Characterization of Polyolefin – Alumina compounded mix for FDC processing

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Abstract

Fused deposition of ceramics (FDC) uses thermoplastic binder and ceramic blend as feed material. The geometry of the fused deposition machine restricts the workability of the FDC feed material, which is in the form of a filament. The feasibility of the usage of these filaments is mainly based on the viscosity at the working temperature and the compressive modulus of the feed material at near room temperature. The polymers based on Polyethylene (PE), having two molecular weights 3,000 (LDWAX) and 341,000 (LDPE) were mixed in various weight proportions by solvent method using toluene as solvent, to develop a binder system for Fused Deposition Modeling of alumina. Variation of viscosity as a function of composition, temperature and solid loading was measured using spindle viscometer and capillary rheometer. Dilatometric thermal expansion of 50 Vol% alumina compounded binders is measured up to 120°C. The pronounced softening of the compounded mixture is observed beyond 70°C, when the volume % of LDWAX is in excess of 50% total binder content. The compression strength decreases from 720 N to 310 N for pellet having 1.2cm diameter and 1.5 aspect ratio, when the percentage of LDWAX varies from 40 to 70% in the binder composition. The suitability of the compounded mix of LDWAX and LDPE binder with 40 Vol. % alumina for FDC is being evaluated in a Stratasys^{TM}1600 machine.

Introduction

The success of the FDC [1-2] or injection molding [3-4] is mainly dependent on the detailed characterization and selection of the proper feed material composition. A multicomponent binder (MB) system containing base binder, plasticiser, and tackifier have been found to be useful in FDC [5]. The advantage of MB over simple unicomponent binder system is its cumulative and variable property with the composition. The different decomposition temperature of each component in the binder system will minimize the cracks in the sample after binder burn out. The role of materials processing [6] and solid loading are the other parameters, which control the property of the feed material. In this paper we restrict ourselves to a particular solid loading of 50 Vol. %.

Though binder systems for FDC is being formulated for Al_2O_3, PZT, SiC etc.[7-8], there were very less instances of minimizing the number of efforts needed to formulate them. The viscosity at working temperature and compressive modulus of the feedstock are the main criterion in deciding the workability of a filament. This can be visualized in Fig 1. The forward force exerted by the rollers and backward drag exerted by the viscous material in side the liquefier will lead to the bending of the filament in between the liquefier and roller [9]. To find out usefulness of the feedstock for FDC, the viscosity and compressive modulus measurements were carried out. The compressive modulus of the feedstock is being compared with the working investment casting wax supplied by Stratasys Inc^{TM}.

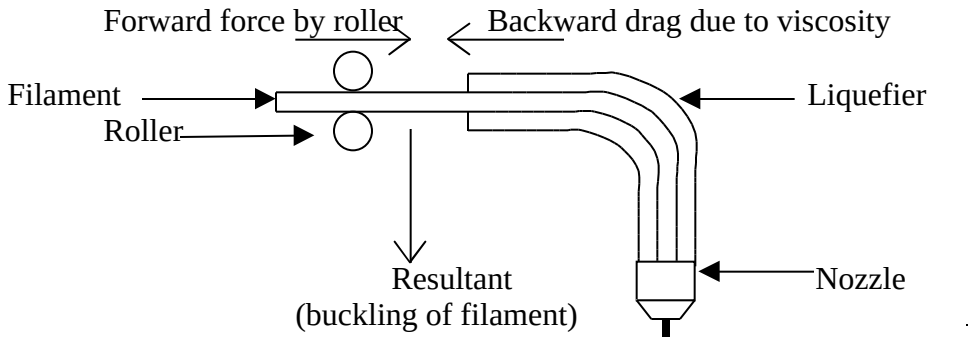

Fig 1. Schematic Structure of roller liquefier array in twin head Stratasys Inc^{TM}. FDM-1600 machine.

PE of two different molecular weights has been blended by solvent method and their viscosity and compression strength values are reported here. The other parameter, which adds to the failure of the filament, is the softening of the filament at inlet of the liquefier. The dilatometric study is done to measure the softening of the material.

Experimental

The molecular weight determination of Low Density Polyethylene (LDPE) and LDPE Wax (LDWAX) was determined out using HPLC-GPC system (Water Inc.). The binder system with LDPE as main binder and LDWAX as plasticiser was blended in different volume (Table 1.) fractions using toluene as the solvent. The blending was performed at 90°C using a mechanical stirrer until the solvent almost removed. The polymer mass was transferred to a tray of aluminum foil. The solvent traces were removed by degassing at 110°C and -650 mmHg in a vacuum oven. The degassed sample was subjected for viscosity measurement using Brookfield viscometer (model- DV-II) with spindle #34, at varied temperature and revolution per minute.

