PROCESS-PROPERTY-PERFORMANCE RELATIONSHIP FOR FUSED DEPOSITION OF CERAMICS (FDC) FEEDSTOCK MATERIALS

N. Venkataraman, S. Rangarajan, B. Harper, M.J. Matthewson, A. Safari and S.C. Danforth Department of Ceramic and Materials Engineering, Rutgers University, Piscataway, NJ, 08854-8065.

ABSTRACT

Fused deposition of ceramics (FDC) is an extrusion based layered manufacturing process. It uses a high solids loaded (>50 vol. % ceramic or metal powder) thermoplastic binder in filament form as the feedstock material. The filament acts as both the piston driving the extrusion process and the feedstock material being deposited in the X-Y direction onto a Z-stage platform. The primary mode of failure of the filament during the FDC process is via buckling. Earlier work has shown that the filament compressive modulus and the feedstock viscosity control the buckling behavior of the filament material in FDC. A study was conducted to investigate the effect of particle/polymer interface on the viscosity and compressive modulus of the PZT filled ECG9 system. The relative viscosity of the untreated and the surface treated particle filled systems increases with solids loading. It is found that both of the surface treated materials (stearic acid and titanate coupling agent) exhibit a lower relative viscosity than the untreated material. A rheological model (Krieger-Dougherty model) was used to investigate the possible reasons for the decrease in relative viscosity due to the surface treatment of particles. The investigaton showed that the coupling agent acted as a dispersant (increasing value of ϕ_m) and thereby decreased the viscosity. The stearic acid may act as a dispersant (increasing value of ϕ_m) and as a lubricant (decreasing value of K_F). The compressive modulus of all the different systems studied showed an increase with solids loading. A generalized Nielsen model was used to describe the relative modulus vs. solids loading behavior for all the different systems studied. Also, the measured compressive modulus of the filled system was found to be insensitive to the modifications in the particle surface treatment.

INTRODUCTION

Solid freeform fabrication involves fabrication of parts directly from CAD files through sequential addition of material. The various SFF processes are distinguished according to the manner in which they accomplish the sequential addition of material. SFF processes can be classified into deposition based processes and directed energy based processes. Some examples of deposition based processes are 3-D Printing [1], Fused Deposition of Ceramics [2], and Sanders Prototyping [3]. Some examples of the directed energy processes are Stereolithography [4] and Selective Laser Sintering [5].

In fused deposition of ceramics (FDC), the sequential addition of material is accomplished via extrusion of a high solids loaded thermoplastic material. A highly (> 50 Vol.%) solids loaded thermoplastic material, in filament form, is fed into a liquefier which, melts the thermoplastic material. The filament acts as the piston driving the extrusion of the molten material through a nozzle. The extruded material is deposited onto a platform in the X-Y plane. Following the completion of a layer, the platform indexes down for further deposition of material. The FDC process is currently being used to fabricate functional components of a variety of ceramic and metallic materials such as: Si_3N_4 , lead zirconate titanate (PZT), Al_2O_3 , hydroxyapatite and stainless steel for a variety of structural, electroceramic and bioceramic applications [6-8].

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In FDC, the filaments act as both the piston driving the extrusion process and the molten feedstock material being extruded. During the FDC build process, if the extrusion pressure (ΔP) exceeds a certain critical value, the filaments tend to buckle. A schematic of the buckling of filaments during FDC is shown in Figure 1.



Figure 1: (a) Schematic showing the buckling of a filament during FDC. The schematic also shows the important process and material parameters involved in buckling (ΔP : extrusion pressure, V: volumetric feed rate, T: temperature, ϕ : solids loading, γ : shear rate, η : viscosity, E: compressive stiffness of filament, ε ': strain rate), (b) schematic showing the section of filament between the rollers and liquefier (of radius, R_{f} and length L_{f}), which buckles under a compressive stress, ΔP .

