Properties of RU955 Si_3N_4 Filament for Fused Deposition of Ceramics

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Abstract

One of the key elements in the FDC process is the development of ceramic loaded fusible filament. The filament is not only material feed stock for deposition, but also serves as a piston to push the fused material through the FDC liquefier. Therefore, the FDC filament has to meet several requirements. It should have enough flexibility to satisfy the automatic feeding requirements, enough stiffness to carry the force for extrusion in the liquefier, and a low viscosity. A series of binders developed at Rutgers University show promising properties and meet these requirements. However, the change of filament properties with time and storage conditions was observed, and they dramatically influenced the FDC process. Systematic experiments were carried out in order to understand filament aging and establish proper storage conditions. The results indicate that moisture in the environment plays an important role in the filament aging. Vacuum treatment at 30°C apparently accelerates the aging process. The mechanisms of filament aging and the method of filament evaluation will be discussed.

I. Introduction

Solid freeform fabrication for ceramics has recently drawn much attention because of the high cost and difficulty of conventional ceramic component fabrication. Several solid freeform fabrication techniques have been developed for ceramic component fabrication, such as three dimensional printing[1], laminated object manufacture (LOM)[2] and fused deposition of ceramic (FDC)[3]. Among these SFF techniques, the FDC process provides a unique ability to form complicated shapes and dense ceramic components. One of the key elements in the FDC process is the development of ceramic loaded fusible filament. Because of the special feeding mechanism in the FDC 3D Modeler, the filament is not only the material feed stock for deposition, but also serves as a piston to push the fused materials through the FDC liquefier. Therefore, the FDC filament has to meet several requirements. The filament should have enough flexibility to satisfy the automatic feeding requirement, sufficient stiffness to carry the force for extrusion in the liquefier, and a low melt viscosity. A series of binders, designated as RU and developed at Rutgers University, show promising properties and meet these requirements. However, the newly fabricated (fresh) filament is sometimes too flexible to drive the extrusion in the liquefier. This filament has to undergo a post-extrusion treatment in order to meet the FDC requirements. Clearly, it is necessary and important to completely understand the change of filament properties with time and storage conditions in order to establish a reliable post-treatment of the filament.

In this work, systematic experiments were designed to investigate the change of filament properties with time and storage conditions. The mechanical tensile testing and viscosity measurements are major characterization methods in this study. A standard storage condition was proposed. Moreover, the mechanisms of filament aging and the method of filament evaluation will be discussion in this paper.

II. Experimental

In order to study the influence of environment, the freshly extruded RU955 filament was divided into four portions. RU955 refers to RU9 binder with 55 volume % GS-44 Si_3N_4 powder (plus 3 weight % oleyl alcohol added as a surfactant). The first portion of the

filament was stored in a glove box, which had almost zero relative humidity (<10 ppm H_2O) at a temperature of 15°C. The second portion of the filament was stored in a dry box, which had a 10% relative humidity and a 25°C. The third portion of the filament was placed in an environment, which was set at 55% relative humidity and 25°C. The last portion was stored in a vacuum oven with 30 mm mercury vacuum and 30°C. Filaments from the four primary conditions and their combinations were characterized by tensile testing and viscosity measurement.

Mechanic tensile testing

The mechanical testing was conducted on a miniature tester (Rheometric, Inc) using a 20N load cell. The cross head speed was set to 1 mm/min. The total filament length was 55mm and the gage length was 33 mm. The diameter of filament was 1.75mm. In order to increase accuracy of measurement, every test condition was repeated at least three times. The stress and strain were calculated from the data of load-displacement and elastic modulus was determined through linear regression of the first 30 data points in the stress-strain curve. In the most cases, the linear relevant factor (R) was greater than 0.996.

Viscosity Measurement

Capillary rheometry (Instron Co.) was chosen to measure the viscosity of the RU955 material because the viscous flow in the capillary was the same flow geometry as in the FDC liquefier. The rheometer had a barrel with a diameter of 9.528 mm and length of 388 mm. The capillary die used for most viscosity measurements had a diameter of 1.422 mm and the aspect ratio (L/D) was 20.29.

