii) micro-extruders for powder slurry delivery of up to 3 different materials, (iii) a laser heating system for powder densification, and (iv) a temperature sensing and control system. The pressure exerted on the porcelain slurry within the micro-extruder was applied via an electric cylinder. The slurries were dispensed onto stainless steel plates with a 1000 μm tip, and the motion and the position control were provided through a X-Y-Z table controlled by a computer through a Galil DMC-1800 multi-axis motion control card.

The rheology of the porcelain slurries was measured using a Brookfield DV II digital viscometer. The zeta potential of the slurries was measured at the National Science Foundation Engineering Research Center for Particle Science and Technology at the University of Florida using a Zeta-Reader instrument. Both the as-received and milled porcelain powders were characterized using an environmental scanning electron microscope (Philips ESEM 2020) to obtain the morphology and size of the powders.

III. Results and Discussion

As shown in Figure 1(a), the as-received porcelain particles (ranging from 5 – 50 microns) are substantially larger than 1 μm and thus not suitable for preparing stable slurries. To achieve a stable slurry, the size of solid particles normally needs to be smaller than or close to 1 μm. Thus, ball milling was evaluated for its potential to reduce the porcelain powder size. Figure 1(b) shows the ESEM image of the porcelain powder after 72-hours of ball milling. When compared with the as-received powder, the size of porcelain particles has been significantly reduced by the ball milling process to the range of 0.5 – 2 microns. With such particle sizes a relatively stable slurry can be easily obtained.

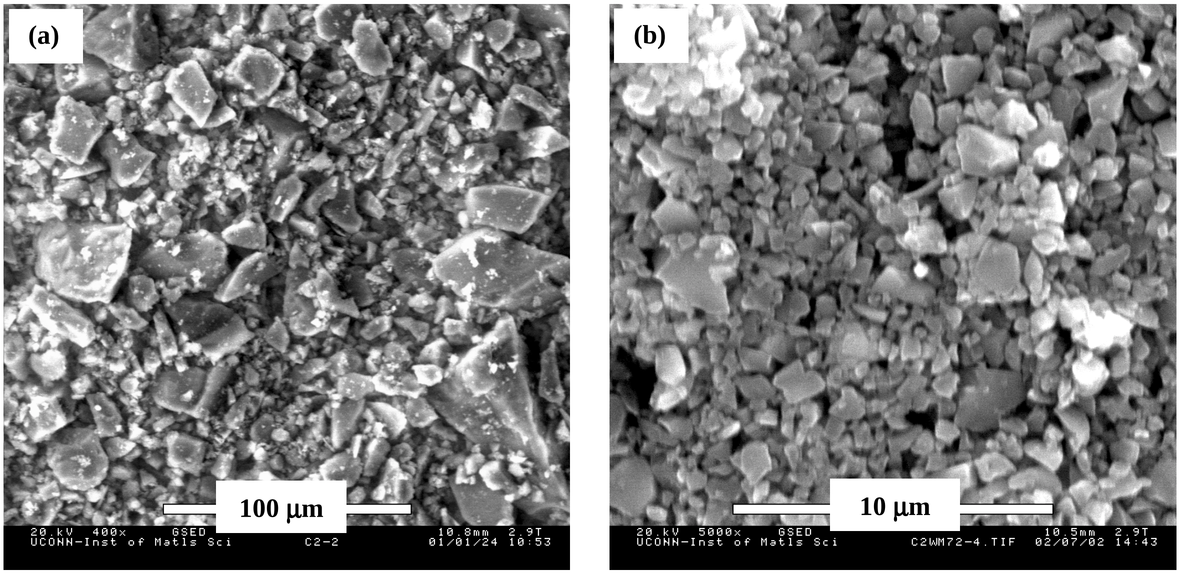

Figure 1. Morphology of the porcelain powder (a) at the as-received condition and (b) after ball milling for 72 hours.

The stability of a slurry, according to the DLVO theory [9], is determined by the balance between the repulsive and attractive forces which particles experience as they approach. The repulsive force depends on the degree of double layer overlap. Figure 2(a) shows the zeta potential versus pH value curve of the porcelain powder suspension. It indicates that the iso-electric point (i.e.p.) of the dental porcelain powder is at about 5.0, which is between the i.e.p. of Al_2O_3 (8.7) and SiO_2 (2.0). Since Al_2O_3 and SiO_2 are the main components of the dental porcelain [8], the zeta-potential of the porcelain powder appears to be controlled by a combined interactive effect of these two compounds. According to "Eilers and Korff Rule", the onset of instability of a suspension is associated with a rapid decrease in the value of the function $\zeta 2/\kappa$ (ζ:

Zeta potential; κ: Debye-Huckel parameter). It can be derived from Figure 2 that between pH value 3 and 7, coagulation of the particles in the slurry will happen quickly, leading to an unstable slurry. For slurries with pH < 3 or pH > 7, the zeta potential of the porcelain powder changes slowly and the surface of powder particles is mainly positively charged (for pH < 3) or negatively charged (for pH > 7). This surface charge provides large repulsive forces between particles and thus the slurry becomes stable.

