Control of the Cross Section Geometry of Extruded Dental Porcelain Slurries for Rapid Prototyping Applications

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Abstract

This study investigates the dependence of the cross section geometry of extruded dental porcelain slurries on the rheological property of the slurry and the extrusion conditions. It is found that a pseudoplastic slurry is a basic requirement for obtaining extruded lines with rectangular cross sections. The cross section geometry of the extrudate is also strongly affected by extrusion parameters including the extrusion nozzle height, nozzle moving speed, and extrusion rate. Proper combinations of these extrusion parameters are necessary in order to obtain extrudates with near rectangular cross sections. The results obtained have been explained in terms of the interactions among the rheological properties of the slurry, the shear rate imposed on the slurry during extrusion, the wettability of the slurry on the substrate, and the forced flow of the slurry during extrusion.

Keywords: Slurry extrusion, dental porcelain, rheology of slurry, solid freeform fabrication

I. Introduction

3D objects fabricated through line-by-line and layer-by-layer approaches require that each line deposited has a rectangular cross section in ideal cases. Lines with such cross section geometry can prevent or minimize the formation of voids between lines and layers. This study investigates the dependence of the cross section geometry of extruded dental porcelain slurries on the rheological property of the slurry and the extrusion conditions for dental restorations via the multi-material laser densification (MMLD) process [1-3].

Currently, there are two general routes for preparing pastes and slurries for SFF. One requires the use of polymers or resins as the binder in order to maintain the shape of the extrudate [4,5]. These polymers and resins are burned out in the subsequent heat treatment while contamination may remain in the extrudate. The second route is to prepare aqueous pastes or slurries without addition of binders and to control the cross section geometry of the extrudate by adjusting the pH value, salt concentration, and volume fraction of solid in the paste [6-11]. Using fine Al_2O_3 powder, Cesarano, et al [7] have shown that when a slurry is pseudoplastic and drying rates are appropriate, the lines extruded yield nearly rectangular cross sections with relatively straight walls and flattened tops. The paste formulation and particle size have also been shown by Du, et al [11] to have strong effects on the extrudability of thin wall thickness tubes and their thickness and uniformity.

Although the effects of rheological behavior of pastes and slurries on the cross section geometry of the extrudate have been studied by several researchers [6-11], the dependency of the cross section geometry on extrusion parameters has never been systematically investigated. To address this issue, the effects of extrusion parameters on the cross section geometry of the extrudate in conjunction with the effects of rheological behavior of dental porcelain slurries have been investigated in this study. The extrusion parameters investigated include the nozzle height of the extruder, nozzle moving speed, and extrusion rate, all of which are experimental variables and thus can be adjusted to achieve the desired cross section geometry. The results indicate that the effects of these extrusion parameters on the cross section geometry of the extrudate can be explained in terms of the interactions among the rheological properties of the slurry, the shear rate imposed on the slurry during extrusion, the wettability of the slurry on the substrate, and the forced flow of the slurry during extrusion.

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 [12], 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 1 to 50 micrometers. To reduce the particle size of the porcelain powder to sub-micrometers, ball-milling process was conducted using a single axis mixer machine loaded with Al_2O_3 balls. After milling, the powder was dispersed in de-ionized water and the submicron-sized particles were separated from coarse particles (> 1 μm) through sedimentation. Only the submicron-sized particles were used to prepare the slurries.

The porcelain slurries were prepared using de-ionized water as the solvent with a solid loading of 40 – 50 vol %. Uniform and stable slurries were obtained by gently mixing the slurry for 24 hours using the mixer machine loaded with Al_2O_3 balls. The porcelain slurry was extruded using a 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 with temperature sensing and control system, and (iv) a X-Y-Z positioning system. The pressure exerted on the porcelain slurry within the micro-extruder was applied via an electric cylinder (model: NV-BN23-105B). The slurries were extruded onto SiC plates with a 700μm nozzle. The motion and position control was provided by a computer through a Galil DMC-1800 multi-axis motion control card. The extrusion variables that could be controlled independently and investigated in this study were the nozzle height of the micro-extruder (i.e., the distance between the nozzle tip and the substrate), the nozzle moving speed (with respect to the substrate, mm/s), and the extrusion rate (i.e., the volume of the slurry extruded per unit time, ml/s).

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 in the University of Florida using a Zeta-Reader instrument. The pH value of the slurry was measured using a Denver basic pH meter. The cross section geometry was defined by the line width and height of the extrudate and its contact angle with the substrate. To measure these geometrical parameters, the porcelain lines extruded were encapsulated using epoxy before cutting and polishing after which these parameters were observed and measured using an optical microscope.

