EXTRUSION METHODS FOR SOLID FREEFORM FABRICATION

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INTRODUCTION

It is becoming clear that current SFF methods are members of a potentially very large family. As with current forming methods, it is to be expected that particular materials and objects will lend themselves best to particular methods. Our group has been working for two years on extrusion methods of freeform fabrication where a reactive slurry is extruded into a pattern to form a series of layers that build up a three-dimensional object. A sketch of the apparatus is shown in figure 1. The slurry may cure chemically either as each layer forms or in a postcuring oven.

As a member of the SFF family, this method offers great versatility in the range of materials that can be formed an in control of the material structure and composition within a part. This paper describes our efforts to extend the application of this method from ceramics to polymer composites, thermoplastics and silica-silica composites.

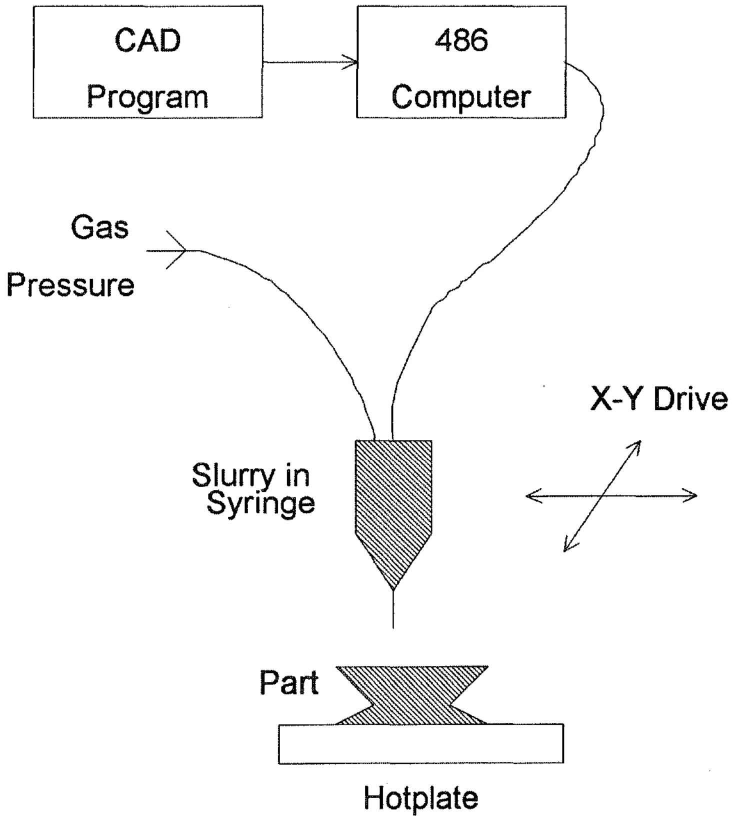


Figure 1: Extrusion SFF Equipment

EXTRUSION SYSTEMS

ACR Systems

The ACR extrusion freeforming equipment comprises a computer-controlled, stepper motor driven and screw-actuated gantry plus a vertical linear slide table. A small positive displacement extruder is mounted on the vertical slide. The extruder is a small stiff piston and cylinder assembly. The piston is actuated by a second linear slide table driven by a stepper motor. Piston and cylinder were originally glass syringes. These have been replaced with epoxy-potted polycarbonate syringes and aluminum pistons. The nozzle (needle) is a shortened Luer-Lok hypodermic needle.

For polymer extrusion, high extrusion pressures increase greatly the weight of the head. To avoid the problems of moving such a large mass a system has been constructed based on a fixed extrusion head and a moving sample table. A computer-controlled massive vertical extruder is mounted above a three-axis table with two orthogonal cross-tables mounted on a vertical stage beneath the extruder. The outlet nozzle of the extruder is a heated block with a machined internal reduction.

AML Dispensing System

Motion control and slurry placement is provided by an Asymtek model 402 benchtop fluid dispensing system. This unit provides an x-y travel of 12" x 12" and z travel of 3.5" with a step resolution of 0.001" on all axes. The maximum head speed is 12 inches/sec, although dispensing is usually limited to 1-4 inches/sec.

Dispensing is through a pinch tube valve connected to a 50 cc syringe. The syringe can be replaced by a feed tube connected to a stationary cartridge allowing a larger supply of slurry. The slurry is pressurized to 5-20 psi from a nitrogen bottle and is dispensed though an 18-25 gauge needle.