FDC trial

FDC trial of filament is the final test for FDC feasibility. The filament was fed into the 3D Modeler using the same conditions for part building. The 3D Modeler monitors the current of the motor that drives the RU955 filament delivery rollers. The value of this parameter, referred to as "torque (τ)", directly reflects the force on the filament during FDC. Filament diameter variation, motor fixture setting and alignment and other non-material parameters all influence the torque value. However, when all those parameters are fixed, the measured motor current directly relates to the force for the filament flow. Therefore, the variation in the motor torque reading can be viewed as resulting from changes in material properties.

III. Results

Mechanical Testing

Figure 1 summarizes the tensile strength of RU955 filament with different storage conditions. In the first two days of aging, the tensile strength of the filaments stored in the vacuum oven and glove box shows an increase with storage time. However, the

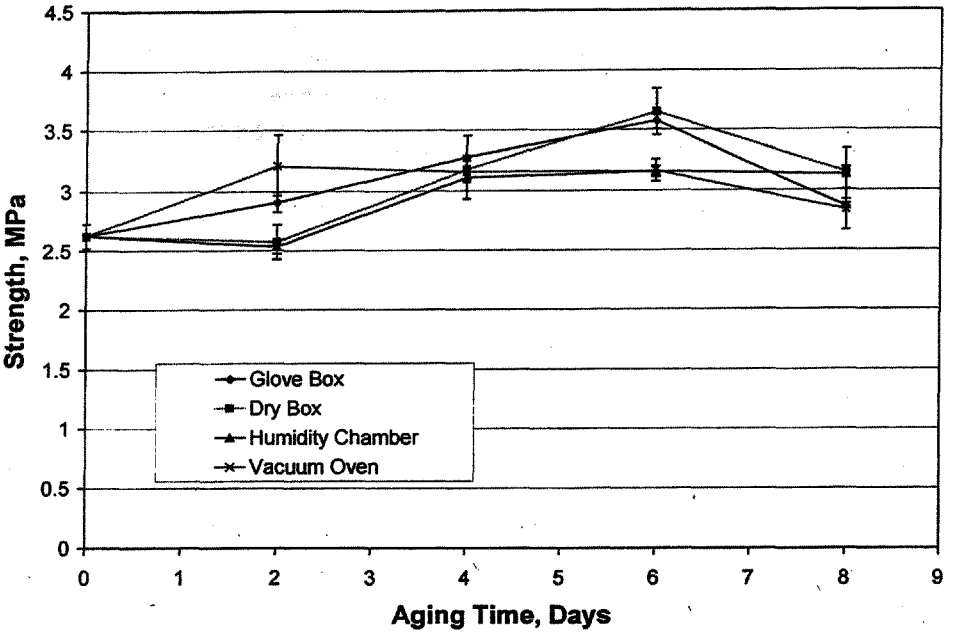

Figure 1. The tensile strength of RU955 filament stored under different conditions.