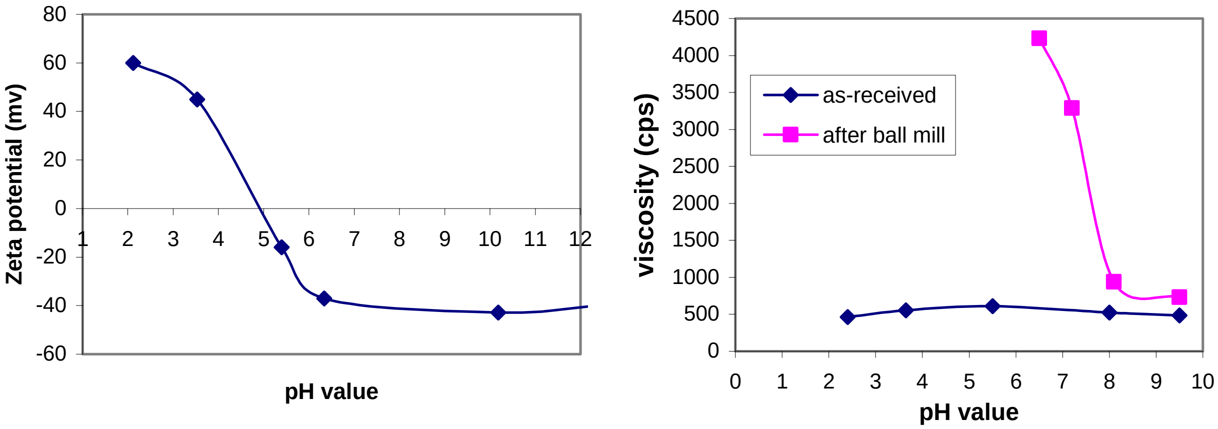

Figure 2. (a) Zeta potential of the dental porcelain powder, and (b) the influence of pH value on the viscosity of the porcelain slurry.

Figure 2(b) shows the viscosity as a function of pH value for the as-received and ball milled porcelain powders. Note that the viscosity of the as-received powder is insensitive to pH value, whereas the ball-milled powder slurry exhibits strong dependency on pH value. The substantially different rheological behaviors of the two slurries are believed to be due to the particle size difference between the two powders. Recall that the particle size of the as-received porcelain powder ranges from 5 to 50 microns, while the ball-milled powder has particles of 0.5 to 2 microns (Figure 1). For coarse particles such as the as-received powder, attractive and repulsive forces between particles induced by surface charges are insignificant in comparison with the influence of the gravity. Therefore, alternation in pH value has little influence on the rheology of the coarse particle slurry. In contrast, for fine particle systems such as the ball-milled powder, attractive and repulsive forces induced by surface charges become important in comparison with the influence of the gravity and thermal vibration. Thus, an adjustment in the pH value of the fine particle slurry, which modifies the surface charges, has large influence on the mobility and interaction of the particles.

Further examination of Figure 2(b) also reveals that when the pH value of the ball-milled powder slurry is larger than 8, the viscosity of the slurry is relatively low. However, the viscosity of the slurry becomes high when the pH value of the slurry approaches the iso-electric point (5.0 for the as-received porcelain). This phenomenon is related to the extent of collision and contact between particles. When the pH value of the fine particle slurry is greater than 8, the surface charge of particles is predominantly negative. Thus, repulsion due to the electrical double layer between particles will reduce their possibility of collision and contact, which reduces the viscosity of the slurry. However, when the pH value of the slurry is close to the iso-electric point, collision and contact between particles are greatly increased by attraction between positive and negative charges on different particles. The viscosity of the slurry is therefore increased significantly.

