

The Role of Materials Processing Variables in the FDC Process

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The Fused Deposition of Ceramics (FDC) is based on the commercially available Fused Deposition Modeling (FDM™) technique developed by Stratasys Inc. The FDC process is being currently developed to make complex ceramic parts in an automated fashion. Although the current focus is on making Si_3N_4 parts, this technique has been successfully used to make electroceramic (such as PZT) and metallic (such as stainless steel) parts.

As feedstock for the FDC process, filaments loaded with 55 vol% GS-44 Si_3N_4 is being used. For the filament to be used in the FDC process, it must possess a unique combination of physical, rheological and mechanical properties. In this paper, we investigate the role played by some of the process variables on these properties. Our current processing sequence to make filaments is as follows - coating of powders with a surfactant, compounding the ceramic and binder, extrusion into filaments and finally treatment of filaments to achieve requisite properties. The study has resulted in improvements to the quality of the filament which can be used for automated FDC. The effect of moisture, agglomerates and filament aging on FDC will be discussed.

1.0 Introduction

One of the most promising ways to fabricate ceramic components to net or near net shape, is through solid freeform fabrication (SFF). Apart from being able to manufacture intricate shapes, this technique has the added advantages of flexibility of design, and is an inexpensive tool for prototyping. This technique is therefore suitable to make complex shapes and novel structures which are normally not feasible using conventional processing routes. Additionally, SFF has the advantage of being material insensitive and therefore finds a variety of applications ranging from macro scale aerospace components[1] to fine scale piezoelectric composites[2].

Many solid freeform fabrication (SFF) or layered manufacturing (LM) techniques are being actively researched and a few have found commercial success. Fused Deposition Modelling[3], Stereolithography[4], 3D Printing/Inkjet Deposition[5] and Laminated Object Manufacturing(LOM)[6] are a few major examples. Most of these techniques were initially developed to make polymeric or paper parts for design verification and form and fit, although recent research activities are directed towards manufacturing metallic and ceramic parts.

The fused deposition process, commercialized by Stratasys™ Inc. (Eden Prairie, MN) as Fused Deposition Modeling (FDM™) [3] is one of the commercially available SFF techniques. In the FDM process, a thermoplastic polymer filament is unwound from a continuous spool and driven through a liquifier, which is heated to a temperature slightly above the melting point of the polymer. The liquifier extrudes a continuous bead, or road, of material through a nozzle (typically 10 - 25 mils) and deposits it onto a fixtureless platform. The liquifier movement is controlled along the X and Y directions by a computer, based on the build strategy of the object to be manufactured. When deposition of the first layer is completed, the fixtureless platform indexes down, and a second layer is built on top of the first layer. This process continues until the whole part is completed. The fused deposition modeling process, which until now has been used to make polymeric parts for

prototyping and investment casting, has been modified at Rutgers University to make ceramic parts directly through a process known as Fused Deposition of Ceramics (FDC). Towards this, ceramic powders are mixed with an appropriate binder to high volume fractions (typically from 50 to 60 volume%) and extruded into a filament which acts as the feed material for the fabrication process. Post processing involves binder burnout and sintering to obtain final parts.

Several important parameters determine the feasibility of manufacturing ceramic parts by FDC and can be broadly lumped into two categories: hardware/machine dependent and material dependent[7]. In this paper, the material dependent parameters specifically related to the processing of feedstock materials will be discussed. "FDCability" is defined as the ability to manufacture a green ceramic part in a continuously automated fashion by FDC. Although such a definition would suggest simplicity, the actual feedstock material, i.e., the filament, must possess a unique combination of physical and mechanical properties to achieve FDCability. The basic requirements for the filament to be FDCable are: (1) sufficiently low viscosity at high solids loading (in the range of 100 - 1000 Pa.s at the FDC extrusion temperatures), (2) filaments free of agglomerates that stop an automated FDC process through nozzle clogging, (3) sufficient filament stiffness to impart the ability to act as a piston to drive the extrusion, (4) sufficient tensile strength for continuous spooling and unspooling operations, (5) high filament dimensional tolerance of 70 ± 1 mil, (6) freedom from surface defects and kinks, (7) a binder with the ability to bond the layers during FDC building and (8) a binder which undergoes total decomposition during burnout.