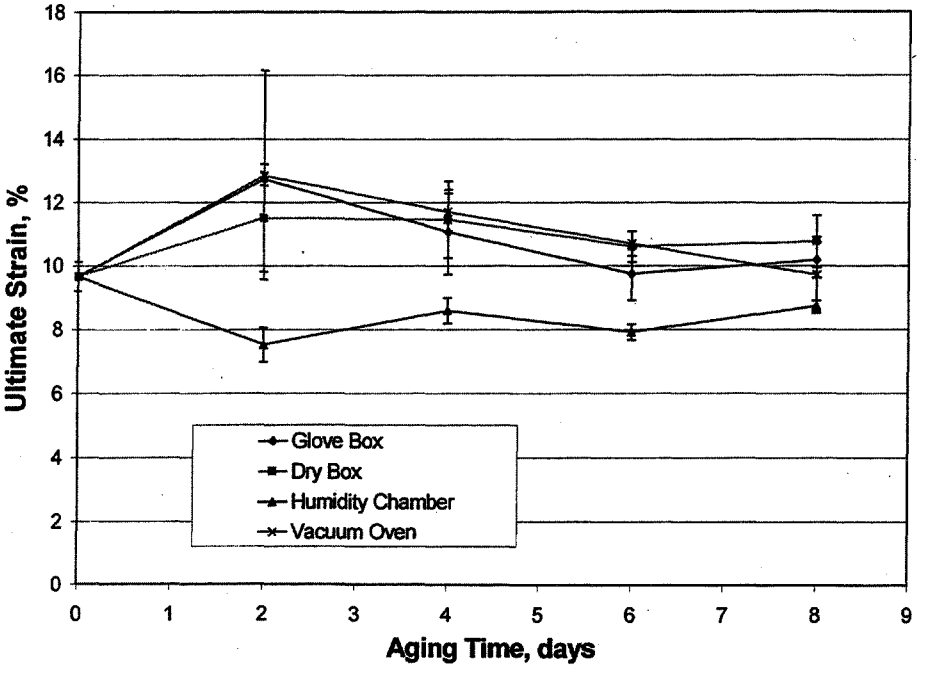

Figure 2. The tensile ultimate strain of RU955 filament stored under different conditions.

filaments in the dry box and humidity chamber showed no increase in the tensile strength for the first two days. The strength of filament stored in vacuum oven stopped increasing after two days of aging. The filaments stored in the other conditions reached the

maximum strength on the sixth day. On the eighth day, the differences among these different storage conditions were not significant. The measured ultimate strain of the RU955 filament showed little change with storage conditions and aging time, except for the storage conditions of the humidity chamber (Figure 2), where the ultimate strain was the lowest for all storage conditions for all aging times. The tensile elastic modulus of the RU955 for all storage conditions increased with storage time (Figure 3). The only exception was the filament stored in the vacuum oven, due to the fact that the elastic modulus of this filament remained almost unchanged with aging time. Generally, the strength and elastic modulus of the filament increased with storage time in the first six days. The ultimate strain of the filament stored in the environment chamber was lower than that for the other storage conditions.

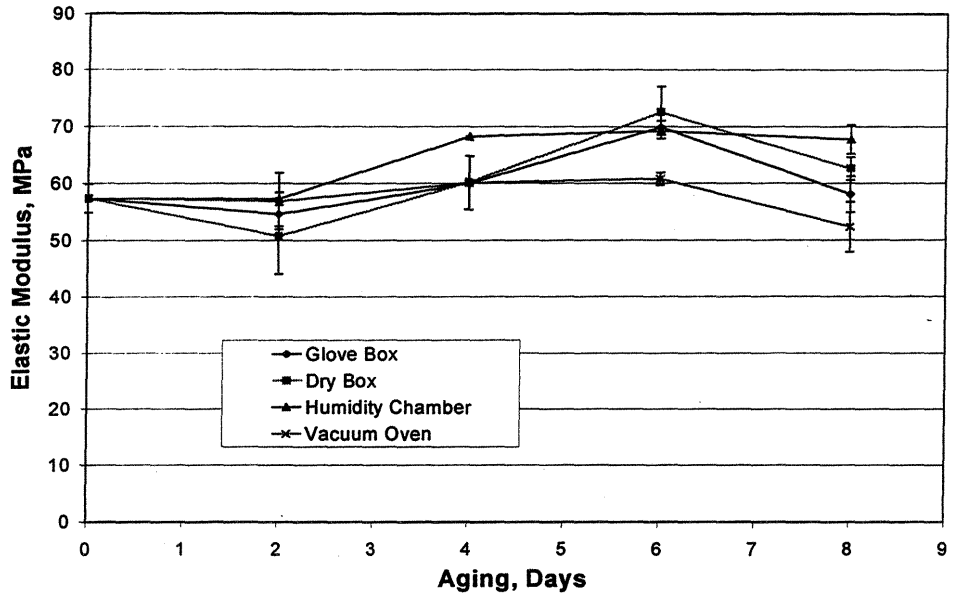

Figure 3. The tensile elastic modulus of RU955 filament stored under different conditions.