III. Results and Discussion

3.1 Rheological Behavior of Dental Porcelain Slurries

Figure 1 shows the zeta potential of the dental porcelain powder as a function of the pH value. 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 [12], the zeta-potential of the porcelain powder appears to be controlled by a combined interactive effect of these two compounds. It can be inferred from Figure 1 that slurries with pH < 3.0 or pH > 8.0 should be relatively stable. This is the case because the surfaces of powder particles with these pH values are mainly positively charged (for pH < 3.0) or negatively charged (for pH > 8.0) [13,14]; the same charges on their surfaces provide large repulsive forces between particles, thereby preventing coagulation and thus leading to stable slurries. In contrast, slurries with pH values between 3.0 and 6.5 would be unstable because coagulation of particles will happen quickly owing to the zero or near-zero net charge on the surfaces of these particles.

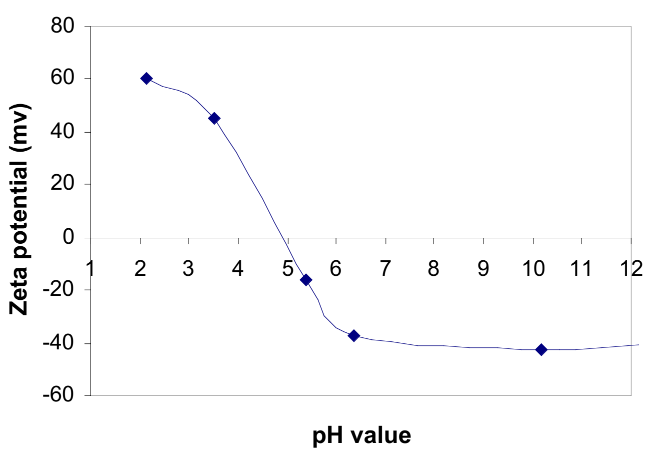
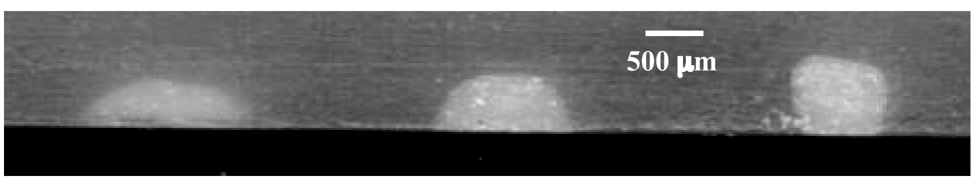


Figure 1. Zeta potential of the dental porcelain powder as a function of the pH value.

Based on Figure 1, clearly, a pseudoplastic slurry with moderate viscosity can be prepared with a pH value near 7.0 – 7.5 because at pH = 5.0 the slurry becomes unstable with high viscosity and at pH > 8.0 or < 3.0 the slurry is very stable. Slurries with pseudoplastic (shear thinning) behavior are highly desirable for controlling the cross section geometry of the extruded line because slurries with shear thinning properties can be extruded with a relatively low extrusion force and solidify in place once the slurry leaves the nozzle due to the removal of shear stresses. Thus, most of the extrusion studies presented below are carried out using dental porcelain slurries with pH = 7.0 – 7.5 unless otherwise mentioned.

Figure 2 compares the cross section geometry of the extrudates with pH values equal to 9.3, 8.0 and 7.0. At pH = 9.3, the slurry is very stable with a relative low viscosity. As a result, the slurry flows continuously after it leaves the nozzle and thus takes on an arch shape with a low contact angle of 40 degrees. At pH = 8.0, the viscosity of the slurry increases slightly and thus the slurry spreads out less on the surface of the substrate, resulting in an increased contact angle of 60 degrees. At pH = 7.0 (approaching the i.e.p.), the slurry becomes pseudoplastic because the low electrical charges of the same sign of the particles allows them to approach to each other, but at the same time prevents them to coagulate. As a result of its shear thinning behavior, the contact angle of the extrudate with the substrate increases to 95 degrees, clearly indicating nearly no spreading after the slurry leaves the nozzle of the extruder. With a contact angle near 90 degrees, the cross section of the extrudate is approaching a rectangular shape which is highly desirable as a “building block” for fabrication of 3-dimensional objects through layer-by-layer approaches.



	pH = 9.3	pH = 8.0	pH = 7.0
Contact angle (degree)	40	60	95

Figure 2. Cross section photos of extrudates with different pH values.

