JULITA JAKUBIAK*), JAN F. RABEK**)

Three-dimensional (3D) photopolymerization in the stereolithography

Part II. TECHNOLOGIES OF THE 3D PHOTOPOLYMERIZATION***)

Summary — A review with 28 references covering 3D computer-aided design (CAD)—computer-aided manufacturing (CAM) devices and techniques used in 3D photopolymerization and micromachining processes applied to make stereolithographic products. The former comprise mechanically scanned devices with a stationary laser spot and optically scanned devices with a moving laser spot, laser types (HeCd; argon-ion) including excimer lasers (Nd:YAG, Nd:YLF) associated with 3D photopolymerization techniques and stereolithography software. Micromachines are reviewed and micromachining processes are described used to make stereolithographic products.
Key words: three-dimensional photopolymerization, CAD and CAM, devices, lasers, stereolithography software, micromachines and micromachining processes.

CAD—CAM devices for 3D photopolymerization

There are two methods of laser irradiation in the 3D CAD (Computer Aided Design)—CAM (Computer Aided Manufacturing) devices [2—5]:

1. The mechanically scanned device with a stationary laser spot (Fig. 1). The laser light spot remains stationary on the surface of the resin vat. The laser drawing speed is adjusted automatically so that the energy deposition is sufficient to photopolymerize the resin composite to the desired cure depth. The first layer formed is adhered to the platform that is positioned slightly beneath the surface of the liquid resin. After completion of the layer, the object is lowered into the liquid resin down at a distance equal to one layer thickness and the next layer is drawn on the top of the preceding layer (Fig. 2). The object is complete after the final top layer has been formed. The platform then rises up out of the pool of the liquid resin and there follow the necessary cleanup and finishing stages.

*) Department of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Cracow, Poland. To whom all correspondence should be addressed.
**) Polymer Research Group, Department of Dental Biomaterial Science, Karolinska Institute (Royal Academy of Medicine), Box 4064, 141 04 Huddinge (Stockholm), Sweden, and Department of Chemistry and Chemical Engineering Technical and Agricultural University, Seminaryjna 3, 85-326 Bydgoszcz, Poland.
***) Part I see [1].

Motorized trolleys micrometrically controlled by a CAD—CAM system, make the laser beam displacements possible along the *x* and *y* axes. The movement along the *z*-axis results from the controlled pumping up of the liquid monomer (Fig. 3a) or lifting up by a motorized trolley (Fig. 3b). The focalizing optics must be lifted up so as to keep the laser beam focalized on the surface of the polymer. A polymerized pattern is thus developed into a thin layer of the monomer solution. It is then necessary to increase the level of the monomer solution after each pass of the laser beam over the monomer surface. The solid object is completed by the layering of many computer generated two-dimensional images on top of the other. The thickness of each layer is controlled by adjusting the monomer solution depth over the most recently completed layer. Since this system depends on a number of motions involving mechanical translation, it is inherently slower than a system of optically translated light beams (Fig. 4). A mechanically scanned pattern device may achieve linear writing speeds of meters per second, while an optically scanned system may attain speeds of hundreds of meters per second.

2. The optically scanned device with a moving laser spot (Fig. 4). The laser light spot moves across the surface of the resin vat in a series of small discrete steps. Motion of the laser light spot is achieved by simply changing the coordinates of the light spot center on the surface of the monomer solution by using scanning mirrors. An electro- or acousto-optic device is necessary to