Table 1. The code for binder and ceramic binder blend with varying plasticiser content.

Plasticiser content in the total binder (Vol.%)	Identity	
	Without Ceramic	With 50 Vol. % Alumina Loading
0	LDPE	-----
40	LDWAX 40%	CLDWAX 40%
50	LDWAX 50%	CLDWAX 50%
60	LDWAX 60%	CLDWAX 60%
70	LDWAX 70%	CLDWAX 70%
80	LDWAX 80%	------
100	LDWAX	------

The 50 Vol.% solid loaded thermoplastic binder containing varying ratio of LDPE and LDWAX with alumina were prepared using solvent method. The average mean particle

size of the alumina was found to be ~0.6μm, (specific surface area: 8-10 sq.m/gm). Alumina powder was ball milled for one hour with 2 Wt.% of strearic acid in toluene medium. The surfactant treated alumina was completely transferred to a stainless steel container and added with calculated amount of LDPE and LDWAX. All the additives were mixed at 100°C using mechanical stirrer. After almost all solvent has been removed, the mixture was transferred to the tray of aluminum foil and degassed at 110°C and –650 mmHg using vacuum oven. The mixture was granulated and its rheology was measured using capillary rheometer CFT-500C type (Shimadzu Corporation) at different temperature with different shear rate.

The pellets having 12mm diameter and 15mm height were made out of binder compounded with alumina at the load of 50kN in 100°C. Investment casting wax (ICW-05, Stratasys Inc^{TM}.) pellets were made into the same dimension pellets as alumina by melting it in the same dye. The crushing strength of these pellets were measured in Darteck-9500 mechanical analyzer with the plunger speed of 0.001mm/s. The thermal expansion measurement of these pellets were carried out in home made dilatometer up to 150°C.

The filaments of 1.7mm of the alumina-binder mix were made using capillary rheometer at 100°C. The extruded 1.5m length filaments were stored in a stainless steel tube till actual fused depositing on the Stratasys 1600 machine. The liquefier fitted with stainless steel nozzles was maintained at 130°C and the filament was introduced into the machine with the flow rate of 40% (Stratasys specification).

Results and Discussion

The decrease in the chain length of the polymer is directly proportional to the interaction between two polymer chains. Therefore the viscosity is intern related to the average molecular weight of the binder. Table 2. shows the decrease in the average molecular weight of the binders and their viscosity at 150°C. This is an important data in controlling the viscosity of the binder on the basis of average molecular weight. We could measure the viscosity of the polymer composite in the range, which is shown in Fig 2, rest of the valves was out of viscometer range. These sets of thermoplastic binders have shown clear expected pseudoplastic behavior in the whole range of temperature, which indicates that there is no effect on the nature of the binder by solvent mixing.

Table 2. The average molecular weights of binder plasticiser mixture at different proportion.

Polymer Composite (% of LDWAX)	Molecular Weight Average (M_w)	Viscosity at 150°C (cps)
0	341000	HIGH
40	205800	85300
50	172000	33900
60	138200	14400
70	104400	5510
80	70600	1800
100	3000	LOW

The viscosity of surfactant treated alumina with binder having variable volume fractions of binder and plasticiser showed a characteristic pseudoplastic behavior as expected. The variation of viscosity as a function of shear rate at different temperature is shown in Fig 3. All the ceramic-binder blends with different plasticiser content were found to have viscosity less than 8000cps at particular temperatures corresponding to them. The preferred working temperature is below 150°C, to avoid the plasticiser loss due to evaporation.

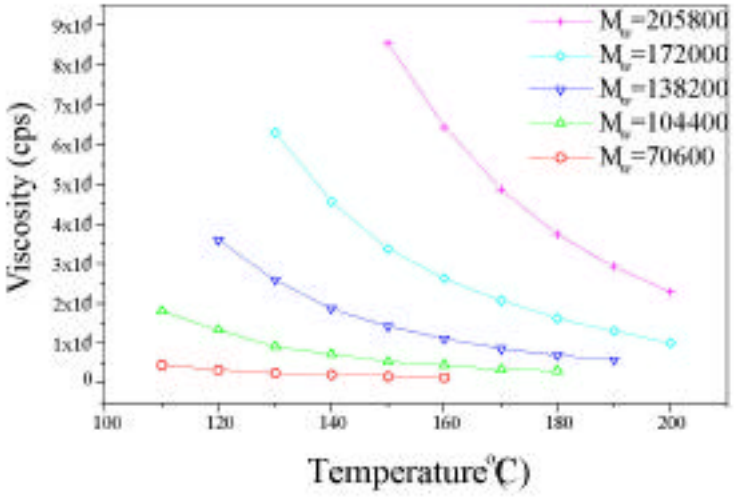

Fig 2. Variation of viscosity at different temperature for different average molecular weight binders

