Development of a Binder Formulation for Fused Deposition of Ceramics

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Abstract

A new binder formulation has been developed for Fused Deposition of Ceramics (FDC) which consists of commercially-available polymer constituents. This formulation was used in conjunction with lead zirconate titanate (PZT) and hydroxyapatite (HAp) powders. Adsorption studies were performed to test the effectiveness of several carboxylic acids and alcohols on the dispersion of these powders in the binder system. In both cases, it was found that stearic acid was most effective as a dispersant for the ceramic powder / thermoplastic system. After a suitable dispersant was chosen, ceramic powders were compounded with the binder formulation to yield 55 vol.% ceramic-loaded materials. The resultant compound was used to make filament suitable for use in a modified Stratasys^{TM} 3D-Modeler. The filament was well suited for FDC usage, and the parts made using FDC contained no detectable filament-related defects.

Introduction

Among the various techniques that have been used for the fabrication of functional quality ceramic components, Fused Deposition of Ceramics (FDC) has shown great promise.[1] In this process, spooled filament with a diameter of 1.75 mm is fed into a heated liquefier via a set of computer-driven counter-rotating rollers. The liquefier motion is computer controlled in the X-Y plane, and material is extruded through a circular nozzle attached to the end of the liquefier. A foam platform moves in the Z direction, allowing material to be deposited layer by layer. The filament, comprised of ceramic particles in appropriate thermoplastic binders, is used for the fabrication of green ceramic components. When ceramic (or metal) powder-loaded filament is fed into the liquefier, the binder softens and melts inside the liquefier, and acts as a carrier for the particles. The cold filament at the top of the liquefier acts as a piston, creating a positive pressure to extrude the molten material out of the liquefier through the nozzle. Components are built layer by layer on the platform, and the bonding between neighboring "roads" or beads of material takes place due the “adhesiveness” of the molten binders, combined with the re-melting of previously deposited layers.

The motivation for this work was to develop a family of thermoplastic binders suitable for the Fused Deposition (FD) of various ceramics and metals using commercially available thermoplastic polymer constituents. Since the compositions of the various binder components are known, specific binder properties can be tailored based on the requirements of the filler phase and the FDC process. Therefore, a detailed understanding of the various polymer ingredients, and their role in the final formulation can be developed. Since the new binder will be a multi-component system, the compatibility of each constituent is critical. In addition to compatibility, it is important that similar processing exists for each component. This includes factors such as melting temperature, decomposition temperature, and decomposition atmosphere. Finally, the binder must exhibit high strength, high stiffness, low residue after burnout, and a relatively low melt viscosity, particularly when mixed with high solids loadings of ceramic or metal powders (50-65 vol.%).[1]

The quality of the feed filament is one of the most important parameters for successful FDC. The critical properties for high quality filament include viscosity, strength, flexibility, and modulus. In addition to forming the part once deposited, the filament also acts as a piston at the entrance of the liquefier, forcing molten material out of the nozzle. If the filament exhibits a low stiffness or high viscosity, buckling will occur just before the entrance to the liquefier, thus making FDC impossible. Filaments with high melt viscosity require either a very high stiffness, or a relatively high operating temperature to lower the melt viscosity to a useable level. Finally, the temperature dependence of viscosity is also important. A high dependence of viscosity on temperature allows the filament to maintain consistent mechanical properties up to its entry into the liquefier. This combination of properties makes the design of a working filament a challenge, particularly for highly loaded systems.

Although a good binder alone is important, it is not the only requirement for high solids loading of ceramic powder. The degree of dispersion of the powder in the molten thermoplastic binder has a dramatic effect on the rheological properties of resultant FDC filament. In general, the better the powder is dispersed in the polymer medium, the lower the resultant viscosity; and by extension, the higher the usable solids loading for a given viscosity range.