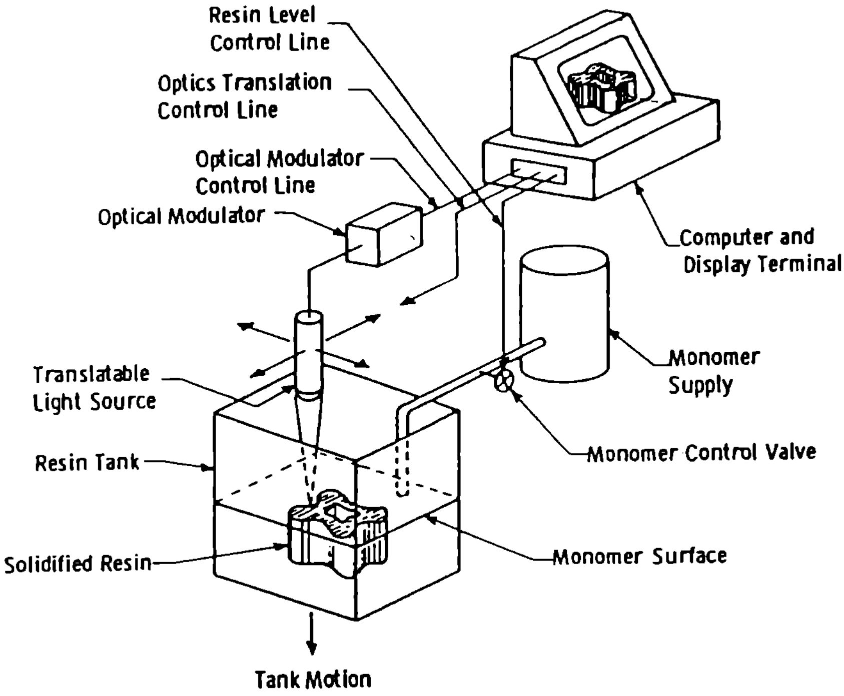

Fig. 1. Mechanically scanned laser 3D CAD—CAM device [2]

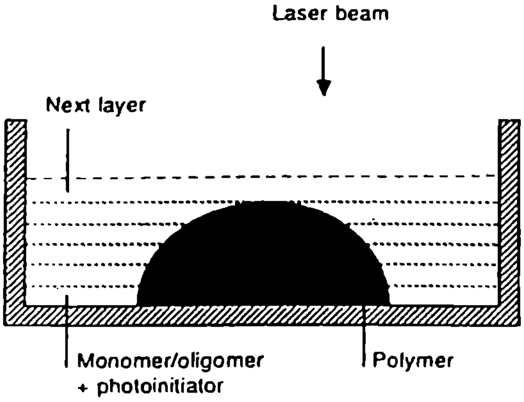

Fig. 2. Layer-by-layer 3D photopolymerization [15]

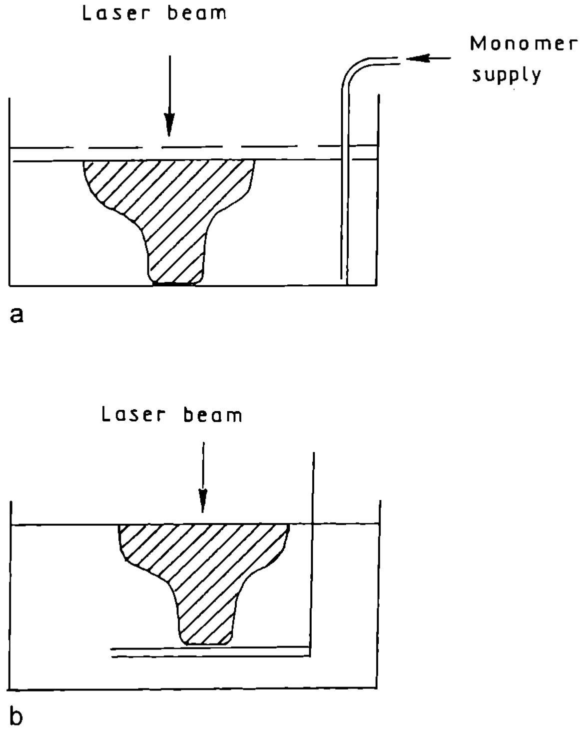

Fig. 3. The movement along the z-axis resulting from: (a) controlled pumping up of the liquid monomer; (b) lifting up by a motorized trolley

turn the laser beam on and off in order to select the area to be irradiated. It is necessary in this system to change the height of the monomer solution surrounding the model as each layer is formed.

Two basic types of lasers are presently used in the 3D CAD—CAM technology [6]. These are the helium-cadmium (HeCd) and the argon-ion laser [7, 8]. These lasers my be tuned to output either ultraviolet or visible wavelengths. However, in terms of power output, the visible capability of these lasers is always several times greater than their ultraviolet capability. In CW operation several to 100 watts are obtained, depending on whether the beam is single mode or transverse multimode. In the 3D CAD—CAM process the HeCd laser will produce outputs of 20—40 milliwatts at a single wavelength of 325 nm. This laser is relatively inexpensive but has a short lifetime owing to the consumption of cadmium. Another disadvantage is the 325 nm wavelength which does not match the major absorption wavelength of many commercial UV photoinitiators [9]. In contrast, argon-ion lasers deliver their UV outputs at wavelengths of 351 nm and 364 nm which are more suitable for UV photoinitiators. These lasers offer signi-