Previous studies [8] have identified a binder material called RU9 for filament processing. RU9 is thermoplastic based binder with 4 components: i) a polymer which acts as a base, ii) an elastomer which lends flexibility to the binder, iii) a wax which lowers viscosity and increases the intrinsic stiffness of the binder, and iv) a tackifier which acts primarily to bond the layers. Also it has been demonstrated that the FDC process can fabricate Si_3N_4 , PZT, Al_2O_3 , hydroxy apatite and stainless steel parts. The skeletal framework for the process has been developed[8], however a better understanding has to be achieved to enable controlled processing and fabricating to high quality parts. This paper will focus on the processing of high quality Si_3N_4 filaments and process modifications made towards this goal. This paper will discuss the build up of requisite filament properties through improved particle dispersion, a more homogenous RU9- Si_3N_4 compounded mix (RU955) and the effect of better filament aging.

2.0 Experimental Procedure

2.1 Processing

The process of Si_3N_4 filament fabrication for FDC is schematically illustrated in the flow chart in Figure 1. Allied Signal's GS-44 Si_3N_4 powder is first coated with oleyl alcohol $\{\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_2\text{OH}\}$ as a dispersant in step I. In step II, the coated powders are compounded with the RU9 binder using a torque rheometer to 55 vol.%. The compounded mix is granulated and finally in step III, the granulated material is extruded into filaments using a single screw extruder. Each of the three steps is described below.

2.1.1 Dispersant Coating

The as received GS-44 Si_3N_4 powder was coated with oleyl alcohol by a solution ball milling procedure. 15 g (3 wt.%) of oleyl alcohol, 485 g Si_3N_4 powder and 1000 ml of ethanol as solvent, along with 1000 g of Si_3N_4 milling media are added to rubber lined ball mill. The mixture is ball milled for 14 hours and then sieved through a #120 mesh to separate the media from the mixture. A drying procedure is performed to remove the

solvent by heating a flask containing the mixture to the boiling point of ethanol (78°C). The evaporated solvent was condensed and removed through a distillation apparatus. After drying, the flask is placed in a vacuum oven for 12 hours to ensure a complete removal of the ethanol.

2.1.2 Compounding of Coated Powders with RU9 binder

The coated powder was compounded with the appropriate amount of binder using a Haake Rheocord torque rheometer. The rheometer has mixing bowls with a capacity of 250 cm³ and Z blades to apply the shear. Efficient mixing was achieved through application of shear and heat. RU9 was first melted at 100°C and subsequently, the powder was added in four increments amounting to 40%, 30%, 20% and 10% by weight of the total powder. High torque results with each powder addition due to entrapment of the binder and the presence of agglomerates. The shear provided by the blades breaks down the agglomerates and lowers the torque. After all powder was added, the temperature was reduced to increase the shear to further breakdown agglomerates. When a stable final torque was reached, the compounded mix was removed and granulated for further processing.

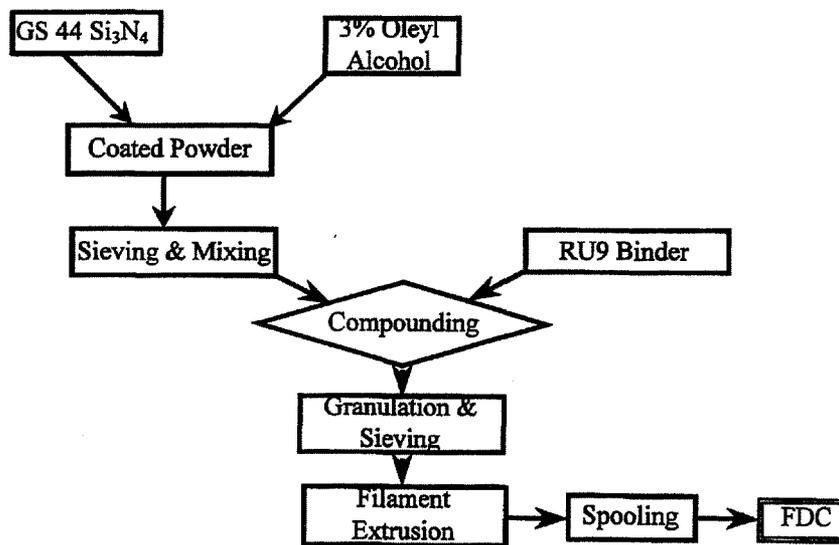


Figure 1. Process flow chart for FDC GS-44 Si₃N₄ filament processing.