Studies have been made on dispersing Si_3N_4 in thermoplastic binders for FDC applications[2]. In this case, oleyl alcohol is coated on the powder surface by ball milling in ethanol to provide dispersion for this system. Oleyl alcohol is a C_{18} hydrocarbon with an OH functional group. In this case, the OH functional group probably hydrogen bonds

Table 1: Binder Formulations

Formulation	Major Binder	Minor Binder	Tackifier	Wax	Plasticizer
ECG 1	100	-----	20	15	-----
ECG 2	100	-----	20	15	5
ECG 3	100	15	20	15	5
ECG 4	70	30	20	15	5
ECG 5	85	15	20	15	5
ECG 6	50	50	20	15	5
ECG 7	100	-----	20	15	5
ECG 8	100	-----	20	15	5
ECG 9	100	-----	20	15	5
ECG 10	100	-----	35	15	5

to the powder surface, thus allowing the remainder of the chain to provide steric hindrance to incoming particles. Since the average size, shape, and surface chemistry varies with the type of powder to be used, there is no guarantee that a surfactant suitable for Si_3N_4 would be suitable in another powder system. Furthermore, the thermoplastic binder formulation used in this work is different from that of the previous Si_3N_4 work.

The adsorption behavior of various hydrocarbons onto powder surfaces have been studied for many years[3,4]. Based on this earlier work, several trends have been established. In general, polar molecules tend to adsorb onto polar powder surfaces, while non-polar molecules tend to adsorb onto non-polar particle surfaces[5]. Oleyl alcohol, like other long-chain alcohols or fatty acids, contains a polar functional group at one end of the chain, and a non-polar hydrocarbon group at the other end. Therefore, these molecules can adsorb onto both non-polar and polar surfaces. A second trend can be seen in the rate at which molecules adsorb into surfaces. Adsorption from solution is strongly dependent on both the concentration of the adsorbing species, and the chemical nature of the medium in which the adsorption takes place. There are situations where the species of interest remains in solution rather than adsorbing onto the powder surface. This occurs when the species is more compatible with the solvent than the powder surface. The concentration of the adsorbing species in solution also plays a critical role.

Since the powders included in this study are oxide ceramics, they have a polar surface. Therefore, we can assume that the polar functional group of the surfactant will adsorb onto the powder surface. In the case of the surfactants tested (oleic acid, oleyl alcohol, stearic acid, and stearyl alcohol), this would be the COOH group of the acids, or the OH group of the alcohols.

The new thermoplastic binder formulation developed for the FDC process is comprised entirely of commercially available polymers, and exhibits properties adequate for usage in combination with lead zirconate titanate (PZT) and hydroxy apatite (HAp) ceramic powder filler. In this paper, the development of high-quality ceramic-loaded feedstock will be outlined. Rheological data from the raw binder will be presented, in addition to thermal and rheological data from a loaded system. Finally, photographs of functional components made using this binder formulation will be presented.

Experimental

Formulations were batched and prepared using a parts-by-weight measuring system. Table 1 lists the various formulations tested within this system. Each formulation consists of at least one poly-olefin base binder, a hydrocarbon resin tackifier, a polyethylene wax, and a polybutylene plasticizer. The various binders, tackifiers, or waxes tested within this system vary primarily in molecular weight. For convenience, the iterations are labeled ECG-1 through ECG-9. The polymers were mixed at 150-175 ^{0}C using a high shear mixer, then de-aired until the entrapped air was removed. Viscosity measurements of the binder formulations were made at 190 ^{0}C using a Brookfield RVDV II+ rheometer with a number 27 spindle in conjunction with a Thermocel adapter.

The adsorption of four different surfactants was measured for the PZT and HAp systems. Oleyl alcohol, stearyl alcohol, oleic acid, and stearic acid were tested. Fifty g/l solutions of each surfactant were made by dissolving the appropriate amount of surfactant

