Stereolithography: Making 3D plastic objects the light way

G. Sudesh Kumar

A combination of chemistry, laser control and computer graphics is providing design engineers and manufacturers with a quick and potentially cost-effective tool for turning computer-generated design data directly into prototype plastic parts.

Model building, prototype construction, soft tooling and pattern-making are key steps in any new product design. These steps are often expensive and time-consuming, and account for over half of the time taken for design. Rapid prototyping refers to a range of new technologies for making, in hours or minutes, three-dimensional prototype parts. One particular version of this 'toolless machine design' is a technique known as *stereolithography*[1], also referred to as 'three-dimensional printing' or 'free-form manufacturing'.

Stereolithography, developed and patented by physicist Charles W. Hull[2] in 1986 is a method that automatically builds complex plastic parts by 'printing' successive cross-sections, positioning one on the top of another until the complete part is formed. The process depends on the rapid curing of acrylic monomers by exposure to UV laser. In other words, it is a photopolymerization technology with a new dimension —the third dimension.

Stereolithography apparatus

Essential parts of the stereolithography apparatus (SLA) (Figure 1) include a vat of photosensitive monomer, a laser that generates a small, intense spot of UV radiation, a galvanometer mirror, X–Y scanner, a microprocessor-controlled elevator mechanism, a computer and software for control. The apparatus requires digitized input data from computer-aided design (CAD), computer-aided manufacturing (CAM), computerized axial tomography (CAT) or magnetic resonance imaging (MRI).

The prototyping process begins when a file containing a 3-D surface or solid model is loaded into the control unit of SLA. Based on the specification, the control unit slices the model into a series of cross-sections from 0.005 to 0.030 inches thick. The control unit then directs the mirrors to focus the beam of light so that it solidifies a

2-D cross-section of the specified thickness on the surface of the movable platform. At the start of the model-building process, the platform of the elevator is positioned just below the surface of the liquid photopolymer. The UV laser spot, guided by the computer data, moves in *x*, *y* directions, causing the monomer to solidify wherever it impinges, and thereby forming a thin, solid cross-section on the platform. When the first cross-section is completed, the platform is lowered a step—as little as 0.008 mm. The just-formed solid layer is covered with a fresh layer of liquid. Instructions for the formation of the next cross-section are received and the process is repeated until the complete part is formed. The duration of the object-making varies according to the complexity of the part geometry, size and type of polymer. After the part is finished, the platform is raised from the vat to allow excess monomer to drain. This green part contains unreacted monomer and should be post-cured thermally or photochemically. Curing may take on an average from 2 to 20 h while post-curing may require 30 min. Currently, moulded parts are of 3″ to 6″ on each side. But the goal is to make much larger parts, and make them faster and more precise.
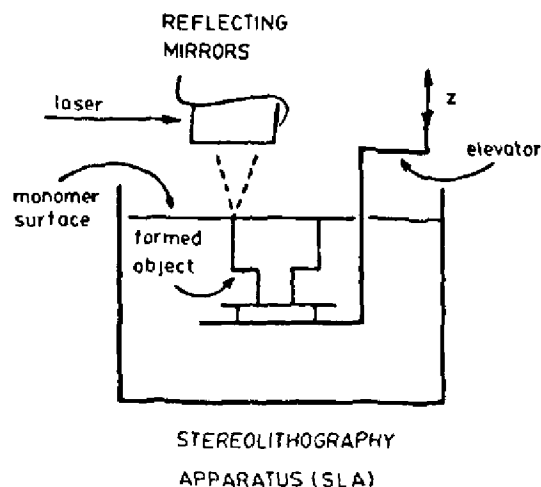

Figure 1. Schematic diagram of a stereolithography apparatus.

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Applications

There are several areas of market application. Most important, at least for now, is industrial design, where models are used to demonstrate form and concept and, engineering design where function is also important. The technique should also be useful to the casting and foundry industry. In architectural design, it could translate blueprints in digital form into a model of a building or a contour map into a site model for area planning.

Design to castings

In the five short years since its product introduction, companies across the globe in industries as diverse as aerospace, automotive, consumer product, computer and electronics have embraced this technology as an integral part of their manufacturing process. Initially, SLA was regarded as the newest design tool for engineers to quickly evaluate their product design. As the technology progressed, it has made rapid transition to the factory floor where numerous case studies attest to its ability in greatly accelerating the productization cycle (Figure 2).