2.1.3 Filament Extrusion

Extrusion of the compounded mix into filaments was performed using a single screw extrusion set up shown in Figure 2. The set up has a 70 mils cylindrical die. Granules of RU955 material were fed through a hopper and passed through four independently controlled heating zones. The screw had a uniform flight thereby transporting material through the barrel at a constant rate. The material was compressed by an increased pressure caused by the diameter constriction from barrel to die. Torque and pressure (see Figure 2 for placement of pressure transducers) were continuously monitored during extrusion. The rotational speed of the screw during extrusion was 5 rpm. Filament exiting the die was carried away by a conveyor belt whose speed was matched to the output flow rate. Two important modifications were made to the set up. First the screw design

was changed from simple constant flight to one with a shear tip (at the die end) to increase mixing efficiency. Second, a breaker plate and #120 mesh screen assembly were added for effective filtration of any debris and agglomerates.

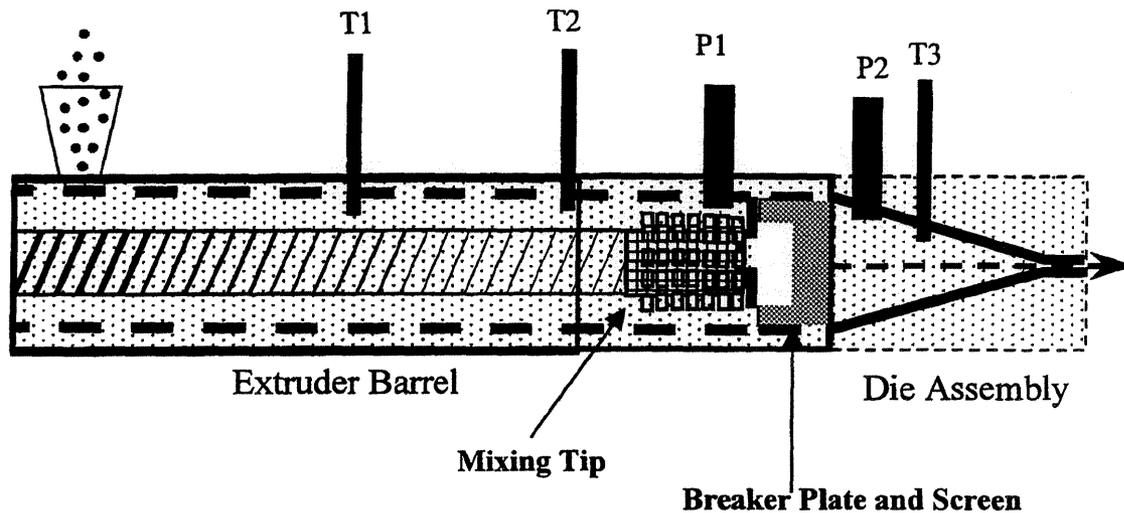


Figure 2. Extrusion set up with a single screw, breaker plate and screen assembly. Temperature and pressure in the melt is monitored at various points along the barrel.

2.2 Process Characterization

2.2.1 Loss on Ignition (LOI) Tests - LOI tests were performed on coated powders and RU955 compounded materials to determine the amount of coating and binder present respectively. LOI was simply performed by measuring weight loss in samples after exposure to temperature in air atmosphere. For coated samples, the temperature was 600°C while that for compounded samples was 700°C.

2.2.2 Particle Size Analysis - Particle size distribution is determined by light scattering method using a Microtrac FRA Particle Size Analyzer. Samples were prepared by mixing 0.5 g of powder and 50 ml of the ethanol and ultrasonicated for 5 minutes before testing.

2.2.3 Viscosity - Viscosity of RU955 materials was measured using an Instron Capillary Rheometer. Capillary nozzles for the measurements had an L/D ratio of 20.3. Measurements were performed at 120°C, 140°C and 185°C. Results from three tests were corrected for barrel drag and averaged, and viscosity vs. shear rate plots were obtained.

