Reviews

Chemical Solid Free-Form Fabrication: Making Shapes without Molds

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Solid free-form fabrication methods are surveyed. This approach of making objects by depositing material layer by layer lends itself to the direct conversion of fluid reactants to a solid part, as opposed to the production of a material and its subsequent processing. Examples are given of the formation of ceramics, metals, thermoplastics, thermosets, and composites. In principle, mobile products can be removed from the layers as they form, allowing a much wider range of reactions to be used. Since the composition may be varied as the object is built up, it is also possible to combine several materials into a monolithic piece.

Introduction

Solid free-form fabrication (SFF) is best known in its stereolithography form as a method of rapid prototyping. In stereolithography a laser photopolymerizes successive thin layers of monomer to build up a solid object. Parts designed on a CAD system can be transformed into solid resin in an 1 or 2 h, at a vertical rate of about 1 mm/min. There is intense interest in using stereolithography or other SFF methods to form molds, for investment casting or injection molding, either from the prototypes or directly. There are anecdotal examples of stereolithography parts being used directly as temporary replacements under circumstances where a component has failed and spare parts are unavailable. As new free-formed materials become available, we can expect that more functional parts will be made in this way.

As a way of making small numbers of parts from conventional materials, free-forming offers the advantages of speed and flexibility for materials that cannot be machined. Many of these methods are also capable of making shapes that cannot be machined, including objects with loose enclosed parts (a ball in a box), convoluted channels, or distributed porosity. This arises from the fact that we are building the whole object rather than only the surface. In principle, it is also simple to embed inserts of a second material, such as a sensor or heater. Beyond this, free-forming has the potential to produce new materials and complex composites that could not be made in any other way. This review will concentrate on this potential impact of free-forming on the synthesis and processing of materials.

In conventional forming, such as for glasses, polymers, or metals, the material is first produced in bulk by chemical processing and is then shipped as a powder or block. With the exception of sintering, solidification in most processing methods occurs by the removal of heat.

Chemical formation of bulk components is limited because of the need to remove reaction products by diffusion. Thus, the reaction either must involve no mobile products, as in reaction injection molding of nylon and polyurethane, or must yield a porous solid, as in reaction-bonded silicon nitride. In addition, chemical processing will frequently involve large volume changes that are hard to accommodate.

The essence of a free-form fabrication method is that either energy or material must be delivered to a point to produce a solid. A series of lines are traced out to make a layer, and successive layers formed to produce a solid part. This layerwise approach lends itself to chemical processing of materials since the diffusional limitations are significantly reduced by the need to form thin layers, one at a time. The time for a diffusional process depends on the square of the diffusion distance. If a solid is formed as a series of layers, this distance is the thickness of one layer, and the time increases only linearly with the number of layers. In addition, chemical precipitation processes frequently involve large shrinkages, which lead to cracking of a solid body if the process is not uniform. It should be possible to accommodate shrinkage within each layer as it is deposited in a free-forming process. Thus, in principle, the many methods for forming thin films of material could be converted to free-form fabrication methods for making large objects.

Chemical processing of materials is the only route available to biological organisms, since cells grow isothermally. This also means that the conversion from chemical in solution to solid part frequently occurs as a single step, rather than the common synthetic approach of producing quantities of powder for processing elsewhere at a later date. Free-forming shares with biology this closer coupling between chemistry and processing.

Mineralization of biological tissues, such as a bone growth or tooth formation, occur at an interface between a layer of cells and the newly mineralized tissue. As the tissue is formed the cells retreat. This method

accommodates the need to supply minerals in solution continuously to the interface. It also allows the properties of the material to be varied locally within the growth plane and between planes. The tissue composition or mineral orientation can be modified by the cells as they deposit successive layers. It is also evident that structural biological tissues are not joined mechanically or by adhesives. A junction is normally effected by a slow transition from one material to the next, as in the mineralization of tendon on the region where it attaches to the bone. This type of graded interface is a consequence of the layerwise processing.

This review primarily addresses the chemical and materials aspects of free-forming methods. The aim is to explore what questions need to be resolved in order to develop this new technology to the full. We will try to do this in a way that is generic to all free-forming methods but will draw largely on our own work in this area. In addition to providing routes to new combinations of materials, full exploitation of the free-forming approach will require a new relationship between design and manufacture. We will briefly discuss some of these questions below.

Current SFF Methods

There are three or four major commercial free-forming systems available currently and many others under development. In principle, there are at least as many potential free-forming systems as there are ways to write or print on a surface. It is reasonable to expect that a large number of approaches will be explored before a small group of standard methods settles out. The annual conference on Solid Free-form Fabrication in Austin, TX, provides a review of developing methods and materials.[1] The World Wide Web has a number of sites that provide good practical surveys of current rapid prototyping methods.[2] It is not our purpose here to compare the merits of different systems. All are still developing, and most have only been applied to one small group of materials. Progress has been driven largely by considerations of developing machines for sale rather than by a desire to explore the full potential of this approach. Much of the development effort has gone into software and engineering to improve precision and speed rather than into materials.

For "desktop" systems, safety concerns will tend to favor free-forming by solidification rather than reaction. In the laboratory or factory, enclosed free-forming equipment should allow the use of most low vapor pressure reagents even by organizations that are not chemically sophisticated.

Stereolithography. Stereolithography was developed by 3D Systems of Valencia, CA, after parallel efforts in several laboratories.[3,4] Apparently similar systems are manufactured by Sony and Ushio in Japan. It has been the subject of a thorough text.[4] As sketched in Figure 1, a He–Cd or argon ion laser traces a shape at the surface of a bath of photopolymerizable monomer. A supporting platform then drops by one layer thickness, a further layer of monomer is swept across the newly solid surface, and the process is repeated. After a few hours, the platform is raised and the completed part removed. Parts are often given a final polish to smooth the surface. Resolution is clearly related to the film thickness and kinetics of photopolymerization[5] and
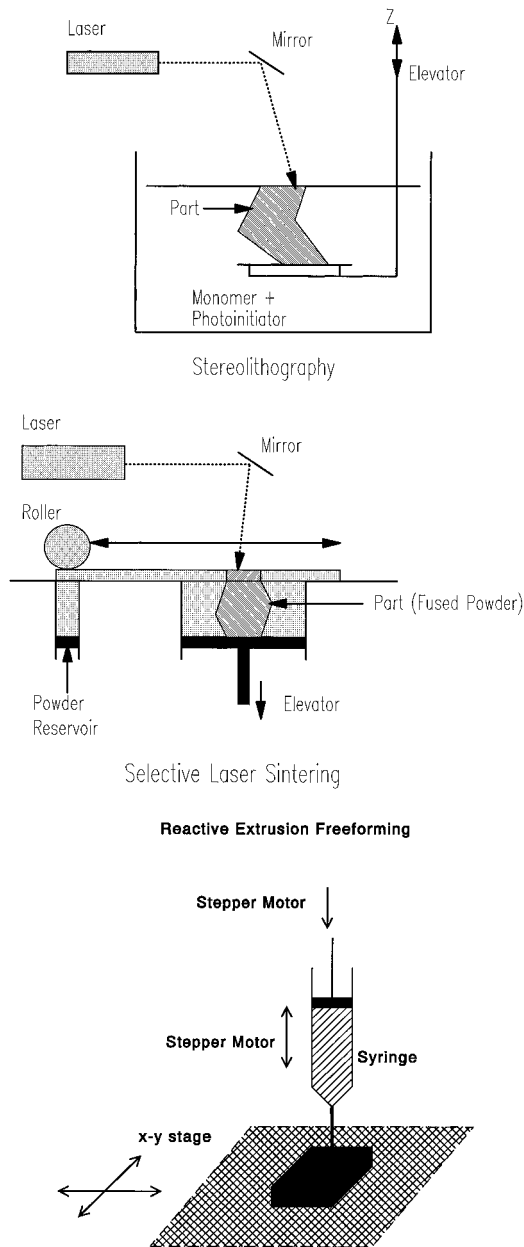

Figure 1. Free-forming methods. (a, top) Stereolithography, a moving mirror tracks a laser across the surface of a bath of monomer. As each layer is written, the elevator drops and a new film of monomer is swept across the existing solid surface. (b, middle) Selective laser sintering, the laser fuses an area of powder, the elevator drops on step, a new layer of powder is rolled across from the reservoir, and the process is repeated. (c, bottom) Reactive extrusion. The syringe delivers a fine stream of material onto the moving hot plate. When a layer is partly cured, the syringe moves up and writes the next layer. Supporting material can be added around each layer if necessary.

diffusion. A typical layer thickness is 200 μm; line widths are similar. Thinner layers increase the part production time, but thicker layers may require longer laser exposure and also longer production times.[4] The maximum part size is really limited by the size of the monomer bath, typically 8 gal, which can contain a substantial volume of resin that is not directly used and represents a large financial investment. Ten inch dimensions are typical, and such a part would take about 20 h to form.

