# Mechanical and Rheological Properties of Feedstock Material for Fused Deposition of Ceramics and Metals (FDC and FDMet) and their Relationship to Process Performance

N. Venkataraman, S. Rangarajan, M.J. Matthewson, A. Safari and S.C. Danforth, Rutgers University.
A. Yardimci*, S.I. Guceri, University of Illinois at Chicago.
* Advanced Engineering Design Center, Baxter International, Round lake, Illinois, USA

## Abstract

Fused deposition of ceramics (FDC) is a solid freeform fabrication technique based on extrusion of a highly loaded thermoplastic binder system. The present FDC process uses filament feedstock of 1.780 mm ± 0.025 mm diameter. The filament acts as both the piston driving the extrusion process as well as the molten feedstock being deposited. The filaments need to be able to provide and sustain the pressure needed to drive the extrusion process. Failure to do this results in failure via "buckling". The filament compressive modulus determines the ability of the filament to provide and sustain the required pressure to drive the extrusion. The viscosity of the feedstock material, nozzle geometry and volumetric flow rates employed determine the pressure needed to drive the extrusion process. In this work the extrusion pressure for a particular material termed PZT ECG9 (52.6 Vol.% PZT powder in ECG9 binder) was measured experimentally as a function of volumetric flow rate and nozzle geometry. The compressive modulus of the material was determined using a miniature materials tester (Rheometrics, Inc., Piscataway, NJ). A process map has been developed. The map is based on the quantity $\Delta P/E$, and predicts the performance of the material in a FDC process as a function of nozzle geometry and volumetric flow rate. In general, it is observed that when $\Delta P/E$ exceeds a critical value, called $\Delta P_{cr}/E$, there is an increased tendency for the filament to buckle. A preliminary fluid flow model for extrusion of PZT ECG9 through a FDC nozzle has also been developed using Polyflow™ software. The model predicts the observed trend in pressure drop with flow rate and nozzle geometry with reasonable accuracy.

## Introduction

Fused deposition of ceramics and metals (FDC and FDMet) is a solid freeform fabrication process based on extrusion of highly loaded thermoplastic binder system. The present fused deposition technique uses filament feedstock of 1.78 mm ± 0.025 mm diameter. A schematic of the fused deposition process is shown in Figure 1. The filament acts as both the piston driving the extrusion process, as well as the molten material being deposited through a nozzle of a particular orifice diameter onto a Z stage platform in the X-Y plane (Figure 1).

The extrusion of a highly particle loaded molten thermoplastic binder system through a nozzle of a given geometry requires the application of a certain amount of pressure. The actual value of the extrusion pressure required depends on: the viscosity of the material, the nozzle geometry, and the volumetric flow rate of the extrusion process. The viscosity of the material will depend on the binder chemistry, solids loading, state of agglomeration, shear rate and temperature.

In the case of the fused deposition process, the extrusion pressure is applied by the filament feedstock. If the required extrusion pressure exceeds a certain critical value, then buckling of the filament ensues (shown schematically in Figure 1). The critical stress value is given according to Euler's criterion as [1, 2]:

$$\sigma_{cr} = \frac{\pi^2 E}{4(L/R)^2} \qquad (1)$$

where: $\sigma_{cr}$ is the critical buckling stress, $E$ is the compressive elastic modulus of the filament,