It has been shown that for a given FDC nozzle geometry, orifice size of the nozzle, volumetric flow rate and liquefier and roller design, a material with a higher ratio of compressive modulus/viscosity (E/η) is less likely to buckle during FDC [9]. A cooling jet was used to maintain the filament near room temperature (25°C). As a result the compressive modulus used in the modulus/viscosity ratio was measured at room temperature (25°C). Also the viscosity in the modulus to viscosity ratio was measured at the liquefier temperature of the filament material. It was found that feedstock materials with a ratio (E/η_a) greater than a critical value (3 x 10⁵ to 5 x 10⁵ s⁻¹) do not buckle during FDC, while those with a ratio less than this range buckle [9]. This establishes that one needs to control the mechanical (compressive modulus) and rheological (viscosity) properties of the filament feedstock material to prevent buckling. Also, in order to enable fast development of filaments of new materials, it is necessary to control the critical filament properties (such as modulus and viscosity) and understand the factors affecting them.

In FDC, the filament feedstock material is a particulate filled thermoplastic composite. The mechanical and rheological properties of these composite materials depend on a variety of parameters, such as: processing conditions, solids loading, the nature of the thermoplastic binder, the particle characteristics (size, size distribution, shape, agglomeration level) and the interface chemistry between the particle and the polymer [10, 11].

The nature of the particle/polymer interface can have a significant influence on the mechanical and rheological properties of particle filled polymer systems [10-14]. For a given particle/polymer system, the nature of the interface can be altered through treatment of the

particle surface with surface agents. The different surface agents can be classified based on their effect on the mechanical and rheological properties of the filled systems [10]. The different types of surface agents are: coupling agents, lubricants and dispersants [10]. The coupling agent is a hybrid inorganic/organic molecule that chemically bonds with both the particles and the polymer to form a particle-polymer bridge [10, 14]. A "true" coupling agent usually increases the viscosity and modulus of filled polymers [10, 13-14]. A dispersant usually modifies the particle surface to make it more compatible with the polymer and thereby enables uniform dispersion [10]. The lubricants can either plasticize the polymer or create slippage at the particle/polymer interface (stress discontinuity) [10]. Both the dispersants and lubricants decrease the viscosity and modulus of filled polymers [10, 15].

In this study, the effect of three different particle surface conditions (untreated, stearic acid and a titanate coupling agent) on the compressive modulus and viscosity of the PZT filled ECG9 system was investigated.

EXPERIMENT

Materials

The polymer used in this study is a multi-component thermoplastic termed ECG 9. It consists of: an amorphous polyolefin as the backbone, a semi-crystalline wax that modulates the viscosity and adds stiffness, a hydrocarbon resin that acts as a tackifier and finally a crystalline polyolefin that acts as a plasticizer imparting flexibility. The details of the binder composition and fabrication procedure have been presented elsewhere [16]. The density of ECG9 as determined by Helium pycnometry was 0.91 g/cm³.

Lead zirconate titanate particles were used as the filler particles. The lead zirconate titanate powder was obtained from TRS, Inc., State College, PA. The particles are equiaxed, with a median particle size of 1.2 μ m. The specific surface area of the powder, as determined by single point BET method, was $1.1 \pm 0.2 \text{ m}^2/\text{g}$. The density, as determined using helium pycnometry, was $7.83 \pm 0.03 \text{ g/cm}^3$.

Two different surface agents were used to modify the nature of the particle surface. One of them was stearic acid $(CH_3(CH_2)_{16}COOH)$ which, was obtained from Fisher Scientific, Inc. The stearic acid has a density of 0.94 g/cm³. The other was a titanate coupling agent, KRTTSTM (Isopropyl, triisostearoyl titanate), which was obtained from Kenrich petrochemicals, Bayonne,

NJ, USA. The chemical formula of KRTTS is as follows [14]:

The density of KRTTS[™] according to the supplier's specifications is 0.95 g/cm³.