Viscosity of RU955 GS-44 filament and RU9 binder

The viscosity of the RU955 filament stored in the dry box (10% R.H.) was measured for three different aging times (Figure 4), 0, 7, and 15 days in the dry box. The plot of viscosity vs. shear rate shows no viscosity difference for storage times up to 15 days. In order to investigate the humidity impact on the viscosity of the RU9 binder, the binder was placed in a dry box with 10% relative humidity (R.H.) or 100% relative humidity environment for 7 days, respectively. The measurement results (Figure 5) show that moisture has a strong influence on the viscosity of the neat binder at 60C, but its influence is reduced as the temperature increases. However, Figure 6 indicates that the effect of high moisture (100% R.H.) on the viscosity of the filament melt persists to 175°C. This suggests that neat binder flow behavior is not sufficient enough to explain the filament melt viscous behavior. Meanwhile, viscosity measurements (Figure 6) also

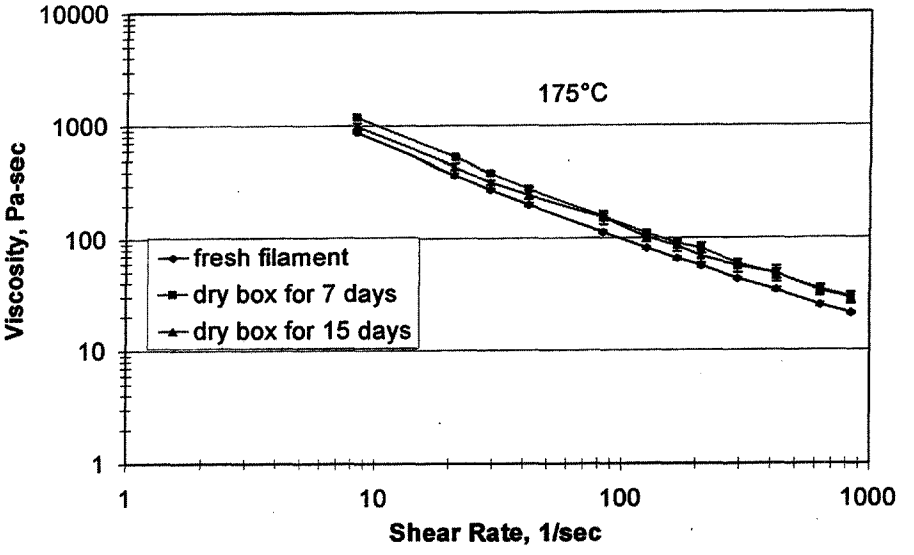

Figure 4. The viscosity vs. shear rate at 175C of RU955 filament stored in dry box for 0, 7, 15 days.

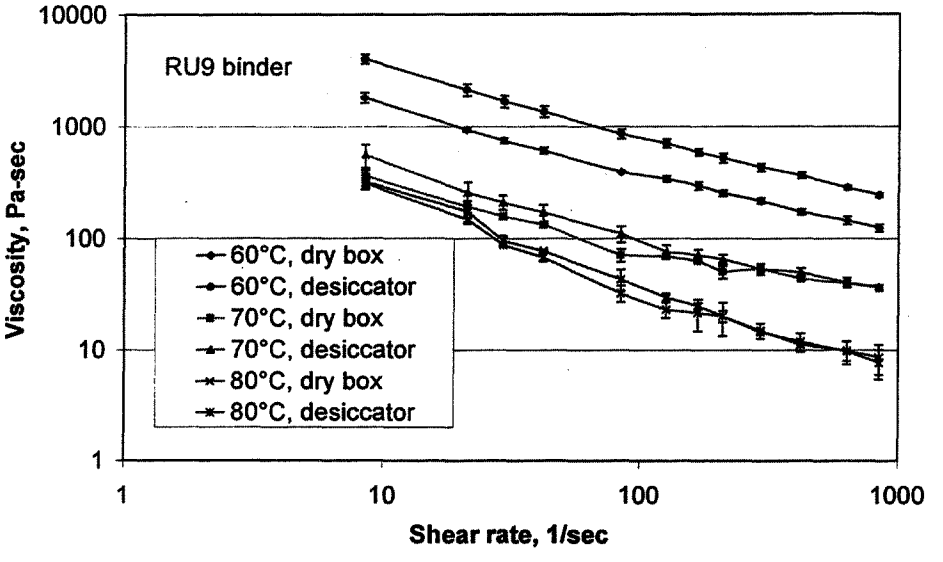

Figure 5. The viscosity vs. shear rate of RU9 binder stored in a dry box with 10% relative humidity and a desiccator with 100% relative humidity conditions, respectively, for 7 days.