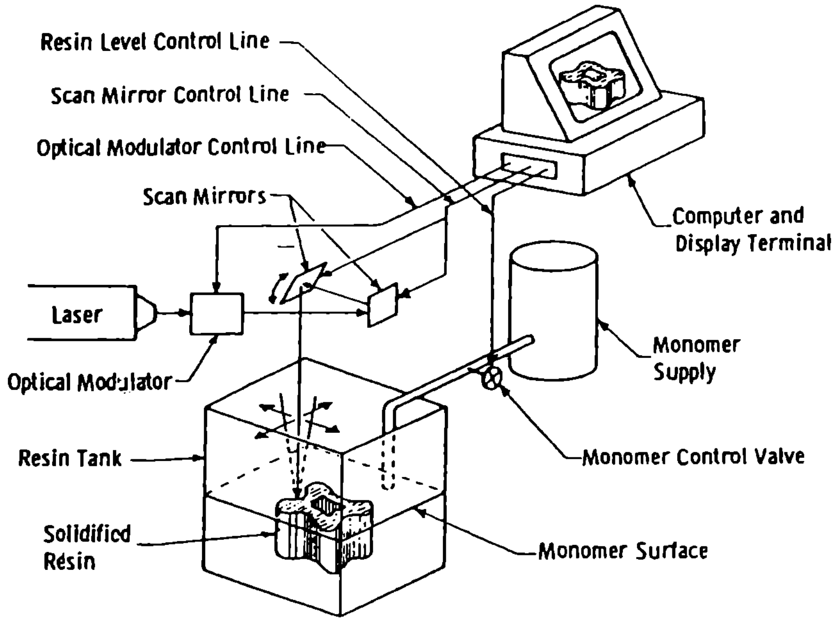

Fig. 4. The optically scanned laser 3D CAD—CAM device [2]

ficantly higher power outputs than do UV HeCd lasers, but they are more expensive because they contain a plasma tube. The power output of an argon-ion laser in the visible range is almost ten times its power output in the ultraviolet range. Replacement of the laser is a significant cost factor in the running of 3D CAD—CAM processes. Visible-light argon-ion lasers are warranted for 2,000 hours and have typically maintained stable power outputs after 5,000 hours. The improved reliability of a visible-light laser will reduce the operating cost. Also the significantly higher power output of a visible-light laser is capable of effecting enhanced vat conversion of the resin. The degree of conversion of the photopolymer formulation in the vat depends not only on the photoreactivity of the mixture but also on the delivered laser power and the laser-scanning technique employed (speed and number of traces).

In some sophisticated research CAD devices excimer lasers are used which emit UV radiation directly, or solid state lasers like Nd:YAG (neodynium-yttrium aluminum garnet, $Y_3Al_5O_{12}$) and Nd:YLF (neodynium-lithium yttrium fluoride, $LiYF_4$) in which frequency multiplication converts their radiation into that of the UV region [7, 8].

The key to the universality of the stereolithographic system design concept is the ability to rapidly direct fo-

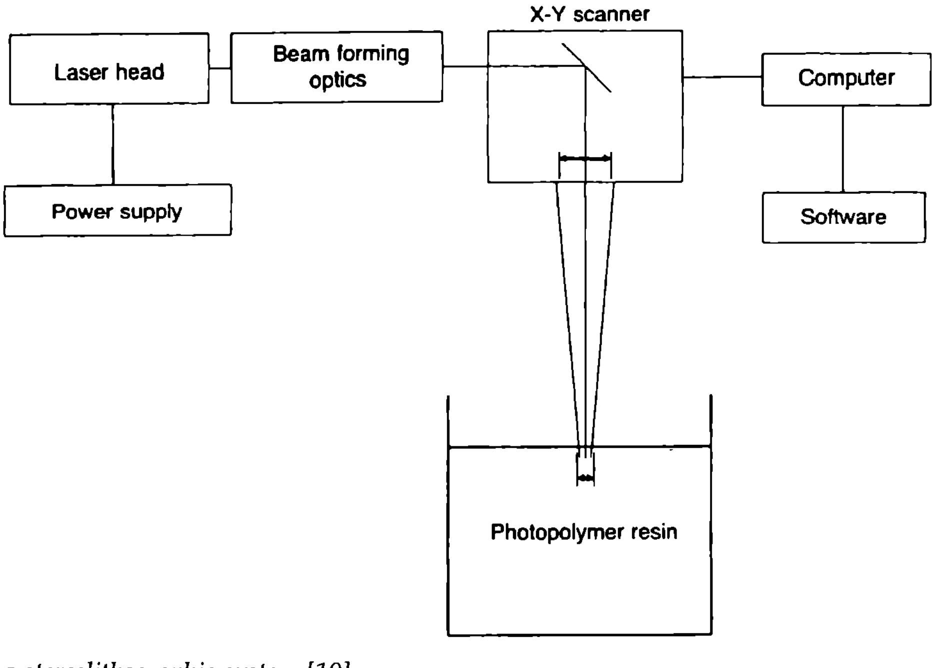

Fig. 5. Elements of a stereolithographic system [10]