Filament Fabrication

The details of the FDC filament fabrication procedure for the stearic acid coated PZT-ECG9 system has been presented elsewhere [9]. In brief, the filament fabrication consists of three important steps: powder coating, compounding and screw extrusion (for extruding filaments). The optimum concentration of KRTTSTM in toluene needed for coating the PZT particles was determined (from adsorption isotherm studies) to be 0.3 wt % (powder weight basis). The PZT powder was then coated with the 0.3 wt % KRTTS[™] solution in toluene. The KRTTS[™] coated powder was then compounded with ECG9 and scew extruded into filaments. The compounding and extrusion conditions used were identical to that used for the stearic acid coated PZT-ECG9 system.

FDC Feedstock Property Characterization

The steady state viscosity of the different filaments was determined at 140°C (the FDC liquefier temperature for PZT) using an InstronTM capillary rheometer. The experimental procedure employed for the measurement of viscosity has been detailed elsewhere [9].

The compressive modulus of the different filaments was measured using a miniature materials tester (Rheometrics, Inc., Piscataway, NJ). The procedure used to measure the compressive modulus has also been presented in an earlier work [9].

The viscosity of the unfilled ECG9 binder was measured at 140°C, using a steady state cone and plate arrangement on an ARESTM controlled strain rheometer (Rheometrics, Inc., Piscataway, NJ). The compressive modulus of the ECG9 binder was measured using the miniature materials tester (Rheometrics, Inc., NJ).

RESULTS AND DISCUSSION

Viscosity Results

The apparent viscosity of the different filled systems was measured using a capillary rheometer at 140°C. In the literature concerning filled polymer systems, the viscosity of the filled system is usually represented by the relative viscosity [10, 17]. The relative viscosity is defined as the ratio of the viscosity of the filled polymer to the viscosity of the neat polymer. In most classical studies, the relative viscosity (viscosity of filled system/viscosity of unfilled polymer) of filled suspensions is defined using the viscosity at high shear limits [17]. This is so as to minimize the effect of the particle network structure and to obtain a shear rate insensitive relative viscosity value [10, 17]. It was determined, that in the case of PZT (stearic acid coated) ECG9 systems the measured viscosity reaches a plateau by a shear rate value of 1000 1/s (upper Newtonian limit). Therefore, the relative viscosity values in the present work (for all the different solids loadings and surface treatments) are calculated using the viscosity values at the highest shear rate used (1000 1/s). The neat binder was found to be shear thinning (with a power law index of n= and has a viscosity of 7.01 \pm 0.2 Pa.s (at 1000 1/s). The relative viscosity of the untreated, stearic acid treated and KRTTS™ treated PZT filled ECG9 systems is plotted as a function of solids loading in Figure 2. As expected, the relative viscosity of all the different filled systems increases with the solids loading. The relative viscosity of the untreated PZT filled ECG9 system is higher than the surface treated cases. The stearic acid coated PZT filled ECG9 system exhibits the lowest relative viscosity values.

The surface treatment of PZT with KRTTS[™] and stearic acid both lead to a reduction in the relative viscosity of the filled system. It was mentioned in the introduction that dispersants and lubricants tend to decrease the viscosity of filled systems [10]. Also, if a coupling agent (such as KRTTS[™]) reduces the viscosity of the system, it may be functioning as a wetting agent or as a lubricant instead of as a coupling agent [10, 18]. It is important from a scientific point of view to try to understand the possible mechanism by which the surface agents (in this study) reduce the viscosity of the filled system. It was decided to try to see whether a model such as the Krieger-Dougherty model could help understand the mechanism of viscosity reduction. The Krieger-Dougherty model is one of the popular models used to describe the behavior of the relative viscosity of filled suspensions. The model is as follows [19, 20]:

$$\eta_r = \left(1 - \phi / \phi_m\right)^{-K_E * \phi_m} \tag{2}$$

where, η_r , is the relative viscosity, ϕ is the solids loading, ϕ_m is an empirical constant known as