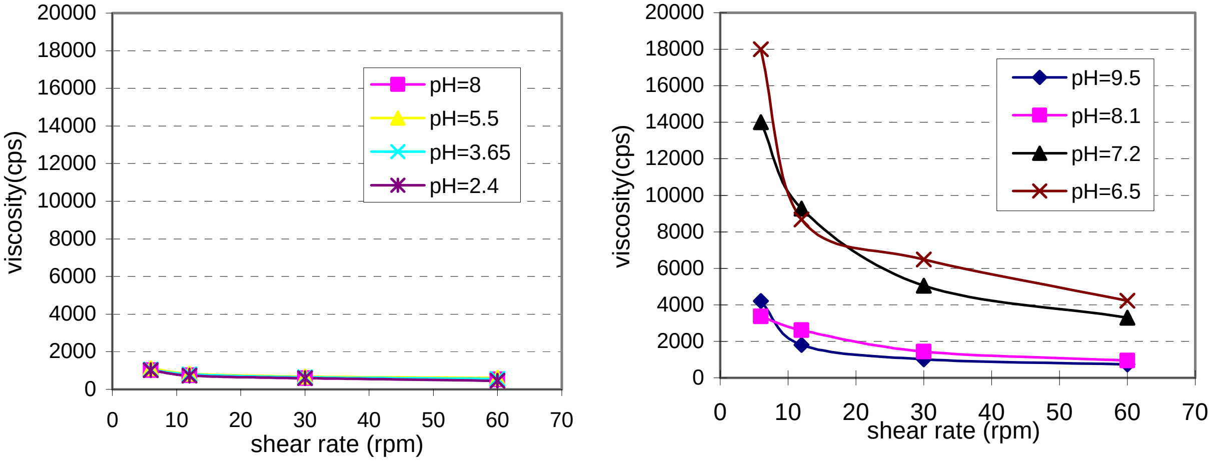

Figure 3. (a) Rheology of the as-received porcelain slurry, and (b) rheology of the ball-milled porcelain slurry. Both slurries contain 50 vol.% of solid loading.

Viscosity as a function of shear rate for the as-received and ball-milled porcelain slurry is shown in Figure 3. In Figure 3(a), the as-received porcelain slurry exhibits a slight shear thinning behavior because the viscosity of the slurry decreases as the shear rate increases. The viscosity curves of different pH values almost overlap, which indicates that pH value has little influence on their rheology, as found in Figure 2(b). In contrast, ball-milled porcelain slurries that have small particle size exhibit a strong shear thinning behavior, i.e., the viscosity of the slurry decreases substantially as the shear rate increases. Furthermore, such shear thinning behavior becomes more potent as the pH value approaches the iso-electric point [Figure 3(b)].

The underlying mechanisms responsible for these phenomena are similar to those discussed earlier for Figure 2. For the ball-milled porcelain slurry, fine particles tend to coagulate when the pH value of the slurry is close to the iso-electric point. Increasing the shear rate increases the rate for breaking up particle coagula, thereby leading to a more uniformly dispersed suspension, and thus a lower viscosity. When pH value moves away from the iso-electric point [e.g., at 8.1 and 9.5 shown in Figure 3(b)], fine particles have already been well dispersed before shearing, and thus the viscosity of the slurry becomes less sensitive to shear rate in comparison with the slurries with pH = 7.2 and 6.5. For the as-received powder, the gravity of large particles dominates their rheological behavior. Therefore, their viscosities are insensitive to pH values, as evidenced by the overlapping of all the curves [Figure 3(a)]. Furthermore, at a given solid loading the large particle slurry has less total particle surface area and fewer contact points between particles in comparison with the fine particle slurry. As such, the large particle slurry tends to have low viscosity and is insensitive to shear rate, as revealed in Figure 3(a).

For solid freeform fabrication of dental restorations, slurries with strong shear shinning properties (i.e., pseudoplastic behavior) are favored because the slurry has relatively low viscosity and friction when passing through the nozzle of the extruder at high shear rates and freeze rapidly after it is deposited onto the substrate due to the increase in the viscosity at low shear rates. However, phase separation and choking at the nozzle could occur if the viscosity of the slurry is too high [10]. Thus, the viscosity and rheological behavior of the slurry should be controlled properly to avoid phase separation and at the same time to allow the shape retention once the slurry has been extruded.