cused radiation of appropriate power and wavelength onto the surface of a liquid photopolymer resin to form patterns of a solidified photopolymer [6]. A block diagram of the elements of a direct laser writing stereolithographic system (Fig 5) shows how a laser beam is sent through a beam-expanding telescope to fill the optical aperture of a pair of cross-axis galvanometer-driven beam scanning mirrors. The beam of the continuous wave laser emitting radiation of power at the suitable wavelength, is positioned by using reflecting mirrors mounted on a pair of orthogonal scanning galvanometers, whose position is directed by a computer. The galvanometers provide vector-scanning mode operation and are located in an axially symmetric position. To obtain high speed, the galvanometer-driven scanning mirrors must be low inertia and small in size. The lasers are focused to provide an illumination spot between 200 and 300 μm in diameter on the liquid resin surface. The laser radiation must have very high radiance to provide a tightly focused spot on the surface of the photopolymer located at a substantial distance. The laser's depth of field at the focus is inversely proportional to the laser wavelength and directly proportional to the focus-spot diameter.

Each method of laser irradiation requires the use of an individual mathematical CAD model:

1. Stationary laser spot [4, 11, 12]: The CAD model allows computation of light intensity, absorbed light, photoinitiator concentration, monomer concentration, and temperature profiles, as a function of time, for the exposed reaction zone and for the surrounding monomer/polymer mixture. This CAD model allows to predict how conical or "bullet-shaped" test pieces will be formed by short-term exposure to a stationary laser beam.

2. Moving laser spot [4, 10, 13]: The CAD model allows light intensities, concentrations and temperatures to be functions of the three spatial coordinates (x, y and z) and time (t). Figure 6 shows a region of exposed material where laser spot is moving along the surface in the positive y-direction ($x = 0$ and $z = 0$). This CAD model allows to predict how temperature profiles vary with time as the light spot moves in the positive y-direction (Fig. 7). The results obtained indicate that, as the laser scans, (a) an appreciable rise in temperature quickly occurs, (b) the maximum temperature reaches a steady state value, and (c) the temperatures decay back to ambient rather slowly. This model can be used to investigate process dynamics in layers varying in thickness, with different laser intensities, exposure time physical and chemical parameters, and kinetic equations. In practice, measurements of concentration and temperature profiles during photopolymerization of a liquid monomer after exposure to a laser can be carried out by employing an interferometric method. A device can measure *in situ* time dependent index of refraction profiles which are then analyzed and converted to thermal and fraction of conversion profiles [14].

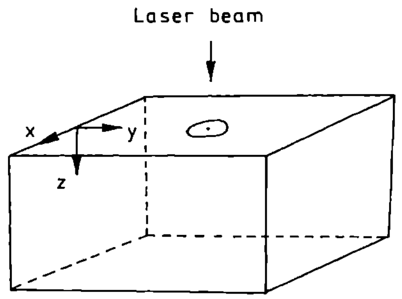

Fig. 6. Region of exposed material used for the development of the moving spot model [13]

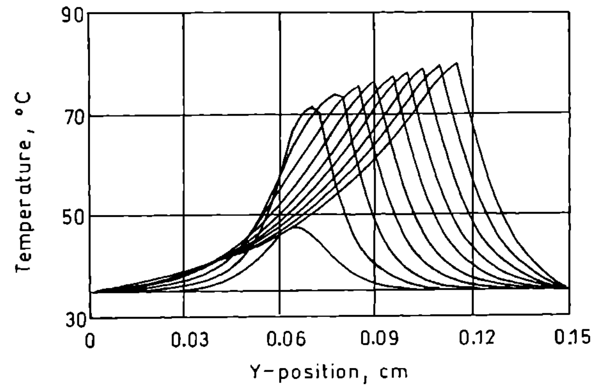

Fig. 7. Temperature profiles along y-axis as obtained from the moving spot model. Plot time increment is equal to 0.1 second [13]

3. In the biphotonic 3D photopolymerization (*cf.* [1]) two perpendicular pulsed laser beams emitting light with energies E_1 and E_2 are focused on the same spot (Fig. 8) [15]. This system removes all mechanical motion of the model and requires only the movements of scanning mirrors, which reduce the time to produce a model. Moving and focalizing two laser beams fast onto the same spot with precision better than 0.1 mm is technically difficult. High-energy laser beams are required to obtain multiphotonic absorptions.