Figure 2: The relative viscosity of untreated PZT (\blacktriangle), KRTTSTM coated PZT (\blacksquare) and stearic acid coated PZT (\bullet) filled ECG9 systems as a function of solids loading measured at 140°C. The solid lines represent the fit to the Krieger-Dougherty models [19, 20].

the maximum packing factor and K_E is an empirical constant called the generalized Einstein coefficient. The value of ϕ_m indicates the packing efficiency of the particles in the suspension [11, 17]. A higher value of ϕ_m indicates a better packing efficiency and thereby lower relative viscosity [11, 17]. In general, the value of ϕ_m will decrease with increasing amount of agglomeration [11, 17]. The value of ϕ_m can also be affected by the particle size and size distribution [11, 17]. For most particle (spheres) filled suspensions the value of K_E is ≈ 2.5 [20, 21]. The typical values for ϕ_m are between 0.52 and 0.74 [19, 20].

The solid lines in Figure 2 represent the best fit curves to the Krieger-Dougherty model. The best fit parameters ($\mathbb{R}^2=0.98$) for each of the different surface treatment conditions are presented in Table I. It can be seen from Table I that the treatment of PZT particles with KRTTSTM leads to an increase in the value of ϕ_m from its value for the untreated case. An increase in the value of ϕ_m implies that the inter-particle interactions have decreased, and therefore the tendency to agglomerate has also decreased [11, 17]. One can conclude from the values of ϕ_m for the untreated and KRTTSTM treated cases, that as expected, the untreated particles tend to agglomerate more than the KRTTSTM treated particles. The KRTTSTM is decreasing the level of attractive inter-particle interactions and thereby reducing the tendency to agglomerate, *i.e.* it acts as a dispersant. One can also see from Table I that the value of K_E is the same for the case of the untreated and KRTTSTM treated particles filled ECG9 systems (2.5). The value of K_E for most filled thermoplastics is usually 2.5. The value of K_E can increase if the particles are non-equiaxed and decrease to a value of 1.0 in case of complete slippage at the particle/polymer interface [11, 17].

Surface Condition	K_E (Generalized Einstein Coefficient)	φ _m (Maximum Packing Fraction)
Untreated PZT	2.50 ± 0.01	0.66 ± 0.01
Stearic Acid Coated PZT	1.49 ± 0.04	0.73 ± 0.01
KRTTS [™] Coated PZT	2.50 ± 0.01	0.73 ± 0.01

Table I. The Best Fit Values ($R^2=0.98$) for the Krieger-Dougherty Model (Relative Viscosity) Parameters Corresponding to the Different Surface Treated PZT Filled ECG9 Systems [19, 20].

The PZT particles used in this study are equiaxed, therefore a value of K_E greater than 2.5 is not expected. As the best fit value of K_E , for the untreated and KRTTSTM treated case is 2.5, one can expect that there is no slippage at the particle/polymer interface.

In the case of the stearic acid treated PZT filled ECG9, the value of ϕ_m is the same as that of the KRTTSTM treated case. This suggests that stearic acid enables more uniform dispersion of the PZT particles in the polymer as compared to the untreated case. Also, the value of K_E is lower than for the untreated and KRTTSTM treated cases. The lower value of K_E (1.49 as opposed to 2.5) suggests that the stearic acid may be introducing some slippage at the particle/polymer interface as compared to the untreated and KRTTSTM treated cases. The exact molecular mechanism by which the stearic acid may cause slippage at the particle/polymer interface is unclear. One possible hypothesis, is that the stearic acid may be plasticizing the ECG9 polymer locally at the particle/polymer interface. This plasticized layer at the particle/polymer interface will have lower viscosity than the bulk ECG9. The presence of this lower viscosity layer at the particle/polymer interface can then manifest as slippage (*i.e.* stress discontinuity). Therefore, the stearic acid may be acting as a dispersant (wetting agent) and also as a lubricant.