2.2.4 Instron QC Test - The Instron capillary rheometer was modified to test the RU955 compounded and filament materials for agglomeration. A 25 mils capillary die was attached and the extrusion was performed at 140°C and 1mm/min constant velocity for a period of 1 hour. The steady state load (P_{ave}) and deviation from steady state (ΔP) were measured. If all other variables remain the same, ΔP is a measure of the degree of agglomeration.

2.2.5 Tensile tests - Tensile tests on RU955 filament were performed to determine tensile strength, strain to failure and elastic modulus of the GS-44 Si_3N_4 filled FDC filament using a Minimat tester. Approximately, 10 cm long filaments were measured for diameter and tested to failure at a stroke rate of 1mm/min. Reported values represent an average of three measurements.

3.0 Results and Discussion

3.1 Powder Processing

The surfactant coating is a crucial step in the filament fabrication process. Earlier studies have shown a dramatic decrease in viscosity due to addition of oleyl alcohol as a surfactant[5]. However Loss on Ignition (LOI) results showed an uneven distribution of oleyl alcohol on the powder within each batch. Table I shows this variability to be $\pm 1.08\%$ indicating that the dispersant coating procedure was not uniform. Indeed this is verified in Figure 3 which shows particle size analysis of the uncoated and coated GS-44 Si_3N_4 powders. The as received powder shows the presence of agglomerates with only 40% of the particles finer than $1\mu\text{m}$, a result of the spray drying procedure used to prepare the GS-44 powder. After coating, this distribution improves only slightly to 50% $< 1\mu\text{m}$ and coarser particles (agglomerates) still persist. As the sieving step before drying should remove agglomerates ($> \#120$ mesh or $125\mu\text{m}$), the solvent drying step is responsible for reformation of soft agglomerates in the 10 -300 micron range. An additional sieving and mixing (S&M) step was therefore introduced to resolve this problem. Six batches of coated powders were sieved using a #60 mesh nylon sieve. The sieved powders were thoroughly mixed on a ball mill for two hours. The improvements made as a result of S&M step can be seen from Table I and Figure 3.

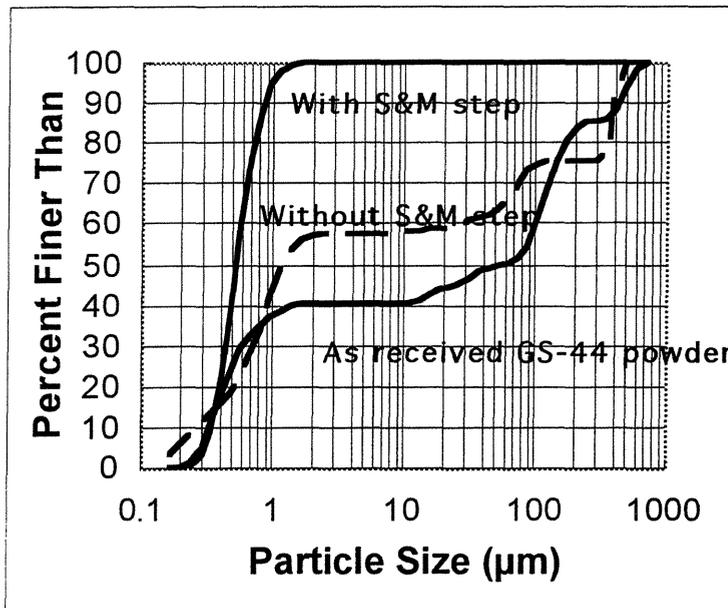


Figure 3. The results of particle size analysis on as received, spray dried, GS-44 Si_3N_4 powder, after coating with oleyl alcohol, and after coating with oleyl alcohol and also adding the sieving and mixing (S&M) step.