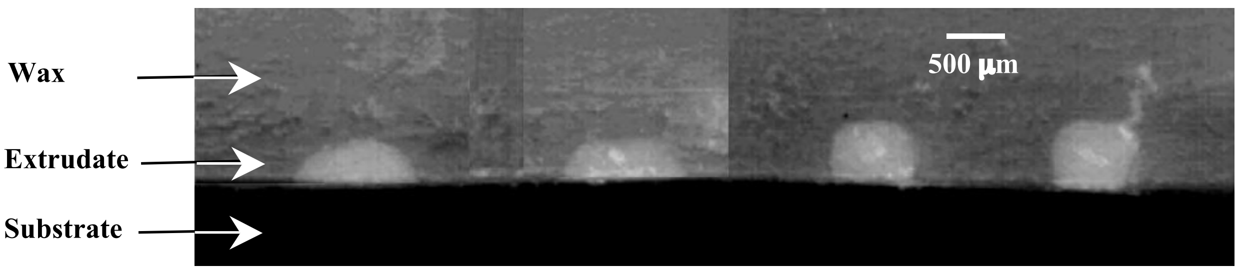
3.2 Effects of Nozzle Height on the Cross Section Geometry of Extrudates

The distance between the nozzle tip of the extruder and the substrate, termed as the nozzle height hereafter, greatly influences the cross section geometry of the extrudate. The distance between the nozzle and the substrate will limit the space within which the slurry can flow. For a certain slurry extrusion rate and nozzle moving speed, there is a critical nozzle height (h_c) above which the cross section geometry of an extruded single line is mainly controlled by the rheological behavior of the slurry and the wettability of the slurry on the substrate. When the nozzle height is lower than h_c, the volume of the slurry extruded will be too large for the space between the nozzle and the substrate. As a result, the slurry is forced to spread in the directions perpendicular to the deposited line along the surface of the substrate, and the resultant shape of the extrudate is not only determined by the rheological properties and wettability of the slurry, but also by the space between the nozzle and the substrate. In contrast, when the nozzle height is larger than h_c, there is enough space for the deposited slurry so that the rheological properties and wettability of the slurry will determine the cross section geometry of the extrudate.

Our experiments indicate that the critical nozzle height can be estimated using the following equation:

$$h_c = \frac{V_d}{v_n D_n} \tag{1}$$

where V_d is the volume of the slurry extruded per unit time (called the extrusion rate hereafter), v_n the nozzle moving speed, and D_n the nozzle diameter. The physical meaning of eq. (1) is that the volume of the slurry extruded per unit time is equal to the volume available per unit time between the nozzle and the substrate. When the nozzle height is lower than h_c, the slurry is forced to take up the space beyond the volume defined by the product of the nozzle height, the nozzle diameter, and the distance traveled by the nozzle per unit time.



Nozzle height (µm):	200	330	670	1000
Contact angle (degree):	40	65	85	95

Figure 3. Cross section of the single lines extruded using a dental porcelain slurry of pH = 7.5 with V_d = 2.5 x 10^{-3} ml/s, D_n = 0.7 mm, v_n = 4.25 mm/s, and different nozzle heights as indicated.

Figure 3 shows the cross section of the extrudates deposited with different nozzle heights. The contact angles of these extrudates with the SiC substrate are measured and presented in Figure 4. When the nozzle height equals to 200 and 330 µm, the slurries spread widely along the substrate with low contact angles, which indicates that the nozzle height is lower than h_c because the slurry has been forced to flow beyond the space defined by the nozzle height, the nozzle diameter, and the distance traveled by the nozzle per unit time. When the nozzle height equals to 670 µm, the contact angle closes to 90 degrees and no spreading is observed. A further increase in the nozzle height (1000 µm) does not alter the shape of the extrudate much with only a small increase in the contact angle. The critical nozzle height calculated using eq. (1) for the extrusion condition shown in Figure 3 is 840 µm which is between 670 µm and 1000 µm tested in the experiment. These results indicate that when the nozzle height is near the critical nozzle height, the contact angle of the slurry on the SiC substrate used in this study is about 90 degrees.

However, when the nozzle height is substantially smaller than h_c (e.g., the cases of 200 and 330 μm in Figure 3), the forced flow is present and the contact angles will be smaller than 90 degrees.