The desire to make investment casting molds from stereolithography parts has led to the "Quickcast"

process where the interior of the part is not solid but formed as a lattice of struts. Excess liquid can be drained out of a hole in the base after forming. In principle, this more compliant part can be used to make a ceramic mold that will not crack due to differential expansion as the resin is burnt out. In practice, strengthening of the ceramic mold is necessary to avoid cracking.

The original monomers were combinations of multifunctional acrylates which formed cross-linked resins. Newer photopolymerizable epoxies offer better properties.[6] The lower shrinkage of the epoxies during postgelation polymerization leads to lower distortion. A major concern in stereolithography is distortion induced by shrinkage during postcuring of the resin. Studies of acrylates showed that the polymerization continued for about 2 days after photoinitiation with the final fraction of reacted double bonds reaching only 30%.[7]

There are efforts to extend this system to other materials such as ceramics. A group at the University of Michigan have produced parts from dispersions containing up to 50 vol % silica in a cross-linkable aqueous acrylamide system.[8] Satisfactory cure depths could be achieved but at the cost of exposure energies about 100 times that of unfilled resins, with a consequent proportional expected increase in build time. Silica is special in having a refractive index close to that of water; light scattering by alumina is much stronger and cure depths are lower.[9] Scattering at a particular wavelength could be decreased by the use of dyes to tune the refractive index of the resin closer to that of the ceramic. Promising results were also obtained with hydroxyapatite suspensions.

There have been attempts to incorporate fibers into stereolithography.[10,11]

Selective Laser Sintering. DTM Corp. of Austin, TX, has developed a selective laser-sintering method. The principle is similar to stereolithography, but the liquid monomer is replaced by polymer powder which is fused by a CO_2 laser.[12,13] A layer of heated powder is spread on a piston and selected areas are fused; the piston is then lowered slightly and a new layer of powder spread and fused. The fused, but still porous, part is finally removed from the powder bed by raising the piston. Layer thickness is typically 25–30 μm with a rate of building of 5 cm/h and an accuracy of about 400 μm. Precision is closely linked to the size of the powder particles.[14]

Polycarbonate has proved very suitable for this process, presumably because of its low melt viscosity and high toughness, but the final parts are only about 60% of full density. A modified nylon has been used to form essentially dense parts.[15] The powder may contain polymer and ceramic so that the fused component is a green body that can be fired.

Bronze–nickel parts have been formed to fractional densities of 65–80%.[16] A number of high-temperature materials have also been formed by fusing polymer-coated powders of silicon carbide,[17] other ceramics, and metals.[18] The porous parts can be converted to high density by hot isostatic pressing (HIPping). There are also schemes for forming composites by partially sintering and impregnating the porous body with liquid metal.[19]

Fused Deposition Modeling. Stratasys Corp. of Minneapolis, MN, developed fused deposition modeling where a 1 mm strand of wax is fitted in a write head attached to an x–y drive, like an inverted pen plotter.[20] The resulting wax parts can be used for investment casting but are rather fragile. (In the investment casting process a machined metal model is used to make a reusable rubber mold. Wax is cast into this mold, and the wax model is coated with refractory cement. The wax is melted out and metal cast into the cement mold, which must then be broken to retrieve the cast metal part.) Steps on the surface, corresponding to the layers, are often noticeable. Polymer materials are also available including a low-melting form of nylon and ABS. Layer thicknesses range from 25 μm to 1 mm with a precision on a 30 cm part of 125 μm. The process tends to leave voids amounting to 10–25 vol %.[21]

Efforts are in progress to adapt this process to ceramics by the incorporation of silicon nitride powder into a thermoplastic binder and extruding as a filament.[22] There are intrinsic difficulties associated with the brittleness of highly filled thermoplastics, coupled with the need for a ceramic loading of 50–60 vol % in order to achieve good sintering.

3-D Printing. 3-D printing was developed at MIT and has been licensed to Soligen Inc., who use it to make molds for metal casting. An inkjet system writes a binder, such as a polymer latex or silica colloid, into a bed of ceramic powder.[23] A layer of powder 100–150 μm thick is spread and then binder sprayed into the zone to be solidified as a stream of droplets. The method is excellent for coarser ceramic powders but is more difficult with fine, submicron powders where capillary forces become significant, and spreading the powder is difficult.

Stainless steel powder can also be formed and sintered.[24] A number of approaches are being developed to form dense ceramics from fine powders including isostatic pressing before firing. Another approach is to replace the rolling on of new layers of powder with a spray of a slurry fine ceramic powder.[25]

Reactive Extrusion Free-Forming. Our involvement with SFF has been with reactive extrusion free-forming. This approach was developed in collaboration with Advanced Ceramics Research Corp. of Tucson, AZ. A motorized syringe is mounted on an x–y drive and writes out a stream of liquid slurry about 0.3 mm in diameter (Figure 2). Setting can occur by thermal polymerization as the material is deposited, by chemical reaction with the atmosphere, by drying, or by photopolymerization. The products of this process are discussed further below. A similar process has been developed at the IFAM Fraunhofer Institute in Bremen and has been used to make parts of stainless steel via free-forming and sintering.[26]

Using a slurry of ceramic powder in cross-linkable acrylate monomer extruded onto a hot plate, we have formed parts from ceramics including alumina and zirconia.[27] These parts are formed at 50–60 vol % ceramic and are then sintered to full density. A similar process has been used to make composite materials with a cross-linked acrylate matrix reinforced by silica powder or chopped carbon fiber.[28] In a modification of the equipment to use a high-pressure extrusion head, thermoplastics and fiber-reinforced thermoplastics have
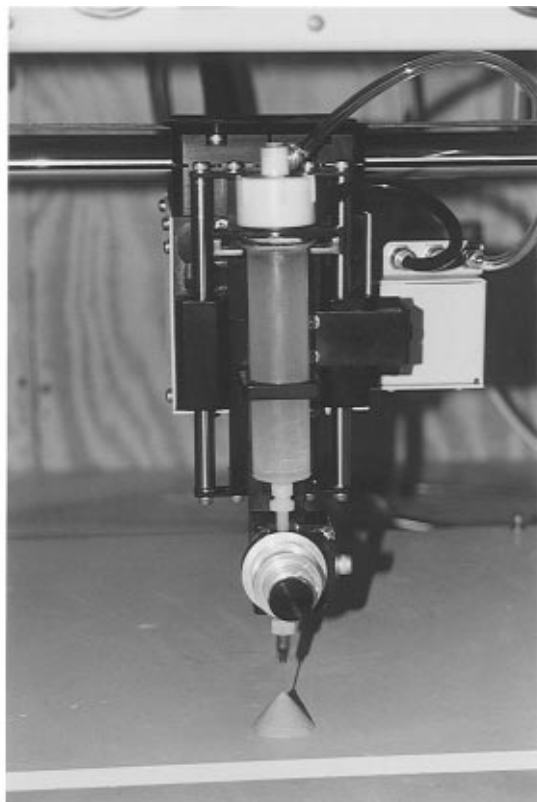
Table 1. Flexural Tests on Free-Formed Acrylate Matrix Composites (Average of Three Samples)

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

and without carbon fiber reinforcement have been formed.[31,32]

Other Methods of Free-Forming. Other approaches include a system of cutting and stacking ceramic green tapes[33,34] or butchers paper and adhesive (Helisys Inc., Torrance, CA).[35] Metal parts have been formed by laser fusion of stainless steel powder carried in a gas stream (Sandia National Labs., LENS process[36]) and by deposition of liquid metal.[37] There are also efforts to make shaped parts by related gas-phase deposition methods, some of which are mentioned below.