Dispensing variables for this system include:
Fluid Pressure
Tip Gauge
Head Velocity
Fill Pattern resolution
Startup delay
Shutoff Distance

The startup delay (time between the opening of the valve and when the head is instructed to move) and shutoff distance (length before the end of a move at which the valve is instructed to shut off) are required to allow the movement of residual fluid in the needle, to avoid blobbing at line ends.

Control is via an IBM PC that handles all aspects of modelling and dispensing in a single integrated package running under Autocad Release 12. The Autocad AME package provides modelling and object slicing, while software routines written in C provide complete control of dispensing operations, converting Autocad data into Asymtek motion commands and issuing machine control statements.

Drawings of an object are prepared as 3-dimensional solid models in Autocad. To fabricate the object, the user manually sets the dispensing tip to the height of the dispensing surface. The control software reads this value, calculates the correct elevation to slice the model and creates a 2-dimensional section. The perimeter of the resulting pattern is dispensed first, then it is filled in a snaking line pattern. After the layer is dispensed, the user is prompted to reset the needle to the new surface height and the process is repeated.

The feedback in the process ensures that the object is fabricated to the highest resolution possible on a layer-by-layer basis, without being subject to additive effects of small changes in dispensing thickness. In principle, surface-sensing equipment could provide this information. Current layer thicknesses are 0.02-0.03 inches.

One promising filling strategy is to dispense the perimeter of three successive layers before filling the interior. The three layers (0.05-0.1" total height) act as a dam, allowing the fill pattern to be dispensed in a much thicker layer without affecting the overall surface resolution. This significantly reduces the total dispensing time and produces flatter, more homogeneous filled regions.

MATERIALS

Ceramic Slurries

Extrusion of slurries of alumina in acrylic monomers was described at the same meeting last year. Slurries could be made with solids contents up to 55% and viscosities of 200 poise. The final parts had good fired density and flexural strength [1].

Filled Resins

Silica-filled acrylic resins could be formed by the same method. In the same way, the slurry cured as each layer was extruded. Table 1 shows the properties of a series of silica-filled acrylics. Ceramic green bodies do not need significant mechanical strength and heavily cross-linking acrylates, such as TMPTA could be used [1]. In the case of composite materials, the high volume fraction of resin places a higher value on good resin toughness. Consequently the highly cross-linked resins based on TMPTA are unsuitable and were replaced by the more flexible urethane acrylates.

Many acrylate and other monomers were investigated before we found a good combination of rapid curing and toughness. Mixtures of a urethane acrylate, hexanedioldiacrylate and N-vinylpyrrolidone were found to give rapid curing (less than 1 minute) and good properties. The resin was reinforced with silica particles plus 1.7 vol.% fumed silica which provided enough viscosity that the larger particles did not settle in the slurry.

We believe that the toughness arises from the polarity of the urethane which allows good bonding to the filler particles. It can be seen that the modulus increases by a factor of three as the filler loading increases to 30 vol.% and that the strength remains high. In many filled polymer systems, where there is poor bonding to the filler, the modulus increases but the strength declines with increasing filler content.

Fiber-reinforced composites

In addition to particulate fillers, short fiber fillers can also be used. As shown in Table

1, 7% carbon fiber (Hercules AS4), chopped to a length of about 100 microns gives a higher modulus but there is some loss of strength. The strength is almost certainly sensitive to the interfacial bonding. Good fiber-resin bonds can be difficult to achieve with carbon fiber.

In situ composites

Other work in our group has been concerned with *in situ* composites where the reinforcing phase grows within the polymer matrix during or after processing. For instance, liquid titanium alkoxides have been blended into polypropylene and co-extruded to form a flexible polymer film. Subsequent treatment of this film in a water bath hydrolyzes the alkoxide and precipitates titania to produce a composite with a very fine titania reinforcement.

Tetraethoxysilane (TEOS) and water, at a 1:4 molar ratio, have been blended with the acrylate monomers to form an extrudable fluid. This both cures and partly hydrolyzes as the layers are deposited to form a composite. A 24-hour steam treatment of the final part was used to complete the hydrolysis to silica. The parts listed in table I contained 7 vol.% silica from TEOS, plus 15 vol.% of silica powder and 1.66 vol.% of fumed silica. The properties are similar to the equivalent 22% silica conventional composite.