In the aerospace industry, for example, developing a complex part using traditional-moulding methods may take six to nine months and cost an average $25,000. In contrast, the same part could be made with stereolithography in about a week, at a cost of only about $4500. APPLE Computers Inc. uses the process to make models of the plastic housings for its computer equipment. This technique allows speeding up the design process by getting the prototypes made faster and allows one to try out a large number of variations on the same design.

Concept to reality

Ciba-Geigy exhibited a kind of sculpture which never existed before and which was the culmination of computer-aided prototyping technologies to print in three physical dimensions forms which were specified directly in mathematical language. The mathematical conditions for a minimal surface imply that the surface is intrinsically stable and strong as a physical surface. Curvatures in directions on the surface perpendicular to each other tend to be equal and opposite. Figure 3 shows the images of this 'toroidesic' surfaces which were modelled in three-dimensional numerical space[3]—an example of abstraction made concrete by stereolithography. (Topologically it is a torus of many handles containing six directional paths of minimal distance.)

Medical images

Potential medical uses include making anatomical models directly from CAT scan or MRI data to provide patterns for making prosthesis or to help surgeons in their operations. In 1989 IBM was involved in an experimental project at the University of Kentucky to explore medical applications of SLA. The first anatomical structure produced was a plastic model of a jaw bone combining information of CAT scan with the SLA. This model aided surgeons in the reconstruction of the jaw bone. MRI data of a patient was fed to SLA to produce a heart model (Figure 4) at the Center for Photochemical Sciences, Bowling Green, USA[4]. This technique allows medical personnel to routinely examine the three-dimensional representations of the actual organs or bones in question. The next major step would be producing prototypes of organs with identical texture, strength appearance and 'feel'.

Current developments

Current development efforts are aimed at improving lasers, computer systems and photopolymers, all with the idea of making better parts bigger and faster. Increasing size of the parts requires advances in photopolymer technology.

Photoinitiation

Precise, powerful and at times subtle in their effects, lasers are increasingly important tools in polymer science[5]. In recent years, the use of continuous and pulsed laser sources to initiate polymerization has increased significantly. In UV lasers such as He/Cd laser, the life time of the laser tube tends to be shorter. Since high power, stable visible lasers are available and convenient, targeting photoinitiation to this radiation is an obvious goal.

Initiators used in photopolymerizations with UV light generate radicals by mostly intramolecular bond cleavage. For example, ketone acetals[6] absorb in the mid-UV, dissociating into a benzoyl radical which initiates acrylate polymerization (Figure 5). The triplet energy of benzoin ethers is about $72 \, kcal \, mol^{-1}$, which is above the triplet energy of styrene, acrylates and other aromatic residues found in unsaturated polyesters. But the excited states of benzoin ethers are not quenched by monomers since the bimolecular quenching rate is too slow and the photodissociation of benzoin ethers to radical pairs from the excited state is so fast that it cannot be quenched. The photodecomposition of benzoin ethers follows the pathway shown in Figure 5. Norrish Type I cleavage is the preferred decomposition pathway for these compounds and a few bimolecular

Figure 3. Wavefront rendering and stereolithography minimal surface model.

Figure 2. Automotive parts made by SLA Full scale model of an automobile wheel (top); an aerospace machine part (below).

reactions of the carbonyl excited state take place. Another important feature of the benzoin ethers is their high thermal stability. This means that they have long shelf lives. Other photoinitiator systems, at least those that are free-radical initiators, take advantage of similar principles.

Most of the visible initiators produce radicals by electron transfer. Eosin, an anionic dye, with a huge absorption at 514 nm, initiates photopolymerization by a first electron-transfer step[5]. The excited triplet state of the dye is quenched by an electron transfer, generally by an electron donor which forms the radical anion of the dye. It has been shown that in the presence of a tertiary amine such as triethanolamine, the absorption due to the red eosin triplet (λ_{max} 600 nm) is quenched, as the yellow radical anion is formed (λ_{max} 405 nm). The

Figure 4. Model of a heart section from MRI data using visible initiators and a mixture of acrylate monomers.
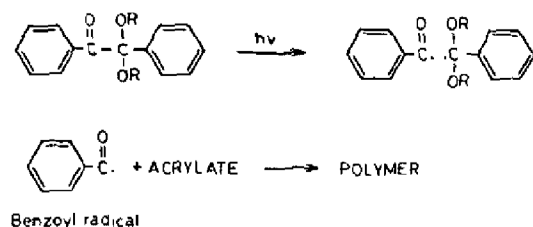
Benzoyl radical

Figure 5. Mechanism of photoinitiation by ketone acetals.

result is an electron-deficient partner and an electron-rich dye residue. The initiating radical is formed from triethanolamine radical cation with a loss of a proton. Therefore eosin/triethanolamine is a well-known photo-initiating system capable of causing radical polymerization at 514 nm, a principal line of argon (+) laser (Figure 6).