These systems all have their advantages and drawbacks for parts production; the interest here is in their implications for new materials.

Chemical Reaction in Free-Forming

As described above, thermal processing based on sintering or fusion and freezing has been used to form ceramics, glasses, metals, and polymers in a variety of SFF machines. Cross-linking polymerization also lends itself well to the process via thermal or photochemical catalysis. While most SFF systems employ conventional thermal processing methods, it is clear that the system should be extendable to produce objects by many types of direct chemical reaction.

This section discusses the relationship between the chemical mechanism and application to free-forming. The next section discusses control of rheology during reaction.

Cross-Linking Polymerization. Cross-linkable resins lend themselves to free-forming processes because they transform from liquid to solid at low extents of reaction and shrink little during curing. Stereolithography initially depended on acrylics and has converted to epoxies. Our reactive extrusion method has used multifunctional acrylates and blends of these with other monomers.

Where it is possible to obtain stable dispersions, ceramic-filled acrylates can be free-formed easily by reactive extrusion.[27] Highly filled monomers show little shrinkage on polymerization.[38] The improved thermal conductivity and lower heat of reaction per unit volume ensures that the temperature rise during polymerization is also limited. Composites can be made at lower loadings of particulate fillers (Table 1). In this case a tougher resin, based on urethane acrylates, is used. Compared to conventional acrylates, these resins have a lower density of reactive groups and so a lower shrinkage.

Table 1 shows an increase in strength and modulus with filler content in line with what would be expected for a filled polymer system.[38] One set of samples were filled by incorporating tetraethoxysilane into the mono-

Figure 2. Reactive extrusion free-forming equipment. (a, top) Moving head writing ceramic slurry onto a stationary substrate. (b, bottom) Fixed, heated, head writing onto a motorized table.

been formed.[29] A process is under development for the production of sintered aluminum parts.[30] Initial samples show an ultimate tensile strength of 100 MPa, an extension to break of 10%, and a density of 2.65 g/cm^3, 92% of theoretical. Epoxy resins (MY721/DDS) with

Table 2. Nylon 6 Formed by Reactive Extrusion SFF, Cured at 165 °C for 4 h, Containing 8 wt % Aerosil R504 SiO₂ as Gelling Agent (Average of 5 Free-Formed or 15 Cast Samples, Range ±10% on Yield Stress and Modulus)

(a) Mechanical Properties, Tensile Test on Rod Sample

sample	yield stress (MPa)	Young's modulus (MPa)	% elongation at break
cast control	83	2250	4.0
free-formed	74	2260	3.0
commercial nylon 6	80	3280	4.0

(b) Thermal Properties by DSC[a]

sample	melt point (1) (°C)	crystallinity (%)	crystallization temp (°C)	melt point (2) (°C)
cast control	216.0	51.1	180.2	214.9
free-formed	218.6	48.0	178.8	218.1

[a] Initial melting point, crystallinity, crystallization temperature on cooling at 10 °C/min, and second melting point on reheating.

mer and allowing this to hydrolyze to silica subsequently. This organic−inorganic hybrid showed a greater increase in stiffness than was seen for the same volume fraction of conventional filler. Chopped carbon fiber was also used as a reinforcement, but the modulus of the cured resin decreased, possibly because of interference with the cross-linking reaction. Fiber-reinforced resins do have the general advantage that the partly cured slurry is tougher, and shrinkage is reduced so that the processing is often simpler.

Linear Polymerization. Cross-linked resins have the disadvantage of being brittle. It would be advantageous to form linear polymers by free-forming. We have had success with poly(vinyl acetate) latex, modified with a fumed silica to provide the right rheology. Extrusion methods have also been applied to molten thermoplastics by fused deposition modeling.[20,29]

Forming a linear polymer during reactive extrusion would require a half-life for the polymerization reaction of a few minutes. This puts severe constraints on the chain length that can be achieved at the propagation rates characteristic of many conventional polymerizations.[39] Those materials which can be formed by reaction injection molding (RIM) will most lend themselves to this approach.

We have had success with a nylon RIM system involving extrusion of liquid caprolactam, sodium hydride as initiator, and isocyanate accelerator plus 8 wt % of a hydrophobic fumed silica as a gelling agent.[40] The mixture is extruded at 80 °C, just above the melting point of caprolactam, onto a hot plate at 100 °C and gels through the thixotropy of the silica suspension plus some slow polymerization. After forming, the parts are immersed in oil to prevent oxidation and are cured at 160−180 °C to induce full polymerization.

Some mechanical and thermal properties of the resulting parts are shown in Table 2. The modulus and elongation to break of nylon 6, like other semicrystalline polymers, are very sensitive to crystallinity and so to the thermal treatment. The modulus of nylon is also especially sensitive to moisture content. The properties given in Table 2 show that free-forming can produce material comparable to commercial RIM nylon 6.

Nylon has the particular advantage for free-forming of strong interchain bonding, giving high toughness at low molecular weights. This makes it easier to achieve good properties in a RIM process than for a polymer where longer chains are needed for toughness.

During the forming, only enough reaction occurs to prevent flow. Most of the polymerization occurs in the subsequent oven treatment. Interestingly, the initiator seems to survive exposure to the air during the forming process, presumably because diffusion of oxygen is slow in the semisolid part.

Alkoxide Chemistry. Since metal alkoxides react rapidly with water to form hydroxide or oxide particles, this can be applied to free-forming. Water can be introduced through reaction with atmospheric moisture during forming, by mixing during forming or by catalyzed reaction after forming of premixed components. The primary problem is in handling the large shrinkage during the conversion from alkoxide and water to oxide.

As part of a project associated with developing manufacturing methods for a lunar base, we wish to make parts from an all-silica system. Any organic material should be recyclable so that the process could, in principle, run with materials indigenous to the moon. Initially this was attempted by reactive extrusion of a mixture of tetraethoxysilane, water, silica, and ethanol. The evaporation of ethanol was intended to provide an initial setting of the slurry by causing it to exceed the critical volume fraction of solids and become rigid. Curing was then intended to occur by heating. These parts slumped badly and could not be formed to a shape.

A second system used ethyl silicate, silica, water, and ethanol. This gelled by evaporation and then was cured by spraying each layer as it formed with an ammonia solution. A high silica volume fraction was critical in order to prevent cracking during curing. Subsequent firing proved unsatisfactory as the silica would not sinter once covered with a layer of alkoxide-derived silica. Replacing the silica with a borosilicate glass allowed parts to be sintered to a density of 100%.

Two organic−inorganic hybrid systems have been formed in our reactive system based on vinyltrimethoxysilane/triethylene glycol dimethacrylate/water and on tetramethoxysilane/poly(vinyl acetate)/tetrahydrofuran with fumed silica as a gelling agent in each case. The first system is set by polymerization whereas the second sets by loss of solvent. The first system free-formed readily, but the second was subject to cracking on drying as the solvent was lost. Successful parts were formed with the second system by writing an open matrix of crossed lines separated by spaces such that each layer dried as individual lines rather than as a solid layer. Highly shrinking materials can generally be formed more readily as an open matrix of lines or as thin-walled shapes.

Gel Mineralization. Many biological tissues form by the deposition of mineral or structural polymer within an existing matrix of water-swollen gel. This could provide a general approach to maintaining shape during free-forming while allowing time for reaction.