These parts show a volume shrinkage of 15% on reaction. For most of these types of *in situ* composites, the shrinkage is a serious problem in forming anything but films and fibers. SFF methods can offer a route to exploitation of this new class of materials since much of the shrinkage can be confined to each layer as it forms, rather than requiring accommodation of the whole part.

Table I: Flexural Tests on Composites

Composition	Flexural Strength, MPa	Flexural Modulus, GPa
Resin	38.3	0.96
Resin + 3.8 vol% Silica	42.8	1.03
Resin + 7.5 vol% Silica	48.8	1.15
Resin + 11.2 vol% Silica	54.9	1.39
Resin + 15 vol% Silica	58.2	1.56
Resin + 22.5 vol% Silica	75.1	2.56
Resin + 30 vol% Silica	61.5	2.89
Resin + 7 vol% Silica from TEOS	50.4	2.10
Resin + 5 vol% Carbon Fiber	27.0	1.24

Ceramic/Ceramic slurries

As part of a program tied to a future lunar base, where polymers would not be available, we have been making ceramic-bonded ceramic materials. A slurry of silica powder, ethylsilicate binder and water is formed in ethanol. Ethylsilicate is related to tetraethylorthosilicate (TEOS) but has been partly hydrolysed under acidic conditions to form linear oligomers. Further hydrolysis and condensation lead to silica which will act as a matrix phase in the final sintered body. The ethanol from the slurry and that released on hydrolysis of the ethylsilicate will be recycled by reaction with silicon derived from lunar sources. The water can also be recycled. Essentially this becomes a process for reforming lunar silica into functional parts.

The hydrolysis and condensation of ethylsilicate can be acid or base catalyzed. Adding catalysts to the slurry produced uneven results as condensation continued in the syringe before dispensing.

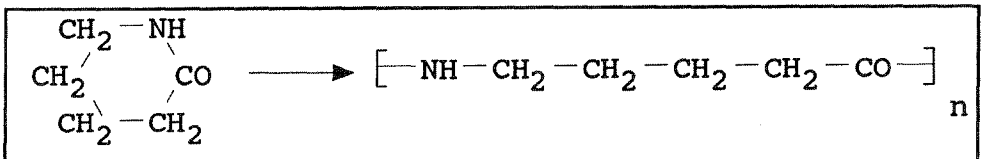
Ethylsilicate, water, ethanol and silica are ball milled with alumina balls for 24 hours and then the slurry is poured into the syringe. Particle loadings of 55-58 vol.% dispense well through a 23-gauge needle at 10-15 psi fluid pressure. After dispensing the layer is briefly treated with a heat gun to remove some ethanol and then is sprayed with aqueous ammonia.

The greenbodies are dried slowly and then fired at 1500°C in air. Fired densities have so far only reached 60% of theoretical and fluxes are being explored to enhance the sintering kinetics.

Thermoplastic Resins

Nylon 6 is a tough engineering thermoplastic that is used for many small parts such as gears, cams and bearing housings. For larger parts the high melt viscosity of Nylon causes problems in filling the mold with polymer of high molecular weight. There has been much development work on reaction injection molding (RIM) methods where molten caprolactam monomer is cast or injection molded and polymerized in the mold. The polymerization can be completed in a few minutes. The low viscosity of the monomer allows large molds to be filled and the high molecular weight product has excellent toughness [2,3]. This low viscosity, rapid polymerization system could be readily adapted to SFF extrusion processes.

Molten caprolactam, at 120°C, is pumped through a needle onto a heated platen to cause polymerization. A strongly basic catalyst, sodium caprolactamate, and an activator, N-acetylcaprolactam, initiate the ring opening polymerization [4]. The reaction occurs rapidly above 150°C and typically produces polymer in 95-98% yield.



Caprolactam Nylon 6

CONCLUSIONS

Extrusion methods of SFF allow considerable versatility in terms of the types of materials that can be formed. Apparatus to carry out this technique is simple and readily constructed. As well as being a manufacturing method, it provides a useful tool for the materials engineer to test the formation of novel materials. In particular the layerwise formation process permits chemical production of materials to final shape without the normal limitations imposed by slow diffusion rates and large shrinkages.

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