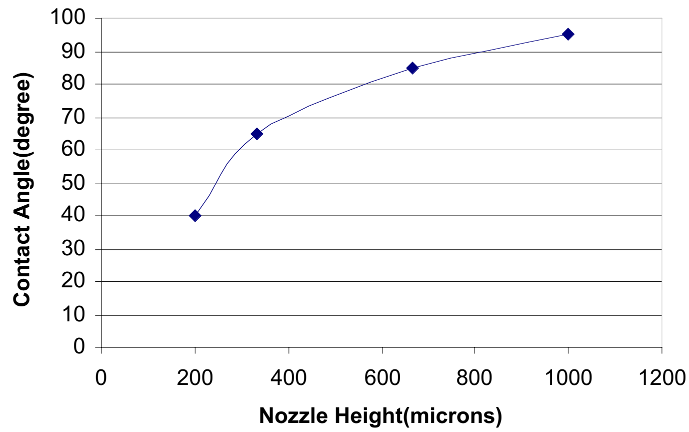


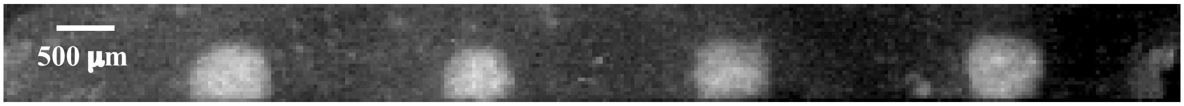
Figure 4. The contact angle as a function of the nozzle height for slurries with pH = 7.5.

3.3 Influence of the Shear Rate on the Cross Section Geometry of Extrudates

Because of the pseudoplastic behavior of the slurry, extrusion conducted with high shear rates will have relative low viscosity, whereas extrusion with low shear rates will have high viscosity. In order to investigate the true effects of the shear rate on the cross section geometry of the extrudate, a set of the experiments have been designed in which both the extrusion rate and the nozzle moving speed have been increased proportionally in order to keep the critical nozzle height [see eq. (1)] and the deposition density constant. The deposition density, D_d, is defined as the volume of the slurry extruded per unit time divided by the product of the nozzle diameter and the moving speed of the nozzle. When both the critical height and the deposition density are kept constant, the change in the extrusion rate provides a genuine evaluation of the effect of the shear rate.

The results from this special set of the experiments are shown in Figure 5. At high extrusion rates (0.01 ml/s and 0.005 ml/s), the contact angles are smaller than 90 degrees. In contrast, at low extrusion rates (0.0025 ml/s and 0.00125 ml/s), contact angles are greater than 90 degrees. This is so because high extrusion rates result in high shear rates which in turn leads to low viscosities. Thus, when high extrusion rates are used, the slurry flows fast after it leaves the nozzle tip. As a result of the fast flow, the slurry spreads out along the surface of the substrate before it freezes and a low contact angle results. In contrast, when low extrusion rates are used, the flow of the slurry after it leaves the nozzle tip is limited because of its high viscosity. As a consequence of this limited flow, a high contact angle results.

It is noted, however, that in spite of the dependency of the cross section geometry on the shear rate, the effect of the shear rate on the contact angle is relatively small in comparison with that of the pH value and the nozzle height. As seen from Figure 5, the variation of the contact angle due to the different shear rates investigated is within 20%, which is much smaller than 100% changes achieved by altering the nozzle height (Figures 4 and 5).



Extrusion rate (ml/s):	0.01	0.005	0.0025	0.00125
Nozzle moving speed (mm/s):	17.5	8.5	4.25	2.125
h_c (mm):	0.84	0.84	0.84	0.84
Deposition density (mm^3/mm^2):	0.84	0.84	0.84	0.84
Contact angle (degree):	85	90	95	105

Figure 5: Cross section of the single lines extruded with different extrusion rates and nozzle moving speeds as indicated, while keeping all other processing parameters constant.

IV. Concluding Remarks

The present extrusion study clearly shows that in order to get favorable cross section geometry of the porcelain powder line in SFF processes, extrusion parameters including the nozzle height, nozzle moving speed and the extrusion rate should be optimized. However, optimization can be achieved only when the slurry is pseudoplastic. The latter can be accomplished by adjusting the pH value of the slurry for the dental porcelain powder to between 7.0 and 7.5. Once the proper slurry is prepared, extrusion conditions can have strong impact on the cross section geometry of the extrudate. There is a critical nozzle height (h_c) for a given set of the extrusion rate, nozzle moving speed, and the nozzle diameter. When extrusion is carried out with the nozzle height above the critical nozzle height, the cross section geometry of the extrudate is mainly determined by the rheological behavior of the slurry and the wettability of the slurry on the substrate. When the nozzle height is lower than the critical nozzle height, the resultant shape of the extrudate is not only controlled by the rheological properties and the wettability of the slurry, but also by the forced flow of the slurry along the surface of the substrate. A rectangular cross section results when low extrusion rates are used. In contrast, an arch-shaped cross section with low contact angles is obtained if high extrusion rates are used.

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