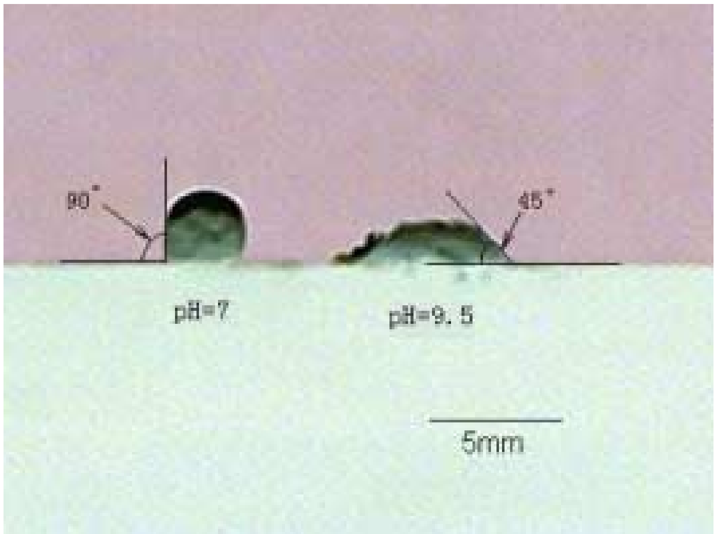

Figure 4. Cross-section of extruded porcelain lines with 50 vol.% of solid loading at different pH values.

Extrusion experiments were carried out to identify the optimum formulation of the porcelain slurry. Figure 4 shows the cross-section of extruded porcelain lines with pH value at 7 and 9.5. Note that the contact angle between the porcelain line (pH=7) and the substrate is almost 90 degrees, which indicates that the slurry is solidified rapidly after extrusion and the shape of the line is kept well because of the sufficient yield strength of the solidified line. For the porcelain line with pH=9.5, the contact angle between the extrudate and the substrate is about 45 degrees. The porcelain line spreads twice the width as that obtained from the slurry with pH=7. Based on the data shown in Figures 2 and 3, it can be concluded that the low contact angle and large width of the porcelain line with pH=9 are due to the wetting of the substrate by the slurry and its slow solidification and low viscosity. Thus, the rheology of the slurry at pH=9.5 should be avoided because it cannot keep the shape of the extrudate well. Such a slurry could also lead to slumping when overhanging features are fabricated because of the low yielding strength of the slurry. The optimal formulation of the slurry can be obtained by modifying the pH value of the stable slurry to be close to the iso-electric point (pH=5.0) in the range from 6.0 to 7.5. In this range, strong shear thinning property can be obtained while the viscosity of the slurry is not too high.

The volume fraction of solids loading also influences the extrusion properties of the slurry. A powder slurry will start to behave like a dilatant solid once the solid loading is increased above approximately 64 vol.% [6]. Dilatant solids have shear thickening behavior, i.e., the slurry exhibits higher viscosities when it is subjected to a higher shear rate. Shown in Figure 5 is the top view of lines extruded from slurries with different solid loadings and extrusion parameters. It is evident that extruded lines become discontinuous or exhibit periodical changes in the line width when the solid loading exceeds 60 vol.% (Lines 1 and 2 in Figure 5). This is attributed to the shear thickening behavior because of the dilatant slurry. As the dilatant slurry passes through the nozzle of the extruder, its viscosity increases. The high viscosity hinders the slurry from being extruded smoothly, and thus the extrusion pressure continues to build up by the coming slurry. When the pressure exceeds a threshold value, the slurry will be extruded in a drop with decreasing viscosity. Thus, periodical drop structure is formed.