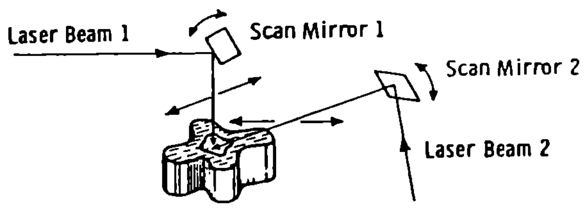

Fig. 8. Principle of the multiphotonic 3D photopolymerization by crossing two laser beams [15]

Stereo-lithography (SL) software is the "brain and central nervous system" that makes the 3D CAD—CAM process come alive [15], whereas photopolymer chemistry, laser physics, optics, viscous fluid dynamics, CAD technology, servo technology, motion and process control, and electrical and mechanical engineering belong to the "SL body". The SL software consists of two components or parts [16]:

— *part preparation software* which involves CAD model verification, model placement and orientation, support generation, assignment of build and recoat attributes, production of cross-sectional slices, and the convergence of all components into the appropriate build file;

— *process control software* which uses the build file produced by the preparation phase to control the entire build process on the SL apparatus.

In the last decade the 3D CAD—CAM technologies have been fully introduced onto the market [3—5, 17, 18]. For technical information on the commercially available 3D CAD—CAM devices, contact Corporate Headquarters 3D Systems, Inc., 26081 Avenue Hall, Valencia, CA 91355, USA, e-mail: woodsm@3dsystems.com, website at http://www.3dsystems.com or European Office, 3D Systems GmbH, Röntgenstrasse 41, D-64291 Darmstadt, Germany, e-mail: info@3dsystems-europe. In Poland, 3D devices are located at the Institute of Mechanics and Construction, Technical University of Warsaw, the Institute of Machine and Automatization, Technical University of Wrocław and ZELMER Works, Rzeszów.

Advantages and disadvantages of 3D photopolymerization

The most important advantages of the 3D CAD—CAM photopolymerization process are [6]:

— rapid translation of a design to a physical form,

— shorter turnaround time and reduced cost of parts and products that require frequent design (*e.g.*, aerospace, automotives, medicine, stomatology),

— rapid generation of new molds and patterns,

— manufacture of parts that are difficult to prepare by conventional milling or casting techniques (*e.g.*, hollow turbine blades or bone joints),

— application to short production runs (<50—100),

— easy replication of three-dimensional electronic data (*e.g.*, mathematical equations, medical imaging, topographical maps).

The most important disadvantages of the 3D CAD—CAM photopolymerization process are:

— Small laser light penetration depth (0.1—0.2 mm) through the monomer layer.

— Variation of the duration of curing and post curing stages with the degree of complexity of part geometry, part size, monomers formulation, and type of the photoinitiation system used. Photocuring can average from 4 to 48 hours, while the post-curing process may last up to 30 minutes [19]. The 3D photocuring of the largest and most complex part is a multiweek and even a multimonth's long oparation.

— Depending upon the power of the laser and the scanning pattern used, the exposure process results in monomer conversions that are far from complete (50—95 %). Additional curing is usually facilitated with a post exposure or heat treatment process.

— Local overheating and bubble formation resulting from thermal effects of photopolymerization which raise the temperature up to as high as 100°C.

— The tendency of the "green" product to swell in the liquid resin. Swelling is highly dependent on the degree of conversion (photoinitiator efficiencies) and resin composition [9, 20].

— The linear and volume shrinkage (*cf.* [1]).

— Curl distortion (*cf.* [1]).

— The thermal strain that causes deformation of the final part.

— The surface tension effects which make it difficult to keep the resin surface perfectly flat.

— Poor mechanical properties of the photocurable resin used as compared with those of general resins applied in plastic molding.

— Computer programming of the three-dimensional models requires a lot of calculation time. The 3D CAD—CAM takes sometimes a long period of time, a matter of weeks, to carry out the total process from design to production.

— High cost of the 3D CAD—CAM devices ($50,000—$500,000) [19, 21].