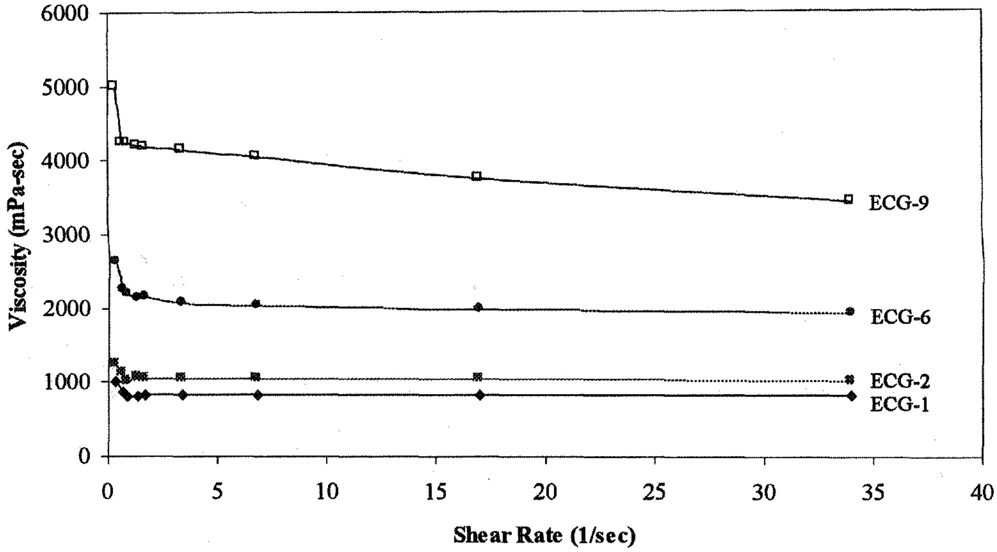

Figure 1: Viscosity vs. shear rate for selected ECG-series binder formulations

in toluene, and TGA analysis was performed to determine the exact concentration of each solution. In the case of PZT, 50 ml of the resultant solution was mixed with 50.0 g of ceramic powder (surface area = 2.58 m^2/g) for 4 hours. For HAp, 50 ml of the solution was mixed with 10.0 g of ceramic powder (surface area = 3.40 m^2/g). After mixing, the slurry was centrifuged for 90 min at 1000 rpm to extract the supernatent. TGA analysis was then performed on the supernatents to determine the concentration of surfactant still in solution after milling and centrifugation. Of the four surfactants, the one with the least surfactant remaining in the supernatent was chosen for further studies.

Once the suitable surfactant was chosen, the coated powder was mixed with the optimized binder, and rheological measurements were made. For this portion of the work, 300.0 g of PZT powder was milled for 4 hours with 300.0 ml of the surfactant solution. The slurry was then vacuum filtered to remove the solvent and any excess surfactant. After drying, 245.42 g of the coated powder was mixed with 19.27 g of binder using a Haake System 9000 torque rheometer in conjunction with a 70 cc mixing bowl.. This corresponds to 55 vol% solids loading. The powder was added in 4 steps spaced 10 minutes apart, with the initial mixing temperature set at 160 °C. High shear mixing was performed at 140 °C for 20 minutes. Hydroxyapatite / thermoplastic compound was produced in a similar fashion. The viscosity of the PZT / thermoplastic compound was measured using a capillary rheometer. The capillary measured 1.016 mm in inside diameter, and 20.32 mm in length. Shear rates of 2.3 to 230 sec^{-1} were measured. Measurements were made at 160, 175, and 190 ^{0}C.

The compounded mixtures were test-extruded at 1 mm / minute and a temperature range of 80 to 95 ^{0}C into filament 1.75 mm in diameter, cut to lengths of approximately 50 cm. In the case of PZT, the purpose was to test the ability to FDC the compounded mixture. For HAp, this filament would be used as the actual feedstock for part production. Once the filament parameters were optimized, continuous lengths of PZT filament were produced using the Haake System 9000 torque rheometer in conjunction with a single screw extruder. Approximately 100 meters of continuous filament was extruded and spooled. This filament was used as feedstock to create green ceramic parts with an upgraded Stratasys™ 3-D Modeler™ machine.

Fused deposition was performed with both materials using a liquefier temperature setpoint of 140-146 °C, and a build envelope temperature of 25-35 °C. Parts were made using both 250 and 300 μm nozzles, depending on part specifications. Build time was 1 to 4 hours, depending on the design. Compositions with 55 vol.% ceramic were used to make the trial parts.