Agarose solutions, at concentrations of a 2−4%, gel rapidly when cooled below 60 °C. We have formed gels containing high levels (1−2 M) of calcium chloride by writing a solution at 70 °C onto a plate at room temperature. The shaped solid gel was then allowed to mineralize by soaking in 0.1 and 1 M sodium carbonate solutions. The resulting mineralized gel contains about 10 vol % calcite. This becomes tough and hard when the excess water is removed by slow drying or extraction with acetone, leaving a solid with 70 vol
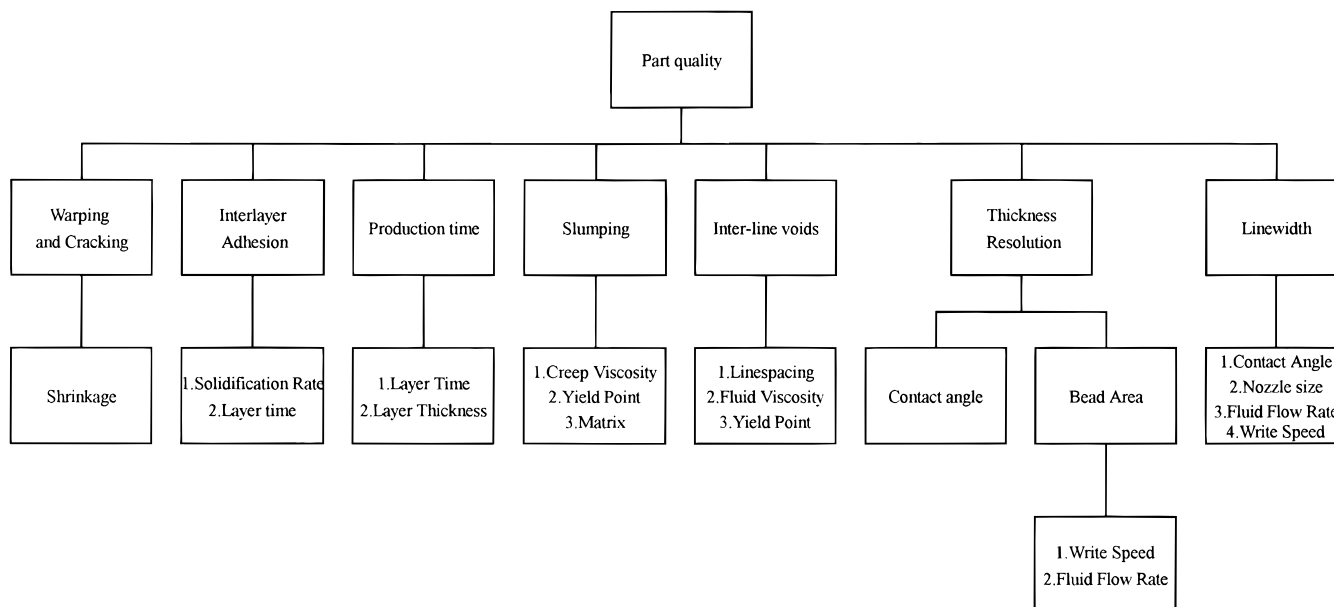
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Figure 3. Effect of material properties and process parameters on reactive extrusion free-forming.

% calcite. This suggests that a cycle based on gel formation, mineralization, and water removal could be used to make composites with high mineral/organic ratios.

We have also formed cross-linked acrylamide gels by extruding viscous acrylamide/bis(acrylamide)/persulfate solutions into an aqueous solution of tertiary amine made viscous with sodium carboxymethylcellulose at 50 °C. Counterdiffusion of the amine and persulfate produces the free radical polymerization initiator. Precision has so far been hard to achieve because the swelling of the reacting acrylamide solution.

Gas-Phase Reaction. There are a number of continuing efforts to use gas-phase laser-induced reaction to form parts. A selective laser sintering system has been used to form alumina shapes by oxidation of aluminum powder in air and to form silicon nitride by laser sintering of silicon in nitrogen or ammonia.[41] A selected-area laser deposition variant is being developed to form silicon carbide by pyrolysis of tetramethylsilane.[42] There are similar efforts to convert laser-induced chemical vapor deposition (CVD) from a film-forming to a shape-making technique.[43−45]

Hence, our current understanding is that solids can be free-formed by chemical reaction if the shrinkages are small or if special measures are taken to accommodate the shrinkage. While systems with a single material feed are convenient, chemical forming would clearly be enhanced by use of two or more material feeds mixed at the point of deposition. This could be achieved by a Y-junction, such as we have already used for materials with variable composition, or by writing successive layers or adjacent lines with different compositions.

General Considerations for Layerwise Processing

In this section we will try to address aspects of the deposition and curing processes that apply to all free-forming techniques. The discussion will be cast in terms of our reactive extrusion approach since we are most familiar with it, but we believe that similar consider-

ations apply to all methods. Thus, line width in stereolithography and selective laser sintering increases as the laser write speed decreases, just as line width in reactive extrusion increases as the writing speed decreases. Likewise, interlayer adhesion depends on similar factors in all these methods. The goal in this section is to understand how the characteristics of a material system of interest impact the ability to free-form a part and what modifications can be performed to achieve acceptable results.

"Acceptable results" in the layerwise processing of a part can be categorized by process *speed* (total build time, including material placement and pauses for curing, etc.), *precision* (accuracy, resolution of object dimensions), and *quality* (closeness to model, final object properties). The impact of key material system characteristics is evident throughout the free-forming process from the initial placement of a liquid as a discrete long bead through the creation of a uniform layer and ultimately to a 3-D body.

Key material system characteristics are the following: (i) liquid properties, including surface tension, visocsty, and yield strength; (ii) solidification kinetics, including reaction rate, mass transfer rate, and heat of transformation; and (iii) shrinkage during reaction. Figure 3 shows as a chart how material properties interact with processing parameters to influence the final part. As with many processing methods, there is a complex tradeoff between the processability of a material and the final properties of the component. The rheology of the slurry is characterized here in terms of the viscosity during extrusion, the yield point under zero shear, and the long-term creep as the remainder of the part is built. Creep is not important if the part is formed in a liquid or solid medium which supports the shape as it forms or if chemical curing occurs rapidly.

Traditional free-forming approaches have selected material systems with object precision as the driving goal. This leads to the extrusion of materials with a high viscosity (1000−10 000 cP)[22,27] or to systems with a solidification time of a few seconds or less. In all cases, reaction shrinkages have been maintained at less
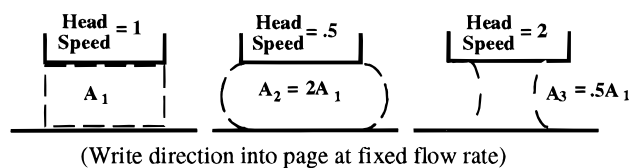
(Write direction into page at fixed flow rate)

Figure 4. Effect of writing speed on beadline geometry under a nozzle, extruding liquid while moving into the paper.

than 2−4%.[14,46] However, the more interesting end of the spectrum for the chemical processing of materials is systems with low viscosity and low reaction rates combined with significantly higher shrinkages. We will discuss the impact of each category of material characteristics on free-forming. This will be followed by the requirements of free-forming software, which must ultimately serve as the control bridge between material characteristics and desired object results.

Liquid Properties. Reactive extrusion shares with other free-forming techniques a relationship between write speed and cross-sectional path area, with operational boundaries defined by the characteristics of the material. The flow of a viscous material through a deposition orifice is controlled by Hagen−Poiseuille flow, in which flow is reduced for high fluid viscosity and small orifice sizes at a given deposition pressure.[47] Once the material leaves the dispensing tip, conditions for stability of the deposited beadline impose a limit to the head speed. The cross-sectional area of the beadline is defined by the ratio of flow rate to deposit head speed. When this area is much reduced below the cross-sectional area of the dispensing tip, the bead will tear, producing gaps in the final part. Excessive head speed also tends to give rise to "castling", wherein irregularities in deposited lines grow into large peaks and troughs in the course of forming multiple layers.