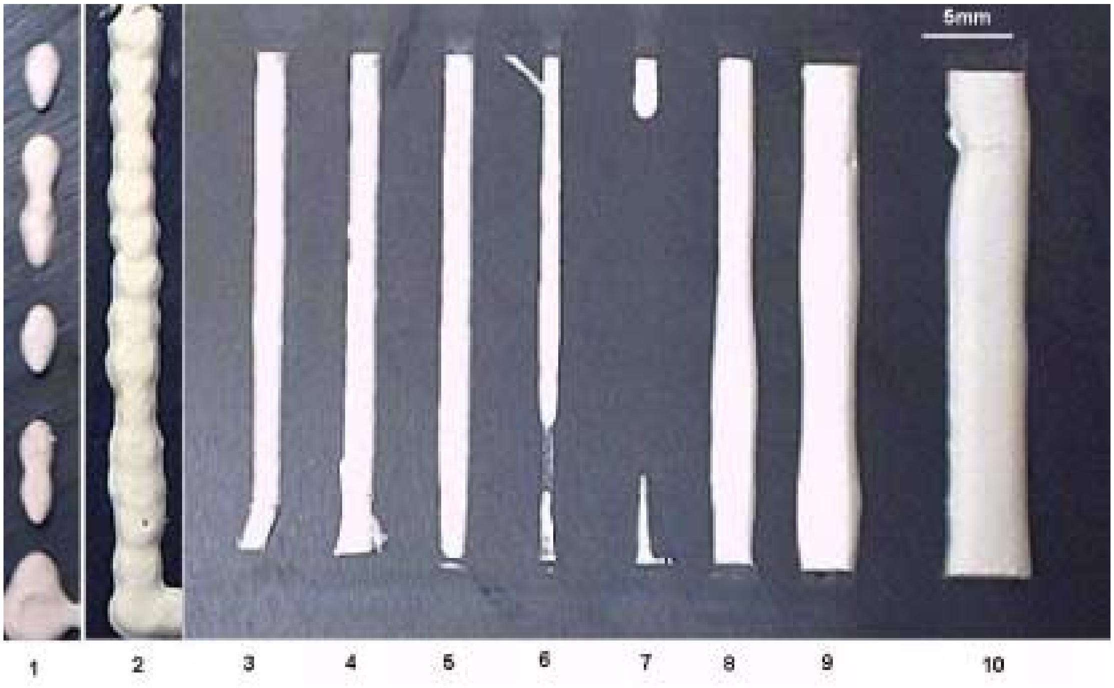

Figure 5. Porcelain lines extruded from slurries with pH=7, but with different solid loadings and extrusion conditions. Keys:

1: periodical structure from slurries with high solid loadings (>60 vol.%)
2: periodical structure from slurries with high solid loadings (>60 vol.%)
3: X-Y table speed 1.6cm/s, extrusion rate 0.02ml/s, 50 vol.% of solid loading
4: X-Y table speed 0.8cm/s, extrusion rate 0.02ml/s, 50 vol.% of solid loading
5: X-Y table speed 0.4cm/s, extrusion rate 0.02ml/s, 50 vol.% of solid loading
6: X-Y table speed 0.4cm/s, extrusion rate 0.01ml/s, 50 vol.% of solid loading
7: X-Y table speed 0.4cm/s, extrusion rate 0.005ml/s, 50 vol.% of solid loading
8: X-Y table speed 0.4cm/s, extrusion rate 0.04ml/s, 50 vol.% of solid loading
9: X-Y table speed 0.4cm/s, extrusion rate 0.08ml/s, 50 vol.% of solid loading
10: X-Y table speed 0.4cm/s, extrusion rate 0.16ml/s, 50 vol.% of solid loading

In addition to the formulation and solids loading of the slurry, deposition rates also influences the extrusion process. Lines 3 to 10 in Figure 5 show the porcelain lines extruded from slurries with 50 vol.% of solid loading under different X-Y table speeds and extrusion rates. The table speed appears to have little influence on the geometry of the extruded porcelain line when the extrusion rate is at 0.02 ml/sec, as evidenced by Lines 3 to 5. However, the extrusion rate has strong impact on the porcelain line. When the extrusion rate is too low (e.g., Lines 6 and 7), the lines are discontinuous, indicating that the amount of the slurry extruded is not enough to cover the substrate area produced by the fast movement of the table. For a table speed of 0.4 cm/s, 0.02 ml/s is found to be the minimum extrusion rate in order to obtain a continuous and uniform extrusion line. Above 0.02 ml/s the width of the extruded line increases continuously as the extrusion rate increases – a phenomenon consistent with the expectation that the more the slurry is extruded, the wider the line is. More works are needed in this area to further investigate interactions among the table speed, extrusion rate and the wetting behavior of the slurry and their effects on the geometry of lines extruded. Nevertheless, some 3D shapes have been extruded from the porcelain slurry using the MMLD machine, as shown in Figure 6.

Figure 6. 3-D samples fabricated via porcelain slurry extrusion.

IV. Summary

Dental restoration via powder delivery by slurry extrusion was studied in this paper. The shape of extrudates before laser densification depends strongly on the formulation of slurries. Modification of pH value has large influence on the fine particle slurry obtained via ball milling. Slurries prepared in a stable pH range can disperse high volume of solids, but have low viscosities and spread uncontrollably when extruded. In contrast, slurries first prepared in a stable pH range and subsequently adjusted to an unstable pH range have exhibited pseudoplastic behavior. Such slurries have a low extrusion pressure to avoid phase separation, and at the same time their yield points are high enough to maintain the shape of extrudates. Solids loading has large influence on the extrusion. Too high solid loading (> 64 vol.%), which causes shear thickening, results in periodical structure of the extruded line. Extrusion rate has substantial influence on the extrudate, whereas the moving speed of the table does not.

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