Although the effectiveness of oleyl alcohol as a dispersant up to 62 vol% solids loading for injection molding compounds has been demonstrated[9], the adsorption mechanism remains largely unclear. More importantly, the effect of moisture on the adsorption is unknown. As a preliminary experiment, weight change of samples of coated powder exposed to 100% RH was monitored periodically for 21 days. Results showed a 1.1% and 1.7% weight gain after 2 days and 21 days respectively. This moisture uptake may affect the particle dispersion and consequently increase the viscosity in loaded systems. Indeed, such increase in viscosity has been observed and will be discussed in the next section. Moisture acts to disrupt the surfactant coating possibly by displacing oleyl

The data in Table I indicates that the homogeneity and distribution of oleyl alcohol on the powders is improved dramatically due to introduction of the S&M step. Also the distribution of particle size (see Figure 3) shifts to $< 1\mu\text{m}$ with the median coinciding with the average particle size of $0.5\mu\text{m}$. At this stage it is not known whether this additional S&M step has any effect on increasing the surface coverage of Si_3N_4 powders by oleyl alcohol although the particle size analysis results indicate that agglomerates have been eliminated.

alcohol on the powder surface. From a processing standpoint, the coated powders should be free from moisture and are therefore stored under dry conditions to maintain a good dispersion.

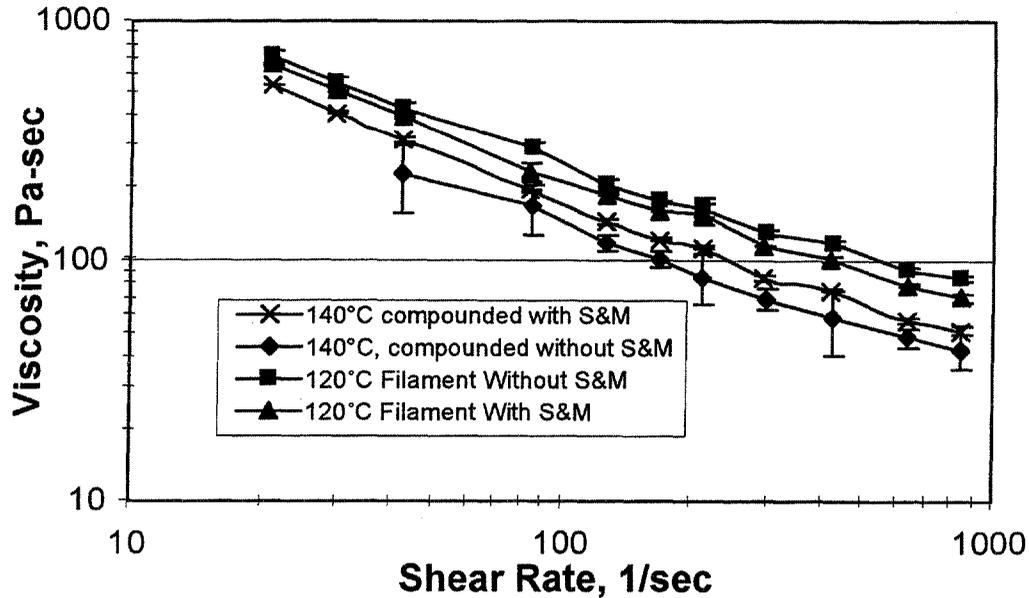


Figure 4. Graph showing the effect of Sieving & Mixing (S&M) on viscosity of compounded (at 140°C) and filament materials (at 120°C).

3.2 RU955 Compounded Materials

RU9 binder and coated GS44 powder were compounded to a 55 vol% solids loading using the procedure described earlier. The addition of the sieving and mixing step had a positive influence on the properties of the compounded materials. Table I shows the load variations during the Instron QC test for the compounded materials with and without the S&M step. Comparison of the results show a 62% decrease in variability of the materials by addition of the S&M step due to agglomerate breakdown.

Table I. Process Characterization Tests Results Showing the Effect of Sieving and Mixing on Coated and Compounded Materials

| | LOI on Coated Powders (% Wt. Loss) | Load Variation ΔP in Instron QC Test (N) |
|------------------|---------------------------------------|---|
| Without S&M step | 2.93 ± 1.08 | 61 |
| With S&M step | 2.86 ± 0.18 | 23 |

Figure 4 shows results from viscosity measurements made on RU955 compounded and filament materials with and without the S&M step. It is seen from Figure 4 that the sieving and mixing step may have a small effect on the viscosity of the compounded and filament materials. The significant result is that the viscosity measurements show a marked decrease in the variability in the viscosity due to S&M as indicated by comparisons of the $\pm \sigma$ standard deviations shown in Figure 4.