The minimum achievable area at the maximum head speed has a similar geometry to the problem of an axisymmetric liquid bridge (Figure 4), which is stable up to a height limit on the order of the square of the dispensing height divided by π.[48] While liquid properties are not directly involved in this stability limit, the impact of exceeding the stability limit and the ability of a material to "neck down" varies based on the Weber number and the Reynolds number of the liquid.[48] The Weber number contains the magnitude of the surface tension, with low surface tension liquids less susceptible to forming individual droplets. Because it is also associated with splashing, the Weber number is an important parameter in the resolution of individual write paths in the 3-D printing process.[25]

Once a bead has been written, it spreads on a self-similar substrate at a rate proportional to the liquid surface tension and inversely proportional to the viscosity and the square root of the bead area. This parameter grouping is the same as that which controls the rate in sintering processes[49] and capillary flow.[50] Spreading will stop at a contact angle determined by the surface tension opposed by the yield strength of the liquid, both of which may be changing during the spreading process as the material solidifies.

The contact angle, in turn, determines the precision of the part in a direct tradeoff between path width and layerwise resolution (Figure 5). A beadline with a cross-sectional area of 1 mm² which achieves a contact angle of 5° will result in a path width of 3.9 mm and layer
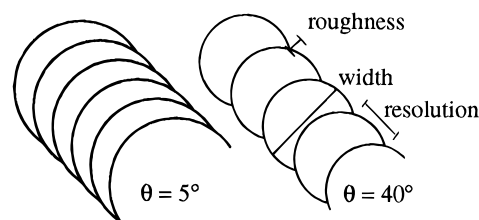

Figure 5. Roughness as a function of liquid contact angle when a stacked series of beads is written.

thickness of 510 μm. Increasing the contact angle to 40°, by increasing the liquid yield strength or solidification rate, reduces the path width to 2.4 mm at the expense of an increased layer thickness of 820 μm.

Also associated with contact angle is the surface roughness of the final part. Many free-formed parts show a stepped surface, especially where the surface is inclined at a shallow angle to the direction perpendicular to the layers (z). This results from the sharp, uniform cure depth of individual layers. Similarly, the reactive extrusion system has an inherent surface roughness created by the cylindrical shape of the deposited bead; the cases presented above have an inherent roughness of 17 and 70 μm, respectively. As with inkjet or laser printing there may be software strategies for dealing with this problem and smoothing the steps. It is also important to note that, in producing a solid, the outer surface (the circumference of a layer) may be written with more care than the interior of the layer. Hence, line width is not necessarily the limiting factor to object build time.

A high viscosity relative to solidification rate is useful in controlling the contact angle and providing time flexibility. The drawback to this, however, is the lack of flow which can create diamond-shaped flaws between individual paths.

A strategy we use extensively in our reactive extrusion process to achieve a desirable amount of flow and a reasonable contact angle is to adjust the rheology to produce a shear-thinning, Bingham plastic liquid with a yield point.[29] For our systems, at least, this is achieved by the addition of a solvent to thin the liquid plus 1−2 vol % fumed silica to develop a shear-dependent rheology; the yield strength of these liquids is established at 5−10% of the ratio of liquid surface tension to beadline cross-sectional area. Viscosities on the order of 100 cP during deposition under shear rates of 100 s⁻¹ allow for dispensing at 10 psi. The fluid viscosity then rapidly increases to greater than 10⁴ cP during the spreading, as the shear rate drops below 10 s⁻¹. This allows a reduced spreading rate and sufficient yield to control the final contact angle. The extreme extension of this strategy is where a stable contact angle is reached after a period of flow by recovery from shear thinning without any solidification occurring; curing is then performed as a separate step on the surface of an entire layer.

Figure 6a shows the increasing strain as stress is ramped at a fixed rate in two viscous solutions of epoxy precursor stiffened with talc particles and with hydrophobic fumed silica. The silica-filled material free-forms readily while the talc-filled material shows excessive flow after deposition. The slurries show similar viscosities, as seen from the similar slopes, at high strain but the fumed silica sample shows much higher viscosity
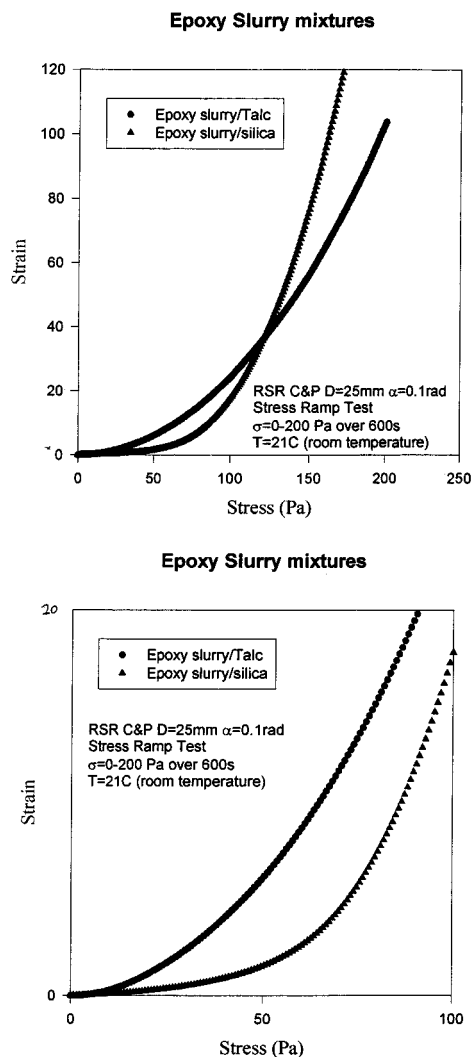
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Epoxy Slurry mixtures

Epoxy Slurry mixtures

Figure 6. (a) Rheology of uncured epoxy resins stiffened with talc (~30 wt %) and with hydrophobic fumed silica (~3 wt %). Strain in oscillating torque as stress is increased to 200 Pa over a time of 600 s. Fumed silica is a satisfactory thickening agent while talc is not. (b) Low stress region of Figure 3.

at low strains. Expansion of the response at low stress (Figure 6b) shows no clear yield stress but does confirm a flattened strain curve at stresses up to about 20 Pa. A similar study of rheology of polymers used in fused deposition modeling has been reported.[51,52]

Solidification Rate. Clearly, solidification during bead spreading modifies the impact of the liquid properties and thus the final contact angle of a bead. Solidification rate also controls the time required between placement of adjacent beads and layers to prevent further shape changes, as well as the interlayer adhesion and shape limitations of the final object.

The spectrum of solidification rates can be classified into none, moderate, and fast, corresponding respectively to no property changes, surface property changes, and bulk property changes of the liquid during bead spreading. No property changes occur during spreading in the "two-stage" solidification strategy, as described above. Under conditions of moderate diffusion rates, the yield strength of the liquid is increased in a surface shell, without changing the bulk properties of the liquid. This occurs in chemically reacting systems or when there is a loss of solvent from the surface during dispensing. If the diffusion is fast enough, the bulk

properties of the liquid change appreciably during spreading, as is the case with solidification due to thermal diffusion.

An obvious objection to a free-forming approach is the long processing time needed to react a sequence of layers. Our rule of thumb has been that reaction should be complete to the point of solidification within 1 min for a layer. This gives reasonable process times for layers that are 0.1−1 mm thick. A typical diffusion coefficient in liquid is $10^{-5}-10^{-6}$ cm^2 s^{-1}, which corresponds to a diffusion length of 0.1−0.5 mm in a minute. This suggests a maximum layer thickness in this range for chemical reactions involving diffusion out of reaction products or loss of solvent. If diffusion, rather than reaction rate, is limiting, it should be possible to write thinner layers faster to obtain faster overall processing. Thermal diffusion is generally much faster than mass diffusion and is unlikely to limit the forming rate in materials that solidify by cooling.