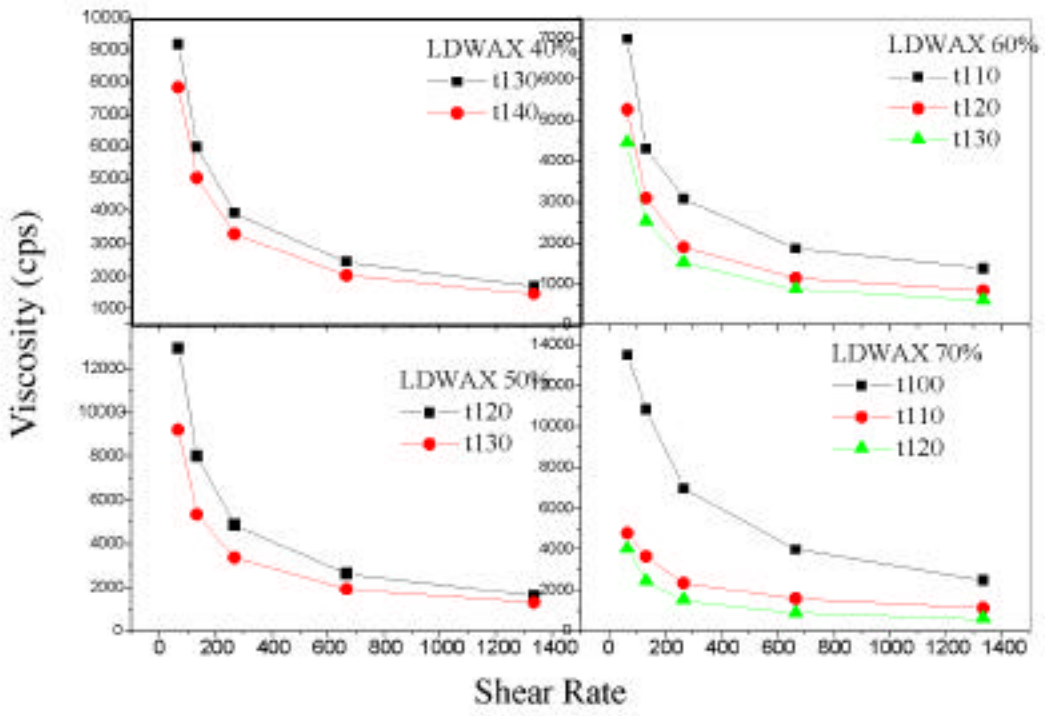

Fig 3. The viscosity behavior of binder with alumina as a function of shear rate at different temperature.

The increase in the plasticiser above 50 Vol.% of binder drastically brings down the long chain interaction in the polymer which causes dramatic change in the viscosity of the material. This is clearly evident from the Table No: 3. There is minimum change in the viscosity of CLDWAX-50% and CLDWAX-40%.

Table 3. Variation in viscosity at 130°C (at different percentage of plasticiser in the total binder content.) as a function of plasticiser content in the total binder system.

Shear Rate	Viscosity (cps)		
	CLDWAX-60%	CLDWAX-50%	CLDWAX-40%
1333.33	591	1306	1691
666.67	866	1931	2440
266.67	1506	3350	3950
133.33	2516	5325	6012
66.67	4447	9187	9187

The increase in the plasticiser content can bring down the viscosity of the material but at the same time decreases the mechanical property, which adversely affects the workability of the filament. This is because of sagging of the filament near the inlet of the liquefier and low compressive modulus of the material.

The thermal expansion measurements with the constant load of 55g shows, at low temperature stiffness of the materials decreases with increasing plasticiser content. This is evident from the Fig 4., the sagging of the sample starts in the range of 65-70°C for the binder having LDWAX more than 60%. But the binder having 50% of LDWAX show the sagging after 80°C. These type of behavior is due to the short range glass transition of the plasticiser at around 55°C. In the case of binders having 40% plasticiser, the sagging will not be found till it softens at100°C. All the samples will collapse at 100°C due to softening of LDPE, during glass transition.