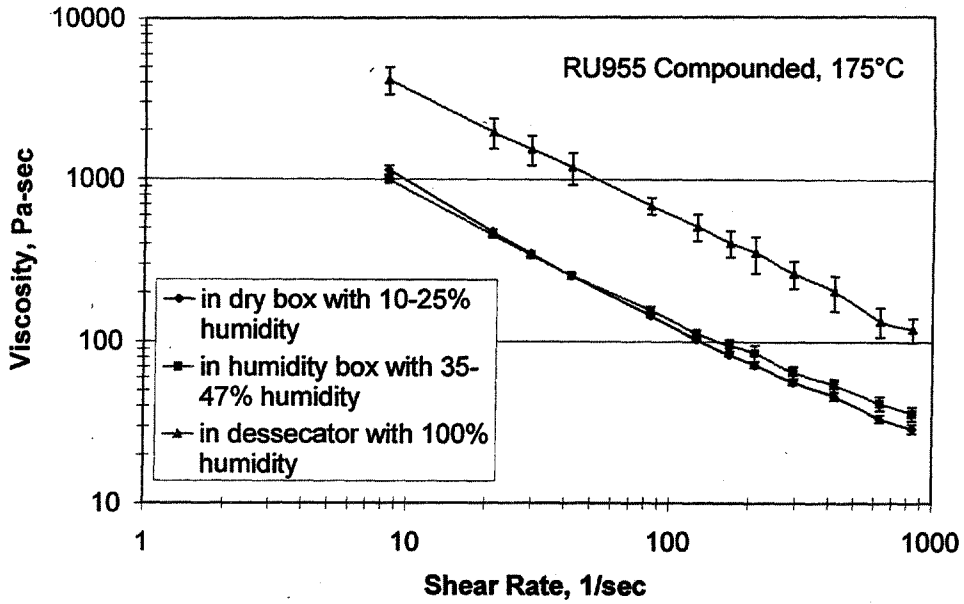

Figure 6. The viscosity vs. shear rate of RU955 compounded material stored in three different humidity conditions for 7 days.

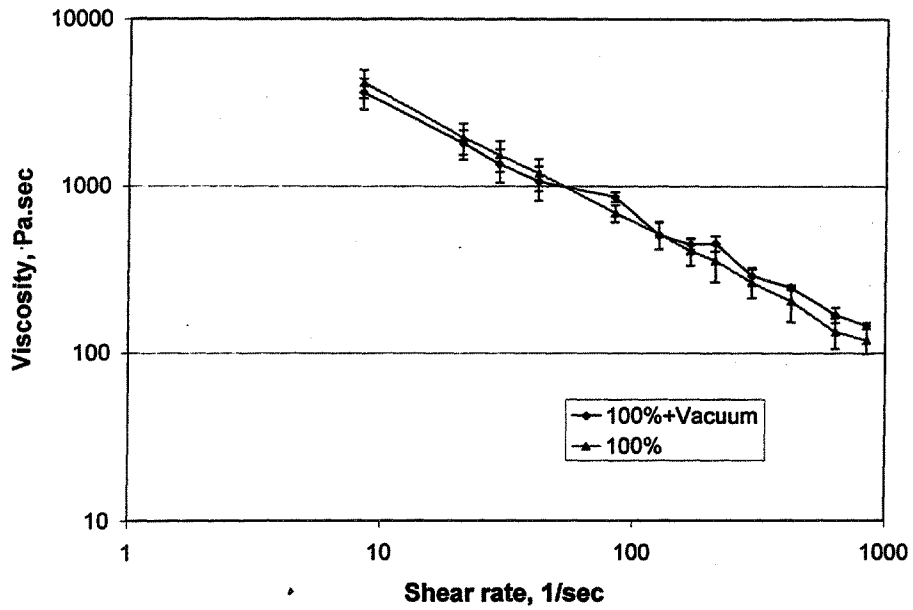

Figure 7. The viscosity vs. shear rate for RU955 compounded materials exposed to 100% relative humidity for 7 days and also followed by a vacuum treatment for 4 days.