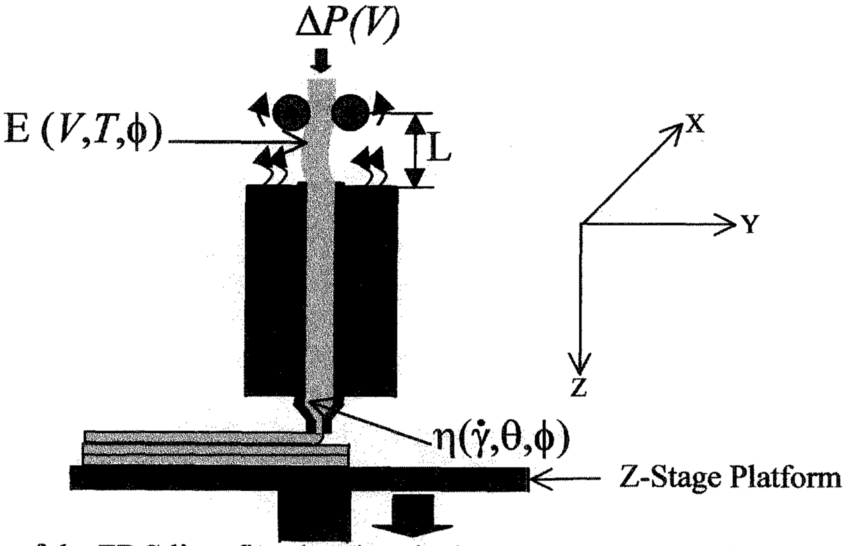

Figure 1: Schematic of the FDC liquefier showing the important process and material parameters involved in buckling ($V$: volumetric feed rate, $T$, $\theta$: temperature, $\phi$: solids loading, $\dot{\gamma}$: shear rate, $\eta$: viscosity of feedstock, $E$: compressive stiffness of filament)

$L/R$ is the aspect ratio of the filament above the liquefier as shown in Figure 1. If $\Delta P$ (Figure1) is the required extrusion pressure for a given nozzle geometry, volumetric flow rate, solids loading and temperature, then the condition for buckling can be represented as [3-4]:

$$1.1\Delta P \geq \sigma_{cr} \qquad (2)$$

The correction factor 1.1 in equation 2 is due to difference in the cross section area between the filament and the liquefier barrel (the barrel diameter is larger than the filament diameter). One sees from Equation 2 that the minimum extrusion pressure needed for buckling of filaments is $\sigma_{cr}/1.1$. For sake of clarity we call this minimum extrusion pressure needed for buckling as $\Delta P_{cr}$ to differentiate from $\Delta P$ which represents any other value of extrusion pressure. One also sees from Equation 2 that 1.1 $\Delta P_{cr} = \sigma_{cr}$, and therefore, applying this condition to equation 1 we find that the quantity $\Delta P_{cr}/E$ is dependent only on the ratio of the length of the filament above the liquefier to the filament radius. This is, therefore, a value characteristic of the particular fused deposition machine design. The quantity $\Delta P/E$ depends on the material used, the temperature of operation, the nozzle geometry and the volumetric flow rate of deposition process. From equation 2 one sees that buckling occurs if 1.1 $\Delta P > \sigma_{cr}$, *i.e.* if $\Delta P/E > \Delta P_{cr}/E$.

## Experimental Procedure

The material used in this study is termed PZT ECG9. It consists of lead zirconate titanate powder (PZT Powder) dispersed in a thermoplastic binder termed ECG9. The details of the binder composition and development have been presented elsewhere [5]. The ceramic powder was obtained from TRS, Inc., State College, PA. The median particle size of the PZT powder was 1.2 μm. The specific surface area of the powder, as determined by single point BET method, was 1.1 $m^2/g$. The density, as determined using helium pycnometry, was 7.83 $g/cm^3$.

The powder was first coated with the dispersant by mixing PZT with a 3 wt% solution of stearic acid in toluene in a Nalgene$^{TM}$ bottle for four hours in a ball mill [6]. $ZrO_2$ media (3/8 inch, cylindrical) was used to avoid contamination of the PZT powder. The slurry obtained at the end of the mixing step was then vacuum filtered to obtain a powder cake which was then dried for 12 hours. The correct proportions of coated powder and binder were compounded at 140°C in a torque rheometer (Haake) to obtain a 52.6 vol.% ceramic-polymer mix. The compounded mix was cooled and then granulated. The granules were stored in a dessicator (25% RH) prior to extrusion. The granules were then fed via a hopper into a single screw extruder (Haake). The pressure and temperature in three zones of the screw extruder were monitored and controlled. A 120 mesh screen and breaker plate arrangement was used to remove agglomerates and also to obtain homogeneous mixing during screw extrusion. A 1.78mm extrusion diameter nozzle was used. The extruded filaments were picked up by a conveyor belt whose speed was matched to the extrusion speed to control the diameter of the filament to 1.780 ± 0.025 mm. The filaments were then spooled and stored in a controlled humidity until further use.