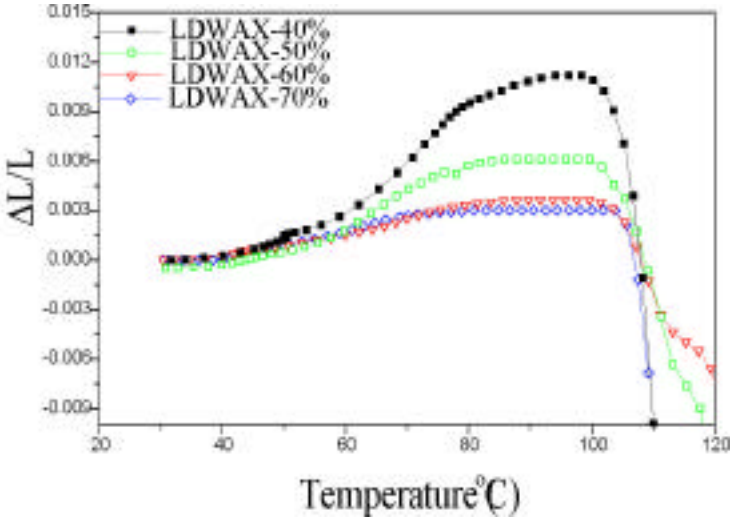

Fig 4. The thermal expansion behavior of 50 Vol% of alumina solid loaded binder with different proportion of plasticiser.

The binder ceramic mixtures were found to have the modulus ranging from 1.1kN/mm to 0.4kN/mm. The working filament ICW-05 filament supplied by Stratasys

Inc^{TM}. was found. to has the modulus of ~0.55 kN/mm as shown in Fig 5. The ceramic binder mixture which are having plasticiser content less than 50% have higher strength and modulus than ICW-05. Though CLDWAX 40% and 50% show higher modulus and compressive strength, they are brittle compared to the ICW-05. The ceramic binder blends show sudden softening once they attain the maximum elastic modulus. The modulus and compressive strength of the ceramic-binder blend and ICW-05 are presented in Table 4. But the ICW-05 shows the deformation in the shape after its maximum elastic modulus, while the sample will be compressed with increasing load. Ceramic-binder can withstand more load compared to ICW-05 without compression, whereas ICW-05 can withstand higher load even after it starts deforming. This tough behavior of the ICW-05 is advantageous over the ceramic-binder blend. The use of other additives such as tackfier, microcrystalline wax to the binder system may help in overcoming this problem.

Table 4. The comparison in between the modulus and compressive strength of ceramic-binder blends with ICW-05.

Materials composition	Modulus (N/mm)	Compressive Strength {until deformation} (N)
ICW-05	550	570
CLDWAX 40%	1100	720
CLDWAX 50%	820	610
CLDWAX 60%	475	350
CLDWAX 70%	410	310

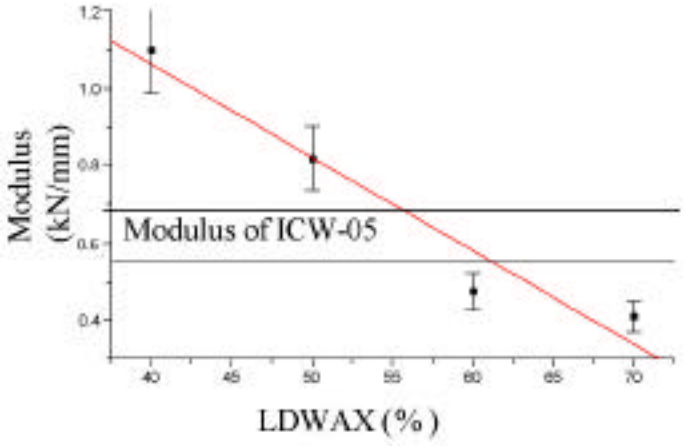

Fig 5. The comparison of the modulus of various ceramic binder (50% solid loading) mixture with ICW-05.

The viscosity of ceramic-binder blend can be adjusted to the required level by controlling the temperature. The mechanical analysis show that the compressive modulus and

the strength of CLDWAX 60% and CLDWAX 70% are lower than ICW-05. The dilatometric curves have shown that the sagging of CLDWAX 60% and CLDWAX 70% will start at 65-70°C, which is not advisable because of their sagging near the inlet of the liquefier. On the basis of these results CLDWAX 40% and CLDWAX 50% have been chosen for the testing on Stratasys machine. The liquefier was maintained at 140°C and the filament was introduced in the speed of 40% (Stratasys Inc. calibration). The filaments of CLDWAX 40% could be extruded through the machine without buckling.

Conclusion

The polyethylene based multicomponent binder system was formulated for the 50 Vol% solid loading. The ceramic-binder blends were characterized by viscosity, dilatometric thermal expansion and mechanical strength measurements to narrow down on a particular composition. The results have shown CLDWAX 40% and CLDWAX 50% are having the required viscosity at 140 and 130°C, and having better mechanical properties than ICW-05. The filaments of CLDWAX 40% could be extruded through the liquefier of FDM. Increasing the number of components of the multicomponent binder system to include tackifier, microcrystalline waxes are being attempted to evolve composition to make FDC process smooth.

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