show no difference for filament stored in a 10% and a 35% humidity environment. It seems that the filament is stable in low humidity conditions (<40% H.R.). In order to investigate the nature of high humidity influence and to control the humidity, vacuum treatment was applied to those filaments exposed to 100% relative humidity. The results

(Figure 7) show that the four days vacuum treatment has little impact on the viscosity of the RU955 filament exposed to 100% relative humidity for a week. This suggests that long time exposure to high humidity may cause a permanent increase on the viscosity of the filament melt. In summary, storage in high humidity has a strong impact on the RU9 binder and RU955 filament. The viscosity of RU9 binder clearly increases after exposure to 100% relative humidity. This increase, however, diminished as the measured temperature increases. In the case of the filament melt on exposure to a 100% relative humidity, the viscosity remains high up to 175°C. Low relative humidity storage (< 40% R.H.) seems to have little influence on the viscosity of the RU955 filament melt. The measurements also indicate that the filament may be permanently changed by exposure to 100% relative humidity and simple vacuum treatment may not be sufficient to eliminate the negative impact.

The Ratio of Filament Elastic Modulus (E) and drive Motor Current (T)

The FDC trials are performed with a 25 mil nozzle at 36% flow rate with the liquefier temperature at 175°C. In the FDC trials, the main focus is on two issues: filament buckling and the surface quality of the extruded road from the liquefier. Obviously, the smooth surface of the roads can reduce the defects and increase the density of the ceramic parts. Testing shows that the filament stored in with 55% relative humidity gives a very rough surface on the roads due to steam generation at 185°C. Without post-vacuum

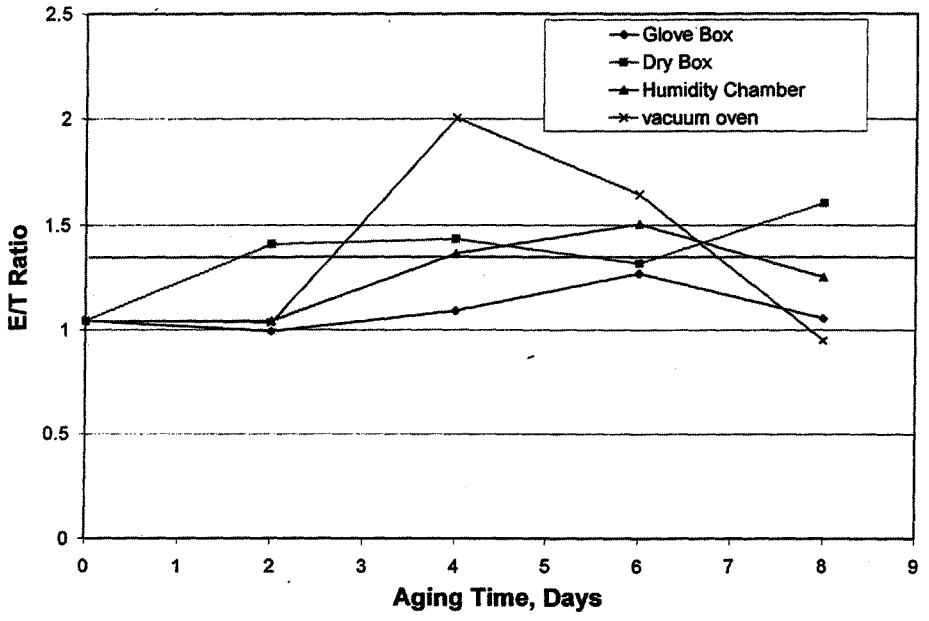

Figure 8. The ratio of elastic modulus (E) vs. motor current (torque τ) against storage time. Filaments, which have the ratio of E/τ of 1.4, show no buckling during FDC trials.