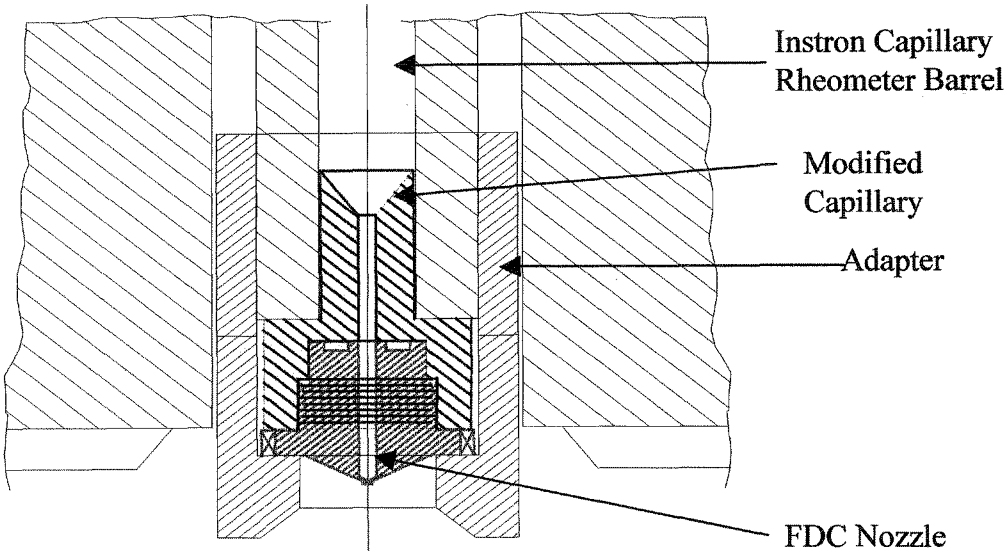

Figure 2: Schematic of modification to capillary rheometer for measurement of pressure drop across FDC nozzles.

The compressive mechanical properties of the filaments of PZT ECG9 were determined using a miniature materials tester (Rheometrics, Inc., Piscataway, NJ). The details of the mechanical testing and modulus determination procedure are described elsewhere [7].

The pressure associated with the extrusion of PZT ECG9 through a FD nozzle was measured using a modified Instron capillary rheometer. The details of the measurement technique are described elsewhere [8]. The modification consisted of an adapter custom fabricated to hold a FDC nozzle. The adapter was fabricated in such a manner as to be able to fit into the Instron capillary rheometer barrel. A schematic of the modified adapter is shown in Figure 2. The barrel was heated along with the nozzle to 140°C (the FDC temperature for PZT ECG9) following which the barrel was filled with PZT ECG9. A precision-machined piston attached to the load cell was lowered from the top end of the barrel. The barrel was then moved at a controlled displacement rate onto the piston following which the material was extruded through the FDC nozzle attached at the bottom. The load corresponding to a particular velocity and nozzle geometry was recorded. The corresponding extrusion pressure was calculated from the recorded load as a function of the volumetric flow rate and nozzle geometry. In this study the volumetric flow rates were chosen to coincide with the typical flow rates associated with the FDC process. The pressure was measured as a function of the nozzle diameter and the aspect ratio of the nozzle. The Instron capillary rheometer was also used to determine the true rheological behavior of PZT ECG9. A simple finite element model using Polyflow™ was also developed to study the physics of flow of PZT ECG9 through FDC nozzle.

## Results and Discussion

The compressive modulus of PZT ECG9 as a function of displacement rate at room temperature (25°C) is presented in Table I.