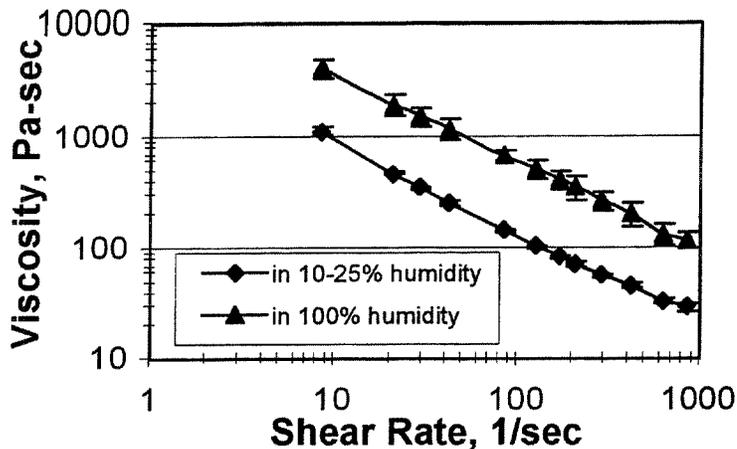


Figure 5. Data showing the increase in viscosity at 175°C of RU955 compounded materials due to exposure to high humidity for 7 days.

Figure 5 shows the effect of moisture on the viscosity of RU955 compounded materials. The viscosity of the compounded material exposed to ~100% RH for a period of 7 days increased by nearly an order of magnitude. This is clearly undesirable for the FDC process and therefore moisture intake into the feedstock materials needs to be carefully controlled. The viscosity of pure RU9 binder (at $T > 100^\circ\text{C}$) is

not significantly affected by humidity, implying that the primary effect of humidity is to increase inter particle interactions.

3.3 Extrusion of Reproducible High Quality Filaments

3.3.1 Homogeneity, Deagglomeration and Dimensional Tolerance of Filaments

The important extrusion variables are temperature profile, shear rate (determined by rpm, temperature profile and die and screw design) and feed rate[10]. The output from a single screw extruder (Q) can be derived as

$$Q = Q_d - Q_p = \alpha N - \beta P/\eta \quad (1)$$

where, Q_d = drag flow transportation of material caused by rotation of the screw, Q_p = pressure flow counteracting the drag flow and arising due to restrictions imposed by the die, N = rotational speed of the screw, α , β = constants depending on screw and die design, P = pressure before die entrance and, η = viscosity of the melt.

Several process improvements were enacted to improve the quality of the GS-44 filled filaments for FDC. A breaker plate and screen assembly was added to the extrusion set up, just upstream of the die entrance. The screen size used was #120 corresponding to 125 μm mesh size opening. The screen therefore acts as an effective filtration agent. Also a new screw design with a mixing tip was introduced. This, in conjunction with the breaker plate assembly, was desired to increase the shear of the material before the die entrance, leading to better mixing efficiency and increased homogeneity in the filament and a further decrease in agglomerate size. Although quantitative estimates of the effect of breaker plate and screen assembly on modulus and viscosity is not available, the combined effect along with the sieving and mixing step is to decrease the agglomeration and variation in viscosity of the filament as seen in Figure 4. An important consequence of these process improvements on FDCability is that nozzle clogging during FDC part building has been eliminated and finer nozzle sizes of 15 mils (compared to 25 mils before) are being utilized, thereby increasing part surface quality and fine feature capability.

Torque and pressure profiles (at the extrusion die entrance) recorded during an extrusion run showed a large fluctuation. The maximum change in pressure was 800 psi (approx. 53%). The existence of variation in pressure leads to variations in the output Q of

the extruder as given by Equation 1. This is significant from the perspective of high filament dimensional tolerance. Deviations from steady flow cause the filament to be extended or compressed at the die exit, which changes the diameter of the filament. Maintaining steady pressure is therefore essential as this will also eliminate kink formation. Although this has not been resolved yet, several factors can minimize the pressure fluctuations. (1) Hardware modifications such as automatic feeding will maintain a constant feed rate and improved screw design should maintain a steady volumetric flow rate of materials through the barrel. (2) By increasing the rotational speed of the screw during extrusion, an increased contribution from drag flow Q_d with respect to pressure flow Q_p will arise, and the overall flow rate fluctuations will decrease. (3) By further increasing homogeneity and particle dispersion, load fluctuations caused by agglomerate break down will be reduced.