treatment, this filament stored in the humidity chamber cannot be used in FDC. In order to quantify the buckling behavior of the filament, the ratio of elastic modulus (E) over the motor current (torque, τ) is used. Figure 8 shows the E/τ ratio against aging time. When

the ratio is over the value of 1.4, no buckling occurred during FDC trials. Any point below this line resulted in filament buckling during FDC trials. By examination of this plot, one can find that all filament stored in a glove box buckled during FDC trials. Filament stored in humidity chambers showed no buckling after the sixth day. In most cases, no buckling was observed for filament stored in the dry box. However, the ratio is very close to the line. The filament placed in the vacuum oven for four days demonstrates the highest ratio of elastic modulus to motor current (torque). The filament showed no buckling during FDC trials and showed it can handle higher speeds of part building. Generally, like most figures of merit, the ratio of elastic modulus over the motor current (E/τ) is an empirical index. It does, however, give us an effective tool to evaluate the filament and to establish suitable filament storage conditions.

IV. Discussion

Mechanical testing and viscosity measurements both show that RU955 material experienced a change in properties with storage condition and time. The increase in the strength and elastic modulus with storage time results from a physical aging of the polymer binder[4,5]. Although crystallization of the wax occurs after RU9 binder melt and solidification, x-ray diffraction analysis shows that the binder in the GS-44 filled filament stored in the glove box remains in an amorphous state. This delay in crystallization may be due to high percent solids loading in the filament that may block the macromolecule movements needed for crystallization.

Viscosity measurements (Figure 5) indicate that water in the neat binder increases its viscosity. However, the influence becomes less pronounced when the temperature of the measurement increases. In FDC, the liquefier operation temperature is 185°C, much higher than the temperature in the measurement in figure 5. Based on the extrapolation from Figure 5, the influence of water on the neat binder viscosity is not expected to be large at the 185C liquefier temperature. However, Figure 6 shows that the viscosity of RU955 filament stored in the 100% relative humidity condition still remains 3 times higher at 175°C. These results suggest that the moisture on the surface of the Si_3N_4 particle and /or the hydrolysis may contribute to the increase of the viscosity. In contrast to the dramatic change of the viscosity in the high humidity, Fig. 6 also shows no difference in viscosity between 10% and 35% relative humidity. Fig. 4 provides evidence of the insensitivity of the viscosity of the filament melt to low humidity, even at a long aging time. Since the water molecules have to diffuse through the binder to attack the particles, the water concentration in the binder has to reach the water solubility of the binder to initialize the interaction between water and particles. This may be the reason that low humidity has no influence on the viscosity of filament melt. When the binder absorbs enough water, Si_3N_4 hydrolysis may occur. The hydrolyzed surface of particles may enhance the interaction between particles. In addition, the concentration of the dispersing oleyl alcohol at the surface of powder may also be reduced when water molecules occupy the surface sites of the particles. Consequently, the viscosity of the filament is expected to increase. When the hydrolysis does occur, the use of a vacuum treatment may be not sufficient to dissociate the hydrolysis produced. Based on this

reasoning, the viscosity of filament exposed to 100% humidity should remain unchanged followed by four days of vacuum treatment.

Although vacuum treatment seems to have no effect on the viscosity of the filament, especially in the 100% relative humidity condition, the mechanical testing results clearly indicate that vacuum treatment has a positive effect. After vacuum treatment, the filament stored in humidity chamber has an increase of almost 20% in elastic modulus, 34% in ultimate strain, and 28% in ultimate strength. It is interesting to point out that the vacuum treatment shows the positive influence only when the filament is freshly fabricated or stored in the humidity chamber.

V. Summary

FDC filaments stored under all conditions show some degree of aging. Water in the binder and on the surface of silicon nitride dictates the filament mechanical properties and viscosity. The current vacuum treatment accelerates the aging process, improves the mechanical properties, and reduces filament buckling. Based on this study, the suitable standard storage condition has been established. The freshly fabricated filament is stored in a vacuum oven at 30°C for four days and then, the treated filament is stored in the dry box at 30°C at <20% R.H. and is ready to be used in FDC 3D molder. Three consecutive batch filaments followed this standard storage procedure and the reproducible and stable process of FDC was achieved.

Acknowledgments

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