Rapid reaction will result in adiabatic heating of the layer, especially in monomer-rich polymerizing systems with poor thermal conductivity. We have observed waves of reaction, which we attribute to such thermal autoacceleration, moving through partly formed parts. Thus, self-heating can limit the overall rate at which material is deposited. In polymerizing systems, thermal runaway may also be associated with the Trommsdorf or gel effect. The reaction rate increases at high conversions as the high viscosity reduces the termination rate.

With the reactive extrusion system, at least, too rapid reaction, in relation to the time to write a layer, also results in poor interlayer bonding and later delamination.

In other systems there are similar tradeoffs controlling speed and resolution. In stereolithography and selective laser sintering these relate to the extent of beam spreading and the cure profile. In 3D printing these relate to droplet size, splashing, and percolation.

Shrinkage during Reaction. Most conversions from the fluid to the solid state involve a shrinkage. This may be very large, as in the evaporation of solvent to form a film, or only a few percent, as in the curing of epoxy resins or solidification of thermoplastics. Shrinkage must be allowed for in the original part design. However, one potential advantage of the free-forming approach is that such corrections may be incorporated into the design and control software.

At one extreme, a material may be extruded as a thixotropic gel which retains its shape during the forming process and then cures later. Caprolactam loaded with 8% hydrophobic fumed silica is such a system.[31] The MY721/DDS epoxy system, containing 20% dioxane and 7% hydrophobic fumed silica, is similar in that there is only a small shrinkage during forming.[32] An equiaxed part then shrinks uniformly during subsequent oven curing with little distortion and no cracking.

Ceramic systems based on a high volume fraction dispersion of powder in monomer similarly shrink only a small extent as the monomer polymerizes during forming. Although highly filled polymers are very brittle, this small shrinkage does not give rise to cracking if adhesion between the forming polymer−ceramic green body and the substrate is weak. Uniform

shrinkage of 30–50 vol % occurs during the burnout and sintering process, as for most ceramics, and usually does not involve significant distortion if the structure of the green body is homogeneous and the heating rate is slow enough to prevent nonuniform temperatures in the part.

Tough polymers can accommodate linear shrinkages of the order of 10%, and ceramic green bodies can shrink by a few percent without cracking, especially if the part has no thin sections. Such shrinkage normally occurs over several layers below the layer being formed, as excess solvent is lost or as crystallization and curing continue. As long as free-formable materials are limited to small shrinkages, they are also limited to materials that can be molded by conventional means.

In principle, it should be possible to accommodate large volume changes by shrinkage along the z axis (layer thickness) in each new layer as it forms. The requirement is that flow must be possible during the time when most of the shrinkage occurs, during layer deposition. Once the material becomes solid, shrinkage will become uniform in three dimensions, and the new layer may crack. After deposition, a final postcuring process can accommodate significant shrinkage if the kinetics are uniform throughout the part.

Chemical solidification reactions that involve loss of products or reaction with the gaseous or liquid environment should thus be confined to the new layers in order to allow rapid diffusion. Some clear examples of such reactive free-forming, with large volume changes, would greatly expand the number of possible free-formable materials.

Curling and distortion is a problem with any process that forms flat parts and is not wholly symmetric through the sheet. Free-forming processes are by nature very asymmetric; the top surface is made when the bottom surface is already solid. In addition to the standard methods of minimizing distortion, such as adding stiffeners, it may be possible to exploit the flexibility of the free-forming system to add a compensatory distortion to one surface.

Cross-linking polymerizations proceed until the glass-transition temperature of the resin rises to ambient.[53] Reaction in the solid then progresses slowly. At the completion of a stereolithography part, for instance, the lower layers will be more fully cured than the upper layers. During postcuring, the different sections will then shrink differently.[4] It is conceivable that variations in composition or conditions during free-forming could be used to balance the residual stresses that cause warping. As parts come to be made of combinations of materials, strategies for control of warping will become crucial.

Shapes. Free-forming methods allow parts to be made that cannot be machined, for instance those with curved internal channels. At first it seems that some shapes will be very difficult to form, a vertical cylinder with two horizontal arms (a toy soldier) being one example. Free-forming in a powder bed or liquid bath has little shape constraint. Stratasys fused deposition modeling allows overhangs to be formed by adding breakaway supports. We have found that some thermoplastic materials can be extruded into space with no support and little sign of sagging. There have also been a number of examples of free-forming parts with enclosed loose components, such as a closed hollow cube
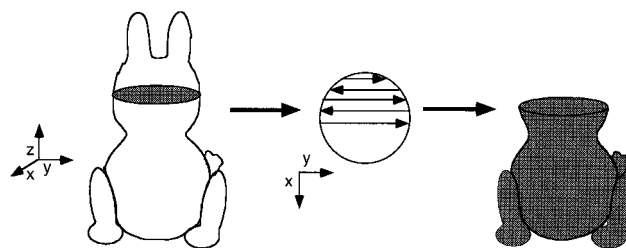

Figure 7. Illustration of a 3D CAD drawing which is then sliced and a path description is written for the slice which is then written onto a forming object.

containing a loose sphere, that could not possibly be machined. Hence, there are no obvious absolute shape limitations.

Free-Forming Software. Much has been published on the software aspects of free-forming.[1] The free-forming software must take a 3D drawing, break this into a series of slices, select a write path for each slice, and then convert this into instructions to the write head (Figure 7). Ideally, a part can be designed using any 3D CAD program and then the information sent directly to any free-forming system. At the machine, the "slicing" and "pathing" programs convert this drawing into instructions to the writing system. This design-to-part flexibility has been quite successful under a limited set of systems when surface data are sufficient to describe the object. There are increased challenges, however, with the expansion of SFF materials, systems, and applications, specifically (1) 3D design software for nonhomogeneous materials, (2) creating models based on data input from existing objects, (3) 3D file interchange format, (4) data manipulation to make a model compatible with a given SFF system, and (5) process control for complex, nonhomogeneous systems where material parameters are continuously changing as the object is built.

Most commercial free-forming machines are designed to be used with a standard CAD program, often Proengineer (Parametric Technology Corp., Waltham, MA; www.proe.com). The ACR extrusion free-forming system uses AutoCAD (Autodesk Inc., San Rafael, CA; www.autodesk.com), a simpler design package, while our experimental systems are programmed from Auto-CAD or Basic. 3D CAD packages are all sufficient for providing the basic solid model required to develop surface data. A basic solid model is also the foundation for concurrent design and analysis; work has been performed on integrating a finite element stress analysis into the design process to allow numerical optimization for structural components[54] or prediction of heat transfer in tooling produced by SFF.[23,24] Beyond this, however, standard finite element packages do not yet seem ready to handle the variation of composition and properties which is possible within free-formed parts.[55]

The de facto standard file format for free-forming has been the STL file, which describes the surface of the object as a series of triangles. STL has allowed for interconversion of object files between the various SFF systems to date. As discussed above, there is a need to move from surface representations to true solid models to perform analysis and design nonhomogeneous internal structures. Conversions between 3D design packages exist through formats such as IGES but are currently limited. A continuing effort is the develop-

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ment of an international standard for the exchange of solid model information, Standard for the Exchange of Product Model Data (STEP).[56] This standard will allow models to be transferred between many different engineering and manufacturing applications, including SFF.

An additional software challenge is the acceptance of 3D input from existing objects. A natural candidate is medical tomography data, which can be converted for use by free-forming systems. Feature extraction and tissue differentiation are currently accomplished based on human expertise, however, requiring much manual modeling.[57,58] Development of automated interpretation is thus required to free-form parts directly from tomography data. There are also various 3D digitizing systems that use a probe or laser to generate a 3D drawing from an object.[59] Touch probes are extremely slow (3−5 measurements per second) but can resolve an object as fine as 1 μm. Optical sensors measure on the order of 50−200 points per second at a resolution of 0.1 mm but have limitations on surface finish to avoid direct reflection of incident light. Once scanned, 3D digitized objects are similar to tomography data. They are currently imperfect surface representations, which work well with simple systems but will require manual manipulation and translation into true 3D models to enable any engineering analysis.