Binder burnout (BBO) was performed in both types of samples using a ramp of 10.0 °C/hr to 550 °C, with a 4.0 hr soak at 550 °C. In each case, BBO was performed in air. After BBO, the materials were sintered at 1285 °C for PZT, and 1100 °C for HAp.

Results and Discussion

Figure 1 shows the viscosity vs. shear rate plots for the binder formulations tested. In each case, the viscosity of the formulations are relatively low, with ECG-9 showing a viscosity approximately 4 times that of ECG-1. Based on viscosity alone, one may conclude that ECG-1 would make the best binder for FDC applications. Instead, ECG-9 was chosen as the binder to be used in future FDC work, primarily due to other factors such as strength and flexibility when mixed in a loaded-system. This point was covered in greater detail in an earlier publication.[6] Figure 2 shows the viscosity vs. shear rate for 55 vol.% PZT / ECG-6 compounded batch. As expected, the material is pseudoplastic, with the viscosity of the mix remaining below 1000 Pa-s throughout the range of shear rates tested.

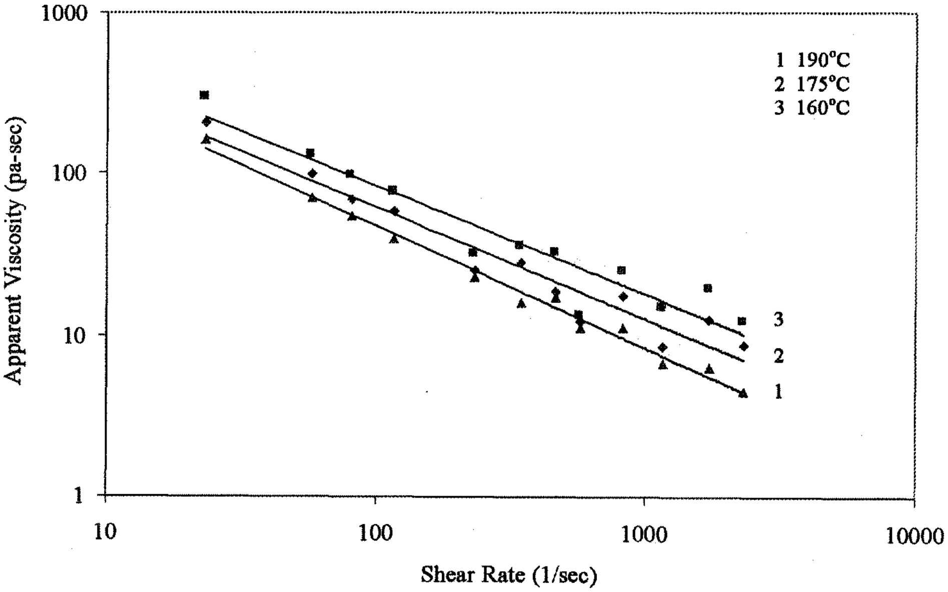

Figure 2: Viscosity vs. shear rate for 55 vol. % PZT / ECG-6 compound

Figure 3 shows the thermogravimetric analysis of the supernatant solutions after being mixed with PZT powder for 4 hours. Clearly, stearic acid adsorbed the most onto the powder surface after being mixed with the PZT powder. A total of 8.1 mg/m^2 of stearic acid adsorbed onto the PZT powder surface from the solution. The data for HAp powder shows similar trends, with stearic acid clearly being the best surfactant of the 4 tested. A total of 26.38 mg/m^2 adsorbed onto the HAp powder surface.

Figure 4 is a thermogravimetric analysis plot of a 55 vol.% PZT / thermoplastic compounded mixture. The solid line denotes the weight % lost as a function of temperature, while the dashed line denotes the slope (ie. rate) of decomposition as a function of temperature. As shown in the plot, the decomposition profile shows a gradual loss of binder with increasing temperature. Of greatest importance is the existence of two rapid increases in rate of decomposition profile. The smaller first spike, occuring at approximately 360 ^{0}C causes open channels to form in the otherwise dense green body. These open channels facilitate removal of the remainder of the binder at approximately 390 ^{0}C, without blistering or cracking which could present an obstacle to the successful BBO of complex ceramic bodies.