Although the choice of photoinitiators is very large, many are highly absorbing and preclude the formation of polymer in anything but very thin films. Accordingly, only very thin slices are formed in each successive scan slowing down the process. In order for a photopoly-merization to occur at any depth below the surface plane of x, y of a highly functionalized crosslinkable monomer solution, the absorbance of the initiator must disappear at a rate that is essentially comparable to that of polymerization. In other words, concomitant bleaching of the initiator is required during the initiation for an effective laser-controlled imaging in all three directions. Neckers et al.[7] reported visible photoinitiators which do precisely that function. These initiators were based on xanthene ring systems.

Another interesting possibility is the application of two-photon photoinitiation in stereolithography. Two-photon reactions involving short-lived intermediates like triplet-state molecules have been explored for holographic recording. As the sensitivity of photoresins is increased for faster curing, they must be handled with rigorous protection from light, and efforts are underway to design 'latent' photoinitiators for this purpose. Spiropyrans and many of its derivatives are characterized by reversible transformations from the more stable 'closed' form to 'open' form upon irradiation with UV to yield a photostationary composition that is both temperature- and wavelength-dependent. The 'closed'
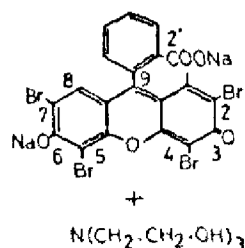

+

N(CH$_2$·CH$_2$·OH)$_3$

Figure 6. Visible photoinitiating system, eosin triethanolamine

spiro molecule itself is colourless or has colour conferred by substituents whereas the coloured form is one in which the spiro ring is 'opened to' give a polar structure stabilized by a number of zwitterionic resonance forms. An equilibrium exists between colourless and coloured forms of spiropyran and that the reaction in either direction can occur photochemically (Figure 7) or thermally. The coloured solutions fade thermally or photochemically to their original state. The interest in using photochromic benzospiropyran in three-dimensional imaging is to use coloured merocyanine form as a visible photoinitiator. The absorption spectra of the two forms, the quantum yield as a function of wavelength for the reaction in each direction, and the rates of thermal reaction and the nature of substituents on spiropyran, are important considerations. The real situation, of course, is much more complex. The idea is to form a coloured ($\lambda_{max} > 500$ nm) merocyanine form from an appropriate benzospiropyran with UV laser and to develop specific conditions wherein only visible wavelength specific to merocyanine effected photopolymerization. A rapid reversal of merocyanine to the benzospiropyran in the absence of UV could be the basis of a two-photon photoinitiation process such that polymerization would occur only at a point where the two different laser sources, one UV and the other visible, intersected. No polymer formation can take place along the UV or visible laser path. Khimura and Sakuragi[8] reported a photochromic benzospiropyran moiety act which is a photoinitiator for radical polymerization under simultaneous irradiation with UV and visible light (Figure 7). This stepwise two-photon excitation of the spiropyran to induce radical polymerization at the intersection of UV and visible lasers may allow formation of an object below the surface layers of bulk monomer.

Photopolymerization

The major themes in stereolithography are to produce

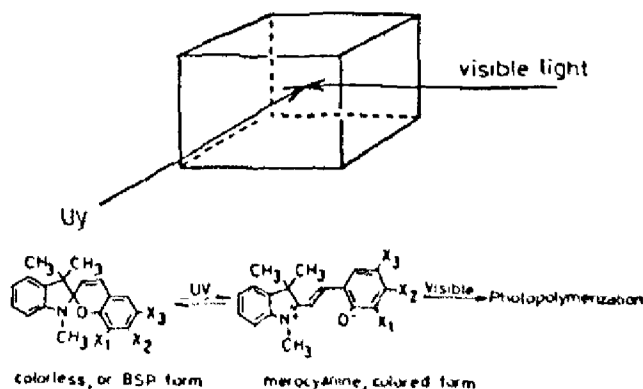colorless, or BSP form   merocyanine, colored form

Figure 7. Two photon photoinitiation. Polymer is formed at the intersection of UV visible lasers beneath the surface

three-dimensional images of a desired texture, mechanical integrity and dimensional stability—soft or rigid, hard or transparent—models that nearly mimic the target object, and with good layer-to-layer adhesion. Clearly, the development of novel photoresin systems is an important target in perfecting stereolithography.