Once a model has been transferred to an appropriate SFF system, it must undergo further manipulation to conform to the system's specific operational characteristics. Examples of this manipulation are optimal part orientation[60,61] and, for parts built without a bath or powder bed, calculation of minimum support structures.[62,63] An additional example of this type of model manipulation is the creation of a negative image of the model for the production of molds and tooling.[23]

Finally, as the range of materials expands, future SFF software will be called upon more to make up for "difficult" material characteristics while maintaining desired object results. Current SFF control software performs simple path planning. An example of this is in systems involving a flow of material; here it is preferable that there are few pen-up/pen-down jumps in each layer and that the write head travels at a constant speed related to the flow rate. Because these control systems often involve simultaneous motion on four or more axes, computation speed can become critical. To get high writing speeds, many systems first generate a set of instructions which are then downloaded to the machine. With the introduction of nonhomogeneous or gradient materials, process parameters will be continually changing. In this case, preprocessing

Table 3. Bending Strength of Tungsten−Alumina Gradient Materials (Four-Point Bend, Two Samples)

	tungsten in tension	alumina in tension
modulus, GPa	218, 227	227, 247
strength, MPa	384, 404	445, 494

of control instructions becomes less desirable. Future systems are thus likely to incorporate sensors to monitor the writing process and provide on-line control.

Prospects for New Materials Synthesis

Gradient Structures. One advantage of the free-forming approach is its ability to deposit a series of materials in successive planes or within planes. A tungsten−alumina functional gradient part was made by depositing first pure tungsten and then tungsten with increasing amounts of alumina up to pure alumina. The green body was hot-pressed to full density in a reducing atmosphere. Table 3 shows the mechanical properties of this material. As would be expected, the bending strength depends on the direction of bending. Also as expected, the metal face is highly conducting and the ceramic face is insulating.

Using the reactive extrusion system, such graded parts can be formed by first setting up a graded reservoir, but a more versatile method is to use a "Y" twinned feed. It is still necessary to match the rheology of the two feed materials and to provide some sort of mixing in the extrusion outlet. When forming gradients of two sinterable materials, such as tungsten and alumina, powder sizes must be selected so that they sinter at similar rates; otherwise, large strains will develop in the part. It would be attractive to sinter individual layers as they are deposited so that widely different materials could be combined into a single part.

The use of the reactive extrusion system to form composites is of especial interest in that the fiber direction follows the writing direction. Our present experience is that the longest fiber must be shorter than the diameter of the outlet nozzle in order to avoid jamming. This would limit fiber lengths to less than 0.1−0.5 mm and provide aspect ratios of 10−50 with conventional chopped carbon fiber. Careful design of the extrusion head may remove this length limitation. Tensile bars can thus be formed with the fiber axis lying along or perpendicular to the tensile axis.[29] This could be extended to the control of the fiber direction to conform to local stress directions, at least in the $x−y$ plane (Table 4). This data is for thermoplastic materials extruded under high pressure. We believe that the lower modulus and strength of these samples, when

Table 4. Mechanical Properties of Thermoplastic Tensile Bars with Write Direction (and Fiber Direction) Parallel or Perpendicular to the Length of the Bar; Compared with Manufacturer's Values for Molded Samples[a]

material	no. of specimens	orientation	modulus exp	modulus manuf	break strength exp	break strength manuf	elongation % exp	elongation % manuf
PEEK	3	parallel	1.7	3.6	59	100	3.3	50
	3	perp	1.8	3.6	88	100	5.3	50
PEEK + 30% carbon fiber	1	parallel	9.4	13	257	233	3.0	1.5
	1	perp	3.6	13	124	233	3.6	1.5
polycarbonate	7	parallel	1.1	2.3	64	70	8.7	130
	6	perp	1.0	2.3	46	70	5.6	130
polycarbonate + 30% glass fiber	8	parallel	3.0	7	106	130	3.8	3.0
	4	perp	1.5	7	61	130	5.8	3.0
PMMA	5	parallel	1.3	3.3	23	41	1.39	1.8

[a] Instron Model 1011; strain rate = 0.2 in./s; load cell = 1000 lb; vertical specimen loading; wedge-action type grip.
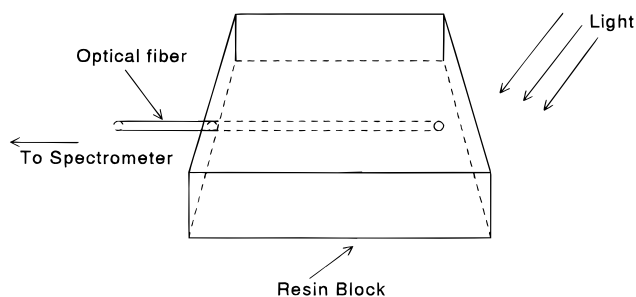
Figure 8. Sketch of embedded optical fiber.

compared to molded material, is due to poor interlayer bonding. The thermoplastic cools very rapidly during extrusion so that adjacent beads do not wholly flow together but trap long pores. Modified deposition methods are being developed to slow the cooling of the bead.

Cima et al. have used free-forming methods to produce slow-release drug formulations where a varying concentration through the tablet, or a particular shape, produces a uniform release rate.[64]

Optimization. This ability to form complex combinations of materials means that the local composition of a part can be adjusted to give optimum performance. This raises a set of difficult questions about whether it is possible to design an object for optimum performance. With the exception of very simple components, it is not usually possible to identify a single simple failure mode for a new part. Hence, it is not possible to focus the optimization on a single property. Also, most finite element analysis packages assume that a single material is being used so it is not really feasible to analyze a series of designs based on an arbitrary blend of two materials. As long as we design with single materials, simple comparisons of properties, such as strength and stiffness, can be quite informative. It is not clear how we will handle the design space for graded components. There is a need for combinations of design, finite element analysis, and free-forming packages that can handle material blends in a unified way.

Porosity. The "Quickcast" stereolithography method[4] reduces the stiffness of a part by replacing the solid interior with a network of struts. In this case, excess liquid must be drained from the part through a small hole after forming. Many free-forming systems would allow controlled porosity to be incorporated in a similar way. Biological materials make considerable use of porosity to provide stiffness with light weight,[65] and there is growing interest in the design and function of cellular materials.[66]

Intelligence. The ability to change materials during free-forming should allow the incorporation of sensors and actuators into parts as they are built. We have produced one example of a component with a built-in optical fiber, but it would be more interesting to free-form the optical paths as part of the process.[32]