Modulus Results

The elastic compressive modulus of the various filled and unfilled systems was measured using the miniature materials tester (at a displacement rate of 1mm/min). The modulus of the



Figure 3 The relative modulus of the various surface treated and untreated PZT filled ECG9 systems vs. solids loading. The solid line correpsonds to the fit to the genralized Nielsen model [11]. The modulus was measured at 1 mm/min displacement rate and at 25°C.

unfilled ECG9 as measured using the miniature materials tester (at 1mm/min) is 7.35 ± 0.21 at 25°C. The relative modulus of the untreated, stearic acid coated and KRTTSTM coated powders is plotted as a function of solids loading in Figure 3.

One can see from Figure 3 that the relative modulus of all the systems increase with solids loading as expected. Also, one can see from the figure that there is no significant effect of surface treatment (or lack of it) on the relative compressive modulus of the filled system. The individual data points corresponding to the different surface treatment conditions were fit to the generalized Nielsen model. The generalized Nielsen model is used to describe the behavior of the relative modulus (compressive, shear or tensile) of filled polymer systems as a function of solids loading [11]. The model is as follows:

$$M/M_0 = \frac{1+AB\phi}{1-B\psi\phi}$$
(3)

where, M and M_0 are the modulus of the filled and unfilled systems representively. The factor A is related to the Einstein coefficient (A=K_E-1), B usually has a value of 1 for rigid filler particles and ψ is a function of the maximum packing factor ϕ_m [11].

There was no statistically significant difference between the best fit parameters ($\mathbb{R}^2 = 0.97$) for the various surface treatment conditions ($K_E = 2.5 \pm 0.01$, $\phi_m = 0.67 \pm 0.01$). Therefore, the current study shows that the measured compressive modulus (using the current technique) is not sensitive to the changes in the state of dispersion (no change in the value of ϕ_m) or the particle/polymer interface condition (no change in the value of K_E) for the stearic acid and KRTTSTM.

In order to decrease the chances of a filament buckling in FDC, a high value of the ratio of the compressive modulus to apparent viscosity is desirable. The experiments conducted in this study suggest that the apparent viscosity of the filaments can be modified (decreased) through the use of surface agents. The compressive modulus however, is not sensitive to changes in the dispersion state or interface conditions for stearic acid and KRTTSTM. Therefore, the compressive modulus is not as readily modifiable as the apparent viscosity. As a result, it seems that decreasing the apparent viscosity of the filled system (filament) may be the only way to increase the modulus/viscosity ratio of a given filament. However, the use of a different coupling agent (with a different molecular structure and chemistry than KRTTSTM) might act as a "true" coupling agent and raise the modulus of the filled system (filament).

SUMMARY AND CONCLUSIONS

A study was conducted to investigate the effect of particle/polymer interface on the relative viscosity and relative modulus of the PZT filled ECG9 system. The relative viscosity of the untreated and the surface treated particle filled systems increases with solids loading. It is found that both the surface treated cases (stearic acid and titanate coupling agent) exhibit a lower relative viscosity than the untreated cases. A rheological model (Krieger-Dougherty model) was used to investigate the possible reasons for the decrease in relative viscosity due to the surface treatment of particles. The investigaton showed that the coupling agent acted as a dispersant (increasing value of ϕ_m) and as a lubricant (decreasing value of K_E). The compressive modulus of all the different systems studied showed an increase with solids loading. The measured compressive modulus of the filled system was found to be insensitive to the changes in the state of dispersion (no change in the value of ϕ_m) or the particle/polymer interface condition (no change in the value of K_E). As a result, it seems that decreasing the apparent viscosity of the

filled system (filament) may be the only way to increase the modulus/viscosity ratio of a given filament, and thereby decrease the chances of filament buckling during FDC.

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