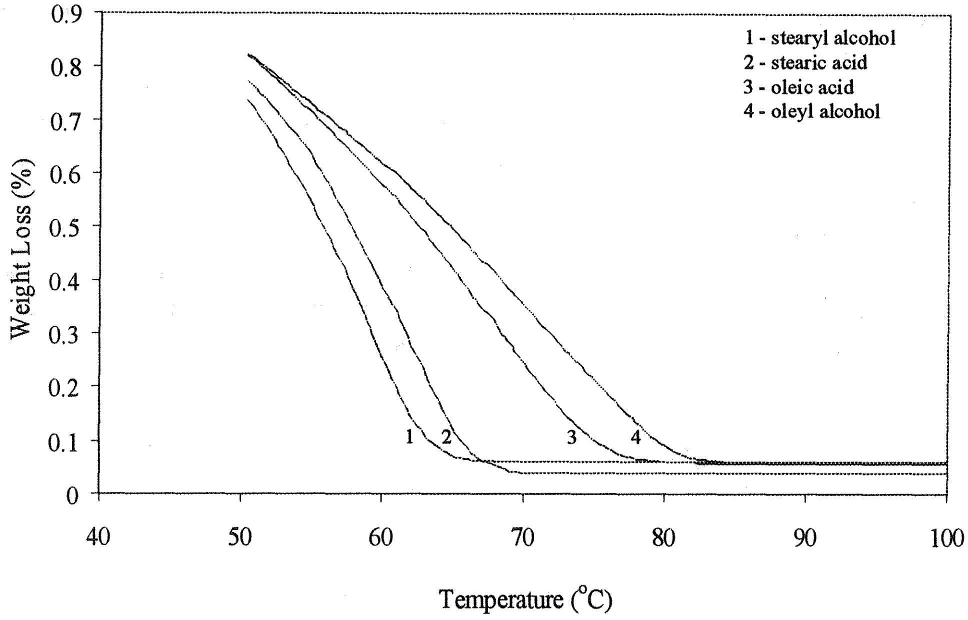

Figure 3: Thermogravimetric analysis of extracted supernatent after mixing with PZT powder

Using the new binder formulation along with PZT and HAp powder, multiple copies of complex designs have been produced using FDC. Figure 5 shows photographs of two such designs. Figure 5a is a photograph of a PZT ceramic part slated for use in Naval towed arrays. Figure 5b is a photograph of a green and sintered PZT design also for use in Naval towed arrays. In each case, the ceramic phase was sintered to near-theoretical density, and was free of defects resulting from FDC processing. In the case of PZT samples, total firing shrinkage averages 18 % in the radial direction, and 24 % in the z-direction.