3.3.2 Filament Aging to Achieve Necessary Mechanical and Rheological Properties

The freshly extruded GS-44 filled RU955 filament has to be aged prior to FDC. Preliminary studies indicate that the aging phenomenon is a time, temperature, humidity phenomenon involving 2 or more processes. Experiments were conducted to study this aging phenomenon and are detailed elsewhere[11]. In this paper, the effects of vacuum aging treatment are discussed.

Table II. Process Characterization Tests Results Showing the Effect of Vacuum Aging RU955 Filament Materials

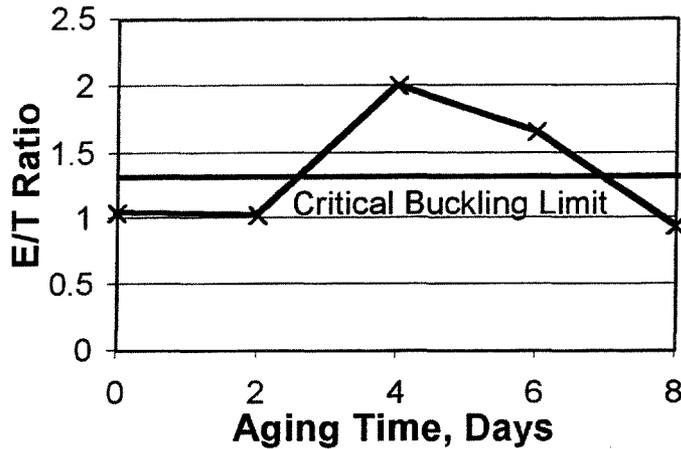
| | Elastic Modulus, E (MPa) | Tensile Strength, σ (MPa) | FDC Motor Current, τ Torque (mA) |
|------------------------|--------------------------|----------------------------------|---------------------------------------|
| Before Aging | 57.4 | 2.65 | 75 |
| After Aging for 4 days | 60.4 | 3.15 | 50 |

Table II shows the properties of the RU955 filament before and after aging. After four days in vacuum, the filament elastic modulus (E) is increased by 5.2 %, the filament tensile strength by 18.7% whereas the FDC motor current (τ) is lowered by 33.3%. The FDC motor current τ is a measure of the resistance experienced by the FDC rollers to push down the filament through the liquifier [12]. If all machine parameters are kept constant, then τ is a measure of the viscosity of the filament. Figure 6 shows the effect of vacuum aging time on the E/ τ ratio. The horizontal line at E/ τ = 1.3 is the critical E/ τ ratio below which filaments buckle during the FDC process[11]. From Figure 6 it can be seen that a 3 day vacuum treatment at 30°C and <0.1”Hg increased the E/ τ to above 1.3. Several factors can contribute to aging and can be related to mechanical properties and/or viscosity of the filament:

(1) Viscosity of “wet RU955 materials” was higher (cf. Figure 4) as seen earlier indicating that H₂O has a significant effect on the filament properties. Vacuum drying may therefore decrease the viscosity by lowering the water content in the filament.

(2) XRD analysis shows that two of the binder components, the wax and the polymer, crystallize over time. This crystallization process would increase the stiffness of the filament thereby increasing FDCability through reduced filament buckling. The kinetics of the crystallization process for the filled binder is seen to be retarded when compared to pure binder and/or its pure constituents. Crystallization in pure components and binder occur within 24 hours at room temperature, but in the case of RU955, there is no evidence of crystallization after a 5 day exposure at room temperature. However, at increased

temperatures of 30°C in the vacuum oven, a crystalline polymer peak in RU955 was observed after 5 days.



At this time, research efforts are currently directed towards understanding the relative significance of various phenomenon on the filament aging. From an FDCability standpoint a suitable filament aging condition has been identified which increases the E/τ ratio to beyond critical buckling limit.

Figure 6. Effect of aging time on E/τ ratio showing that a four to six day vacuum treatment at 30°C increases the filament E/τ ratio to above critical buckling limit (1.3).