Table I: Compressive Modulus of PZT ECG9 (25°C, 50% RH) as a Function of Displacement Rate

| Modulus (MPa) | Displacement Rate (mm/min) |
|---|---|
| 58 ± 8 | 0.1 |
| 80 ± 11 | 1 |
| 101 ± 23 | 10 |
| 134 ± 17 | 20 |

The data indicate a statistically significant increase in compressive modulus with displacement rate. The details of the compressive mechanical behavior of PZT ECG9 as a function of temperature and storage time have been described elsewhere [7]. As mentioned before, for a fixed geometry, the filament critical buckling stress is directly proportional to the compressive elastic modulus. In this work, the compressive modulus corresponding to the lowest displacement rate (0.1 mm/min) was chosen as a conservative estimate. The true rheological (true wall shear stress vs. true wall shear rate) behavior of PZT ECG9 as determined by the capillary instron rheometer is shown in Figure 3. The Herschel-Buckley type equation was determined to be the best fit. The constitutive equation for a Hershel-Buckley fluid is[9,10]:

$$\tau = \tau_y + K\dot{\gamma}^n \tag{3}$$

The best fit parameters for PZT ECG9 which were used in subsequent finite element modeling are given in Table II.

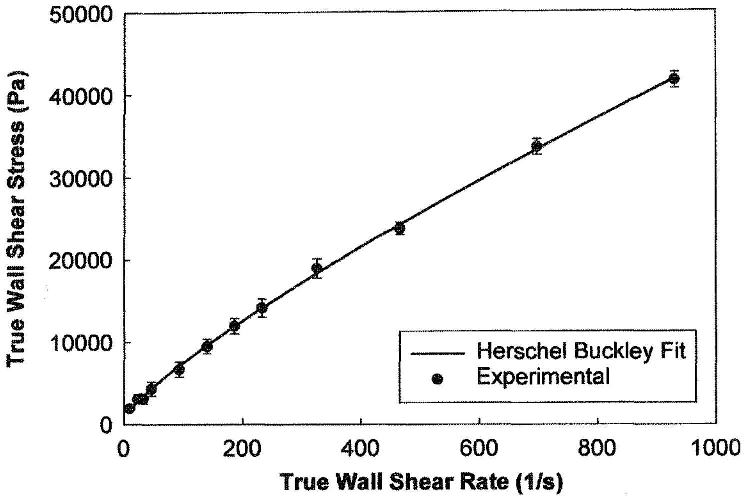

Figure 3: The true rheological behavior of PZT ECG9 at 140°C as measured using a capillary rheometer.

A schematic of the domain used in finite element model is shown in Figure 4. The domain represents the modified capillary Instron rheometer used for measurement of extrusion pressure of PZT ECG9 through the FDC nozzle. A commercial computational fluid dynamic software (Polyflow™) was used for solving the model under the following boundary conditions: isothermal, axisymmetric, no slip at walls and a fully developed flow at the inlet. The predicted pressure drop values for PZT ECG9, as calculated using Polyflow™, are shown in Figure 5

Table II: Best Fit Parameters to Herschel-Buckley Equation for PZT ECG9 at 140°C

| Parameter | Value |
|---|---|
| $\tau_y$ | 716 ± 290 Pa |
| K | 165 ± 21 Pa.s$^n$ |
| n | 0.8 ± 0.02 |

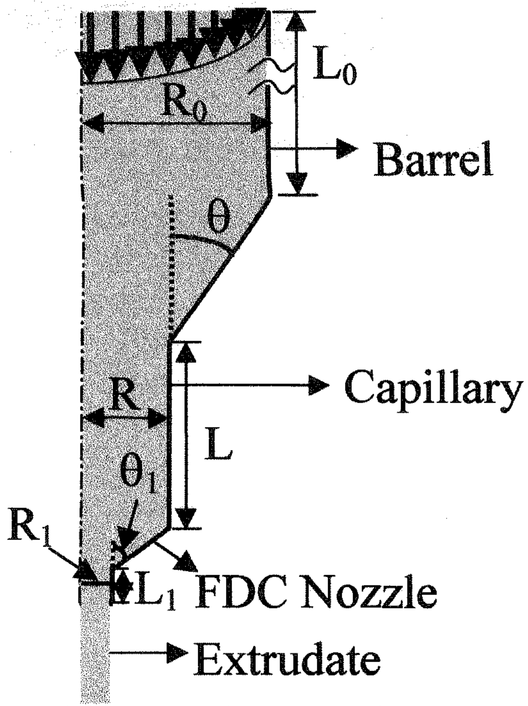

Figure 4: Schematic of domain used in finite element modeling. The values of the various parameters are: $L_0$: 50 mm, $R_0$: 4.7625 mm, L: 35.2 mm, R: 0.965 mm, $\theta$: 33.5 °, $R_1$: 0.127 mm, $L_1/R_1$: 2, 4, 10, $\theta_1$: 59°.