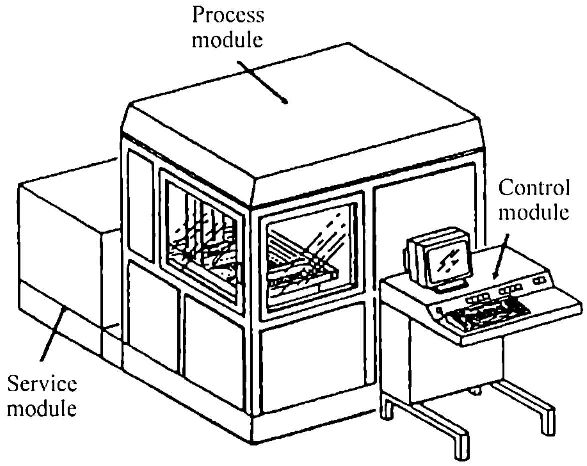

Fig. 9. Simplified 3D CAD—CAM SLA-500 Build Station diagram [3]

Nevertheless, by the end of 1994, only the 3D Systems had installed as many as *ca.* 500 3D CAD—CAM devices [5]. Figure 9 shows a simplified diagram of the 3D CAD—CAM SLA-500 Build Station (produced by Corporate Headquarters 3D Systems, Inc., USA).

Micromachining process

There is a special 3D CAD technology to produce "micromachines" like a micro-motor 100 μm in diameter, a tiny gear train or a turbine and others [22—28]. Typical micromachines consist of parts made with a precision of about 0.1 μm to 100 μm. The micromachines have found wide applications to surgical operating tools, artificial organs, turbine or piping inspecting tools, very light aerospace devices, highly integrated robots, precise stationary machines, precise and sensitive mechano-electronic sensors and so on. A micromachinig device is shown in Fig. 10 [3]. This forming device is connected with a control computer and works in the sequence shown in Fig. 11. The sequence is the same as that in the 3D CAD—CAM process. The scanning device can control exposure conditions more precisely than the photomask method does (Fig. 12).

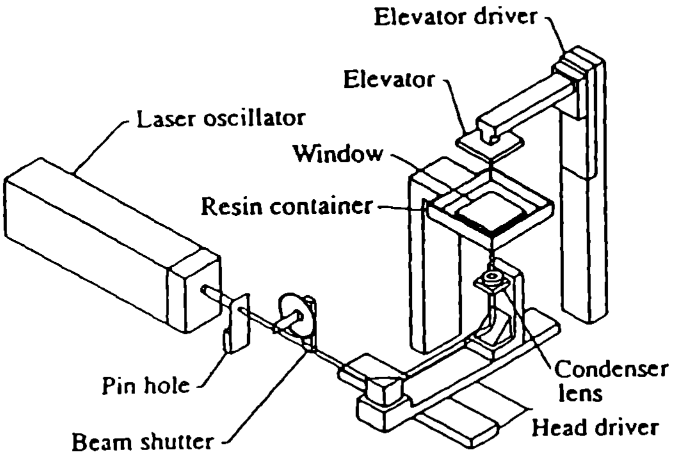

Fig. 10. A micromachining device [22]

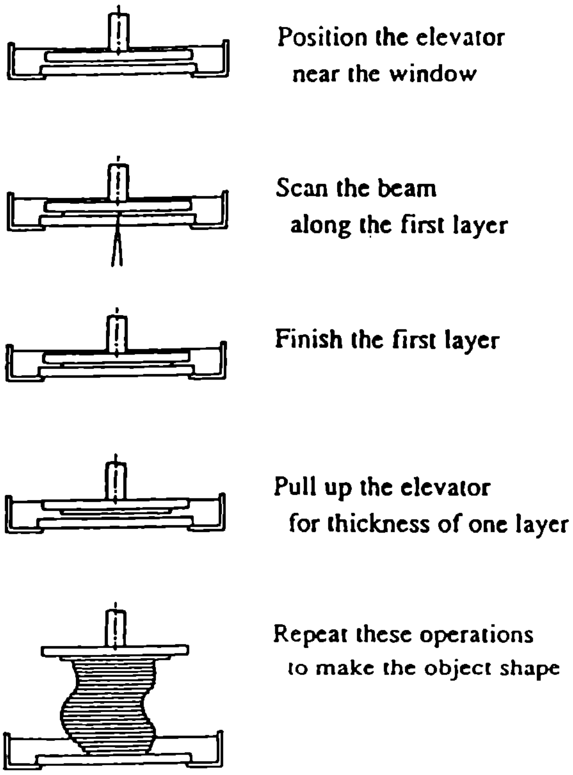

Fig. 11. Forming sequence [22]