An epoxy plate was formed using the system MY721/27% DDS gelled with 7 wt % fumed silica. Halfway through the forming, an optical fiber was placed on the surface with one end just inside the edge of the sample (Figure 8). More resin was then deposited over the fiber. After forming and precuring, the fiber was used to monitor the resin curing and water uptake by illuminating the outside of the sample. That part of the light that was picked up in the fiber was passed into a near-infrared spectrometer. Figure 9 shows the effect of water uptake on the spectrum.
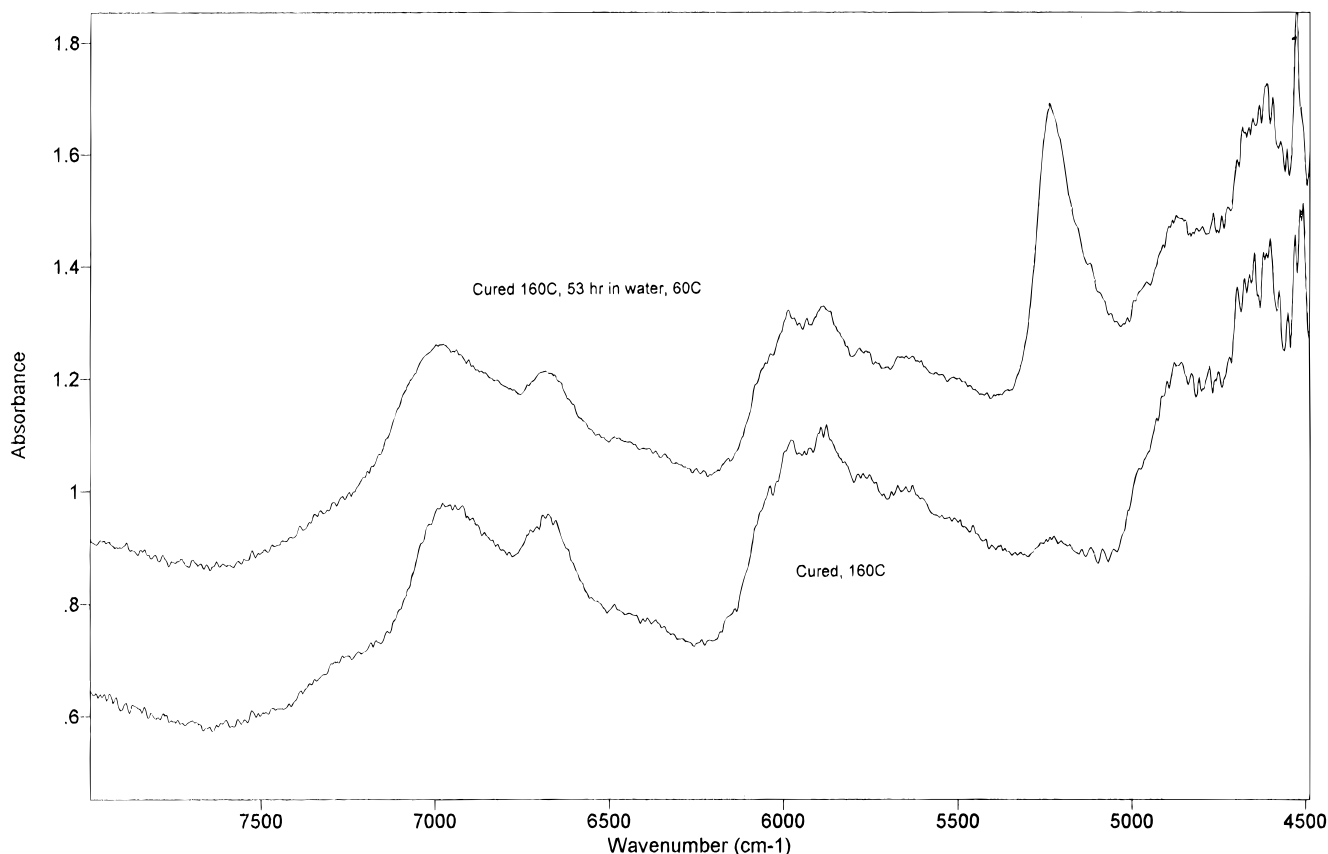

Figure 9. Water uptake by epoxy as monitored by an embedded optical fiber.

Biomimetic Materials. The biological materials mentioned in the Introduction represent one goal of free-forming. A part, such as a human femur, contains a mixture of dense bone and cancellous bone in an arrangement that is apparently optimized to combine the lightness and stiffness of a tubular strut with the broad end sections needed to keep light loadings on the joint. The bone ends are covered with cartilage, a soft material, to allow motion without excessive wear or friction. In addition, the bone contains pathways for nerves, sensors in the synthetic world, and blood vessels. If we substitute piezoelectric actuators for the blood vessels, all the components of bone would be useful as part of an active ("intelligent") strut.

Beneath this gross scale structure, bone is a structural hierarchy.[67] At the micron level, the collagen and hydroxyapatite structure is arranged into plates or concentric cylinders, which may have an important role in toughening the system by allowing microcracking. At the 10 nm level, the material is a composite of highly oriented mineral plates in a collagen matrix. We envisage that these lower levels of the hierarchy could be integrated with the free-forming process in that structure at the micron scale will be driven by phase separation and at the nanometer level by the basic chemistry during a free-forming operation which specifies structure at the millimeter scale.

There has been discussion of the importance of structural hierarchy, for instance in liquid crystal polymers or in car tires.[68] We have not really had the ability to control the different levels of these structures independently. A combination of reactive processing and self-assembly should allow parts with the complexity of a bone to be free-formed.

It is possible to free-form gels in either air or water. We have successfully formed agarose gels, which set rapidly on cooling, and cross-linked acrylamide gels, by extruding a solution of monomer and free radical initiator into a solution of accelerator. It is possible to include a calcium salt in the agarose gel and react the final part with a soluble phosphate or carbonate in order to mineralize it. A 2% agarose gel, containing 23 wt % $CaCl_2$, was free-formed and then was treated with a 6% sodium carbonate solution to produce a gel containing 18 wt % calcite. On immersion in acetone, the gel shrinks strongly as water is lost. The final part is 90% calcite and 10% agarose.

Many variants on this approach are conceivable. To achieve high volume fractions of mineral, it may be sufficient simply to remove the water from the final gel. Water loss may also be driven by osmotic changes if there is binding between the gel and mineral. However, the biological route may be to replace water with mineral in order to avoid shrinkage. This would require a feed of more salts than can simply be included in the starting material. These types of gel-mineral interactions have not been explored.

One difficulty with free-forming biomimetic materials is the large design space which makes optimization very difficult, as discussed above. We no longer have to design only shape, but also properties and orientation. This may require some kind of evolutionary approach parallel to that which occurs in biology, but, one trusts, somewhat faster.

Biomedical Materials. There is a clear opportunity for the application for free-forming methods for surgical prostheses since individually shaped parts can be made in a short time. X-ray tomography could directly provide the data to design the replacement part, thus raising the possibility of manufacturing simple prostheses during the course of an operation.

There is much interest in the role of porosity in allowing tissue ingrowth to provide better bonding to a prosthesis. Current free-forming methods could be used to design the size and orientation of porosity on the scale of 100 μm and up.

The ability to free-form gels also implies that animal or bacterial cells can be incorporated into built objects. This in turn means that functional organs could be formed.[64]

Future

Free-forming methods have already had a major impact on design and prototyping and will have a great impact on mold building. Burns[59] has given enthusiastic scenarios of the future of free-forming methods in manufacturing. The emergence of a laser printer-like technology for manufacturing small parts seems quite feasible. At this level, questions of speed, precision, and resolution are most important and will depend on software, machine design, and materials. This approach will also favor local, flexible, small-scale manufacturing with low capital investments as opposed to mass production. In the development of free-forming as an engineering tool, little attention has yet been given to the potential for materials synthesis.

In the context of new materials, these methods do allow control of microstructure at the level of 100 μm and higher and so will foster the development of new classes of composites. Among the underlying problems that will need to be tackled are the design and optimization of complex composites and properties of graded interfaces. Combinations of ceramics or refractory metals and polymers will depend on our ability to develop localized sintering of the high-temperature materials without destroying the polymer. These methods also provide the ability to incorporate sensors and actuators in materials with their associated connections, but how this will be exploited is still unclear.

The methods all place a premium on rapid reactions leading to solidification. This is in contrast to many chemical processes for the production of raw materials that depend on reactions with a time scale of hours rather than seconds. Thus, in polymers, at least, it may be that new routes need to be explored which would have been regarded as unsuitably fast for bulk synthesis. Current processes depend on either a liquid stream in air or reaction in a fluid or powder. Vapor-phase deposition processes, powder jets, and wet spinning are clearly all possible.

It is natural to think that atomic or nanoscale methods might be used to build large structures, using a scanning tunneling microscope, for instance, as a higher resolution version of free-forming.[69-71] However, sequential processing on this scale will be very slow. Biological processing could be viewed as a hierarchy with cells directly controlling structure at the scale of 100 μm while self-assembly and chemical composition control structures at finer scales. Hence, it seems

reasonable that synthetic parts will be formed by a similar hierarchy of processes, each controlling structure at a different level. For instance, a single particle deposition system[72] could be incorporated as an interchangeable head on an SFF system.

In recent years there has been much development of new materials chemistry where it has not been clear how this would be applied to real components except in the form of thin films. Free-forming methods offer the possibility of a much closer integration between chemistry, design, materials, and processing. It will be interesting to see how this opportunity comes to be exploited.

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