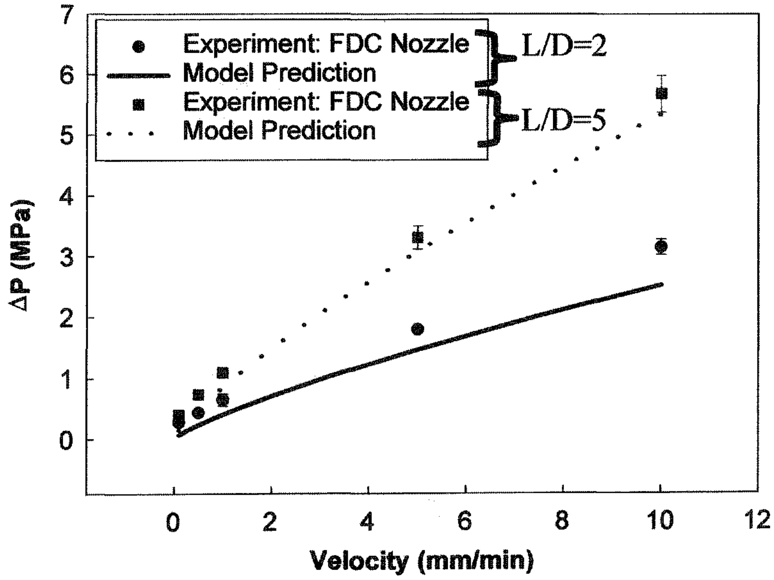

Figure 5: Experimental (symbols) and predicted (lines) pressure drop values as a function of average velocity at the inlet for flow of 52.5 Vol.% PZT in ECG9 binder in the modified capillary rheometer.

along with the experimentally determined values. One can see from Figure 5 that the finite element model accurately predicts the trend in the experimentally determined ΔP values. The model tends to underestimate the magnitude of the pressure drop values (by ~ 30%). The lack of exact agreement between the experimental value and predicted value could be because the model does not accommodate for non-idealities such as end effects, non-isothermal effects and viscoelasticity of the material. The nozzle used in the measurement of the pressure drop values is not heated and therefore, the experimental pressure values are expected to be higher than the model predictions. The model also predicts that greater than 90% of the pressure drop occurs at the nozzle, and less than 10% in the barrel and modified capillary, implying that the major contribution to the measured pressure drop is from the FDC nozzle. The pressure drop for PZT ECG9 as a function of nozzle diameter and aspect ratio were measured for various volumetric flow rates. The quantity ΔP/E was calculated for the various nozzle diameters and aspect ratios as a function of volumetric flow rates. The measured pressure drop values and compressive modulus (at room temperature corresponding to 0.1 mm/min displacement rate) were used to