The width of the solidified polymer along the thickness is affected by the shape and intensity distribution of the irradiated laser beam and diffraction and ab-

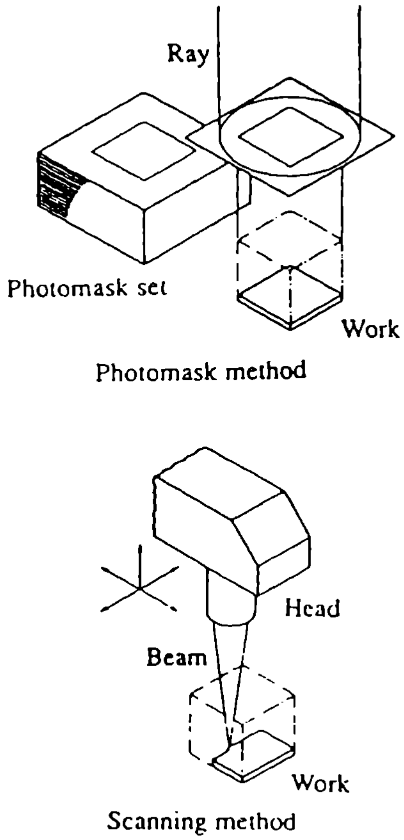

Fig. 12. Methods to realize partial exposing [22]

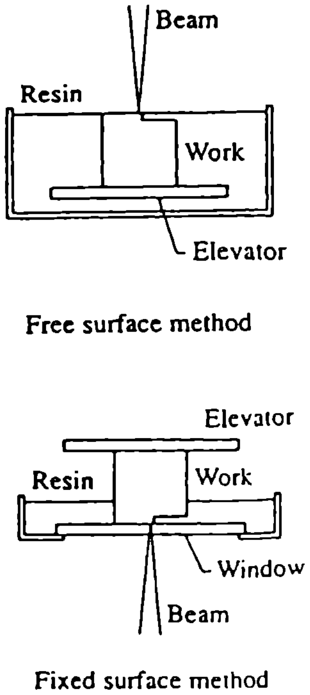

Fig. 13. Methods to control resin surface [22]

sorption of light within the polymer [23—25]. In order to produce micro-polymer structures with a high aspect ratio, a constant width of the solidified polymer along the depth is essential. When a laser beam is irradiated onto the liquid resin, the solidified width of a polymerized sample changes along the depth.

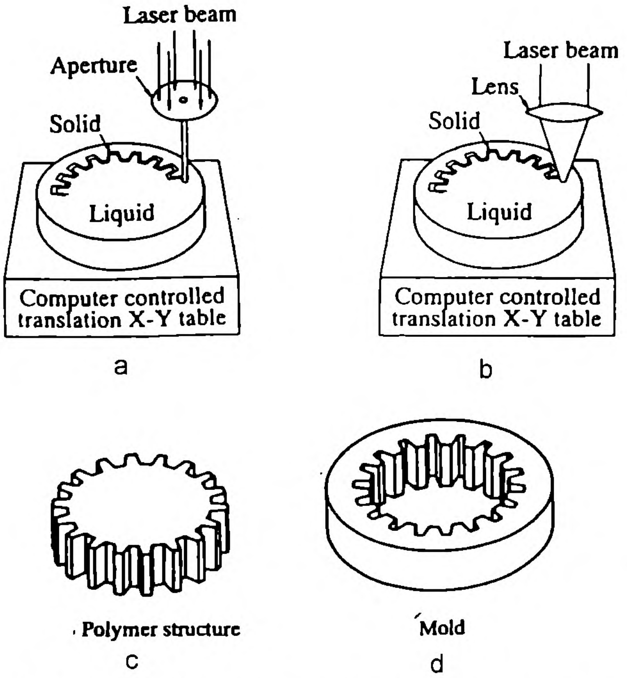

Fig. 14. Schematic diagram of the manufacturing of a micromechanical gear part by the photomask method [23, 26]