In terms of macromolecular engineering, both the polymerization step and cross-linking step may be carried out simultaneously by UV or visible radiation as in current methodologies or the two processes may be partly or completely decoupled. One way to effect this latter approach is to use systems that are sensitive separately to both visible and UV radiation. It is our interest to achieve the required cross-link density of a polymer network by a combination of dye-sensitized photopolymerization using a visible laser and final shaping and dimensional stability of the object by photocrosslinking using UV radiation (Figure 8). Kumar and Neckers[9] reported a *two-photon photopolymerization* involving dye-sensitized homo- and co-polymerization of oxime acrylates with polyfunctional acrylates followed by UV cross-linking of the residual acyloxyimino pendant groups.

Typically, all the polymerizations were carried out with the argon-ion laser at 514 nm. The mixture to be polymerized consisted of an initiator/cocatalyst (e.g. eosin, triethanolamine), monomer mixture (e.g. bisphenol diacrylate and pyrene-1-carboxaldehyde oxime acrylate) and traces of N-vinylpyrrolidone. Where the laser strikes the monomer solution, solid polymer formed and the length of the polymer spike so obtained in the direction of the laser beam increased. The visible initiators employed effectively underwent concomitant bleaching. Acrylate derivatives of various oximes were used as *comonomers with photolabile pendant groups* for the following reasons: 1) A wide range of oxime acrylates having desired absorption maxima in UV range may be prepared by a one-step procedure from corresponding oximes. 2) Polymers bearing O-acyloxy-imino pendant groups are expected to be photolabile and should participate in photocrosslinking. 3) Selection of monofunctional, low-viscosity monomers as reactive diluents introduces a new formulation latitude. Parallel sets of experiments for shorter periods were carried out as above and the resulting soft gel was irradiated with He–Cd laser (325 nm) to produce much harder spikes. UV-induced cross-linking might proceed by two mechanisms. Intermolecular attack of carboxy radicals generated by the photocleavage of the side chains

$$> N = O - \overset{\displaystyle O}{\overset{\|}{C}} - Ⓟ$$

($> N = O-C-$Ⓟ) on the unreacted double bonds of another chain is a possibility. In other words, the macroradical generated on the polymer acts as a grafting site, leading to intermolecular crosslinks.
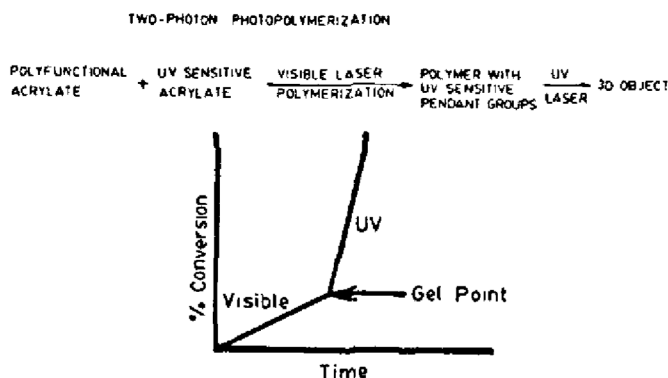

Figure 8. Two photon photopolymerization showing visible light initiated prepolymer formation and UV-induced crosslinking.

Alternatively, carboxyl macroradicals might react with each other, leading to crosslinking.

This two-photon technique makes it possible to achieve differential crosslinking of the polymer network and thus parts can be grown with physical differentiation, for example, between hard and soft areas. Since the polymerization proceeds with kinetically controllable bleaching, the possibility of recreating selectively stained tissues also exists.

Conclusion

Stereolithography is helping designers and manufacturers to overcome a traditional bottleneck in product development. Global markets for new products are becoming increasingly competitive and it is vital for companies to be able to revamp and fine-tune their wares rapidly. The advances in these free-form manufacturing practices are certainly taking product design out of the traditional mould.

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