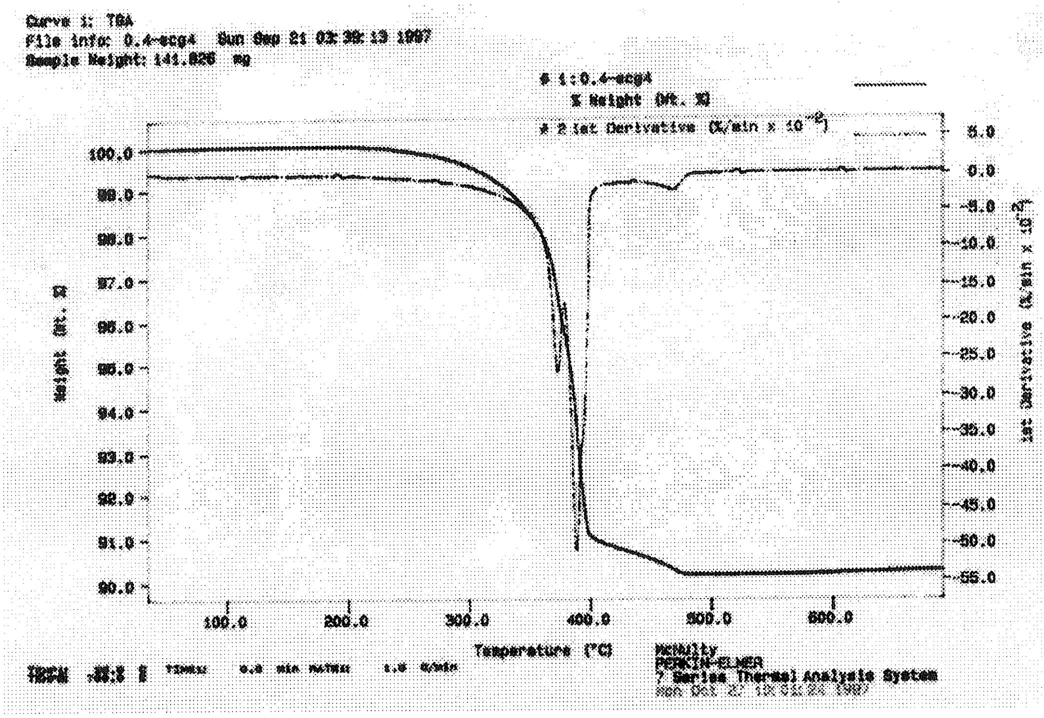

Figure 4: Thermogravimetric analysis of 55 vol.% PZT / thermoplastic compound

For HAp samples, shrinkage averages 13 % in the radial direction, and 14 % in the z direction.

Conclusions

A new binder formulation has been developed for use in Fused Deposition of Ceramics (FDC). This binder formulation consists entirely of commercially available polymers, and exhibits rheological and thermal properties suitable for FDC applications. In addition, stearic acid has been found to provide adequate dispersion for both a lead zirconate titianate-based system and a hydroxyapatite-based system. In both cases, functional ceramic prototypes were manufactured using a Stratasys 3-D Modeler^{TM}. Parts made using this new polymer were of high quality, and showed no signs of binder-related flaws after sintering.

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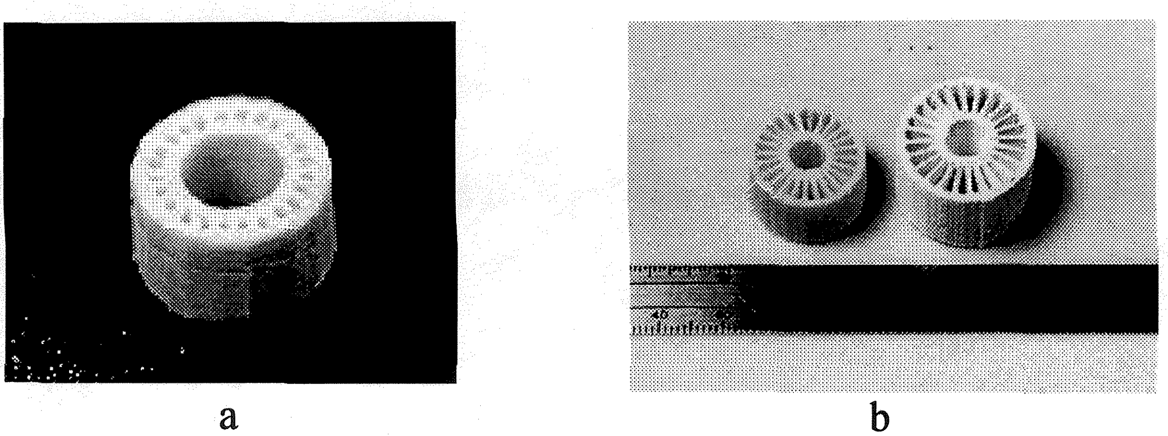

Figure 5: a) Photograph of sintered PZT part made via FDC
b) Photograph of green and sintered PZT parts made via FDC

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