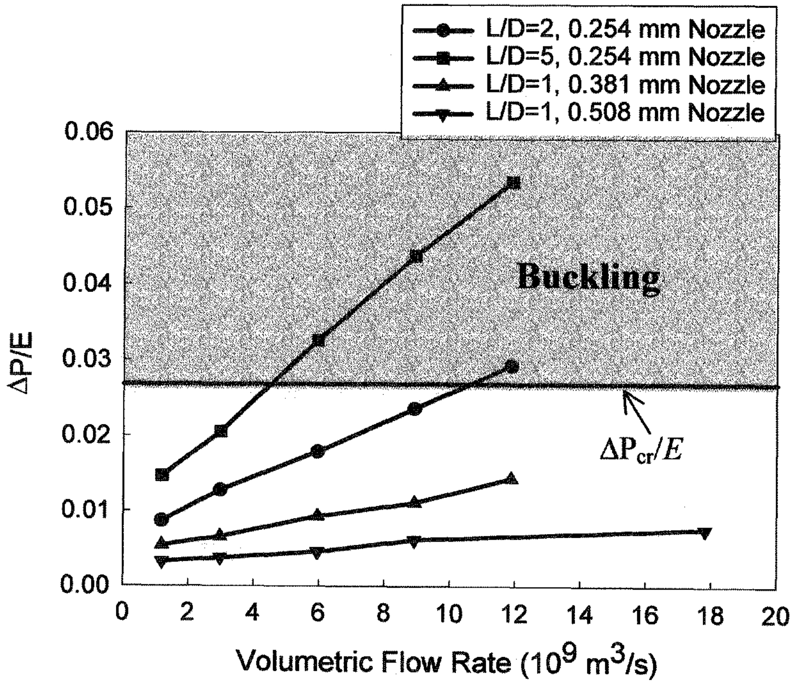

Figure 6: Process map for PZT ECG9 showing the variation of the dimensionless quantity ΔP/E (measured at 140°C) with FDC nozzle diameter, aspect ratio and volumetric flow rate.

develop a process map. A plot of ΔP/E as a function of volumetric flow rates (the process map) is shown in Figure 6. A line corresponding to $\Delta P_{cr}/E$ is also plotted on the process map. According to the theory, if ΔP/E exceeds $\Delta P_{cr}/E$ buckling should occur in the FDC process. This condition is shown in the process map as the shaded region above the $\Delta P_{cr}/E$ line. The process map predicts that with increasing volumetric flow rates, the tendency to buckle in FDC increases, as has been confirmed via independent tests. A series of independent testing have also established that PZT ECG9 does not buckle even at very high volumetric flow rates in FDC for the 0.508 mm diameter nozzle. This is confirmed by the fact that the line corresponding to the 0.508 mm diameter nozzle for PZT ECG9 lies below the critical limit, for even up to very high flow rates. The PZT ECG9 used with a 0.254 mm diameter nozzle in FDC was found to buckle at lower volumetric flow rates than the 0.508 mm diameter nozzle. This is qualitatively confirmed by the observation that in Figure 6 the line corresponding to the 0.254 mm diameter nozzle crosses the critical line at a lower volumetric flow rate. The volumetric flow rate at which PZT ECG9 buckled with a 0.254 mm diameter nozzle is 2-3 x $10^{-9}$ $m^3/s$, which is about 1/5th the predicted value.

In the actual process, there is a temperature gradient in the filament above the liquefier. This will result in an elastic modulus gradient in the filament above the liquefier. There is also a rate dependence of the elastic modulus. The theory used in the development of the current process map does not include these effects and also it does not include possible effects of agglomeration on the elastic modulus or pressure drop. Therefore the process map in its current state gives only a good qualitative indication of the effects of nozzle geometry and volumetric flow rate on the performance of PZT ECG9 in the FDC process.

## Summary and Conclusions

In this work the pressure needed for extrusion through a FDC nozzle for a particular material termed PZT ECG9 was measured experimentally as a function of volumetric flow rate and nozzle geometry. The pressure drop was found to increase with nozzle aspect ratio and volumetric flow rates, as expected. The pressure drop also increases with a decrease in nozzle diameter. The compressive modulus of the PZT ECG9 filament material was determined using a miniature materials tester (Rheometrics, Inc., Piscataway, NJ). A process map has been developed. The process map is based on the quantity $\Delta P/E$ (extrusion pressure/compressive modulus) that predicts the performance of the material in the FDC process as a function of nozzle geometry and volumetric flow rate. In general, it is observed that when $\Delta P/E$ exceeds a critical value, $\Delta P_{cr}/E$ there is an increased tendency to buckle. The predictions of the process map have been confirmed qualitatively via independent tests. It should be noted that $\Delta P_{cr}/E$ depends only on the ratio of the filament length above the liquefier to the radius of the filament. A preliminary fluid flow model for extrusion of PZT ECG9 through FDC nozzle has also been developed using Polyflow™ software. The model predicts the observed trend in pressure drop with flow rate and nozzle geometry with reasonable accuracy. The model also predicts that greater than 90% of pressure drop occurs in the FDC nozzle implying that a change in nozzle geometry will affect the pressure drop and therefore the tendency to buckle in a significant manner.

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