4.0 Summary and Conclusions

Several process modifications have contributed towards the build up of requisite filament properties for continuous FDC. The quality and homogeneity of filament fabrication has been improved considerably due to the introduction of sieving and mixing step and the breaker plate and screen assembly. Specifically, the filament is more homogenous with lower $\pm \sigma$ (standard deviations) in viscosity, lower agglomeration and high dimensional tolerance of 70 ± 1 mils. It is now possible to extrude over 1200 ft of continuous spoolable and FDCable filament. The resulting filament, after adequate aging, has been qualified by continuous and automated FDC. The filament was continuously FDCed for 16 hours using a 15 mils nozzle[11]. There was no nozzle clogging (due to agglomeration) or filament buckling (due to either agglomeration or high viscosity/low stiffness).

Acknowledgements

The authors would like to thank the Office of Naval Research (ONR) and the Defense Advanced Research Projects Agency (DARPA) for their financial support under contract # N0014-94-0115. The authors would also like to thank R. Clancy and Dr. P. J. Whalen at AlliedSignal Research and Development for their valuable discussions and contributions. Laboratory assistance from G. Zuo, L. Ordonez, G. Walker, R. Jaico and M. Miller is greatly appreciated.

References.

1. M. K. Agawala, A. Bandyopadhyay, R. van Weeren, A. Safari and S. C. Danforth, *Ceramic Bulletin*, 75 [11], 1996, pp. 60-65.
2. A. Bandyopadhyay, R. K. Panda, V. F. Janas, S. C. Danforth and A. Safari, *J. Am. Cer. Soc.*, 80, [6], 1997 pp. 1366 - 1372.

3. W. Walters, *Solid Freeform Fabrication Proceedings*, 3, Ed. H. L. Marcus, J. J. Beamen, J. W. Barlow, D. L. Bourell and R. H. Crawford, University of Texas, Austin, TX, 1992, pp 301-308.
4. P. F. Jacobs, *Rapid Prototyping & Manufacturing: Fundamentals of Stereolithography*, Chapters 4 & 8, Society of Manufacturing Engineers, Dearborn, MI, July 1992.
5. E. Sachs, M. J. Cima, and J. Cornie, *Solid Freeform Fabrication Proceedings*, 1, Eds. J. J. Beamen, H. L. Marcus, D. L. Bourell, R. H. Crawford, and J. W. Barlow, University of Texas, Austin TX, 1990, pp 24-47.
6. M. Feygin and B. Hsieh, *Solid Freeform Fabrication Proceedings*, 2, Eds. H. L. Marcus, J. J. Beamen, J. W. Barlow, D. L. Bourell, and R. H. Crawford, University of Texas, Austin TX, 1991, pp 123-130.
7. M. K. Agawala, A. Bandyopadhyay, R. van Weeren, N. A. Langrana, A. Safari, S. C. Danforth, V. R. Jamalabad, P. J. Whalen, R. Donaldson and J. Pollinger, *Solid Freeform Fabrication Proceedings*, 7, Ed. D. L. Bourell, J. J. Beamen, H. L. Marcus, R. H. Crawford, and J. W. Barlow, University of Texas, Austin TX, 1996, pp 335-343.
8. M. K. Agawala, R. van Weeren, A. Bandyopadhyay, A. Safari, S. C. Danforth, and W. L. Priedeman, , *Solid Freeform Fabrication Proceedings*, 7, Ed. D. L. Bourell, J. J. Beamen, H. L. Marcus, R. H. Crawford, and J. W. Barlow, University of Texas, Austin TX, 1996, pp 451-458.
9. D. J. Shanefield, *Organic Additives and Ceramic Processing*, Kulwer Academic Publishers, 1st edition, 1995, pp 251-254.
10. G. Challa, *Polymer Chemistry An Introduction*, Ellis Horwood, West Sussex, Great Britain, 1993, pp 172-182.
11. G. Qi, C. Dai, S. Rangarajan, S. Wu, A. Safari and S. C. Danforth, to be published in *Solid Freeform Fabrication Proceedings*, 8, Ed. D. L. Bourell, J. J. Beamen, H. L. Marcus, R. H. Crawford, and J. W. Barlow, University of Texas, Austin TX, 1997.
12. C. Dai, G. Qi, S. Rangarajan, S. Wu, A. Safari, N. Langrana and S. C. Danforth, to be published in *Solid Freeform Fabrication Proceedings*, 8, Ed. D. L. Bourell, J. J. Beamen, H. L. Marcus, R. H. Crawford, and J. W. Barlow, University of Texas, Austin TX, 1997.