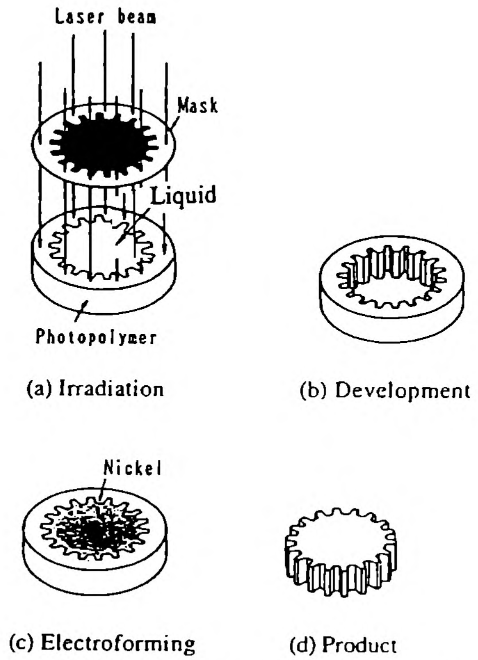

Fig. 15. Schematic diagram of the manufacturing of a micromechanical gear part by the scanning methods: (a) direct shaped beam writing; (b) direct focused beam writing [25, 26]

The depth solidified in the resin is linearly increased according to the light density in the exposure spot. It is hard to control the position of the threshold light amount as designed to form a microscopic object, since the light is hardly attenuated by absorption in such a short path. In the micromachining process, a very precise control of the exposure light amount is required [25, 27]. The "fixed surface method", but not the "free surface

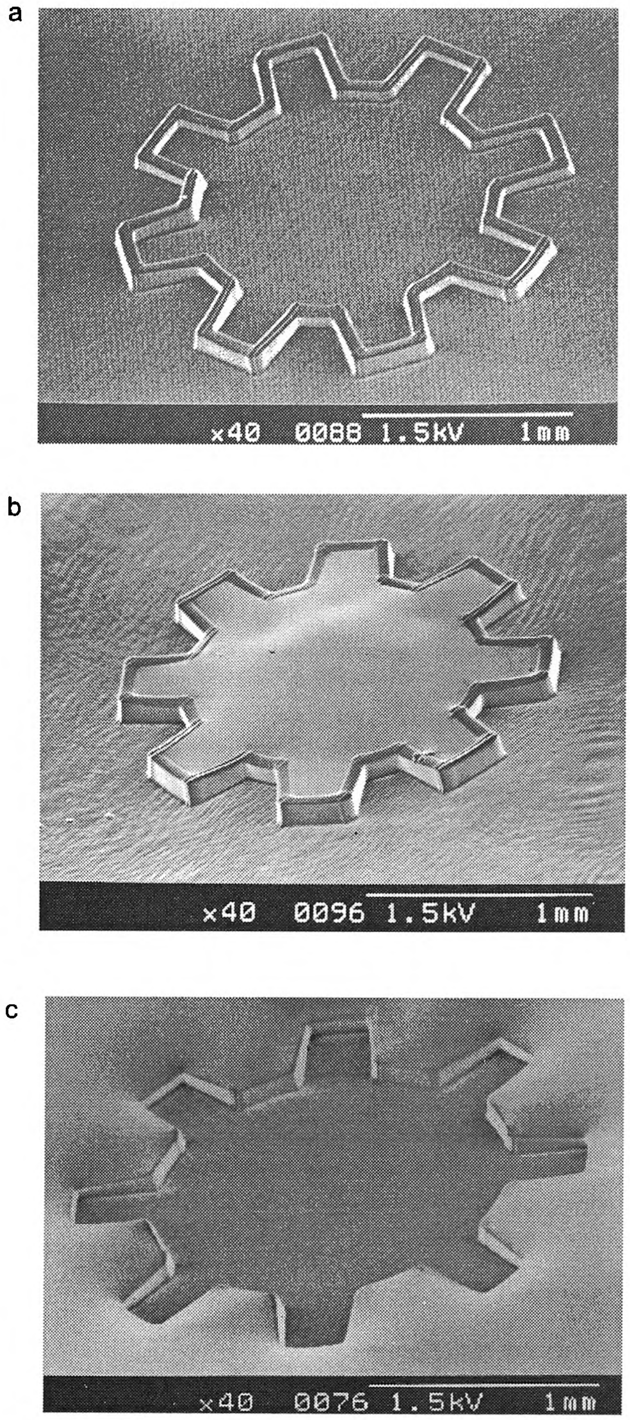

Fig. 16. Polymer microstructures: (a) direct beam writing, (b) polymer microstructure, (c) mold [25, 26] (provided by Prof. K. Yamaguchi, Department of Mechanical Engineering, School of Engineering, Nagoya University, Nagoya, Japan)

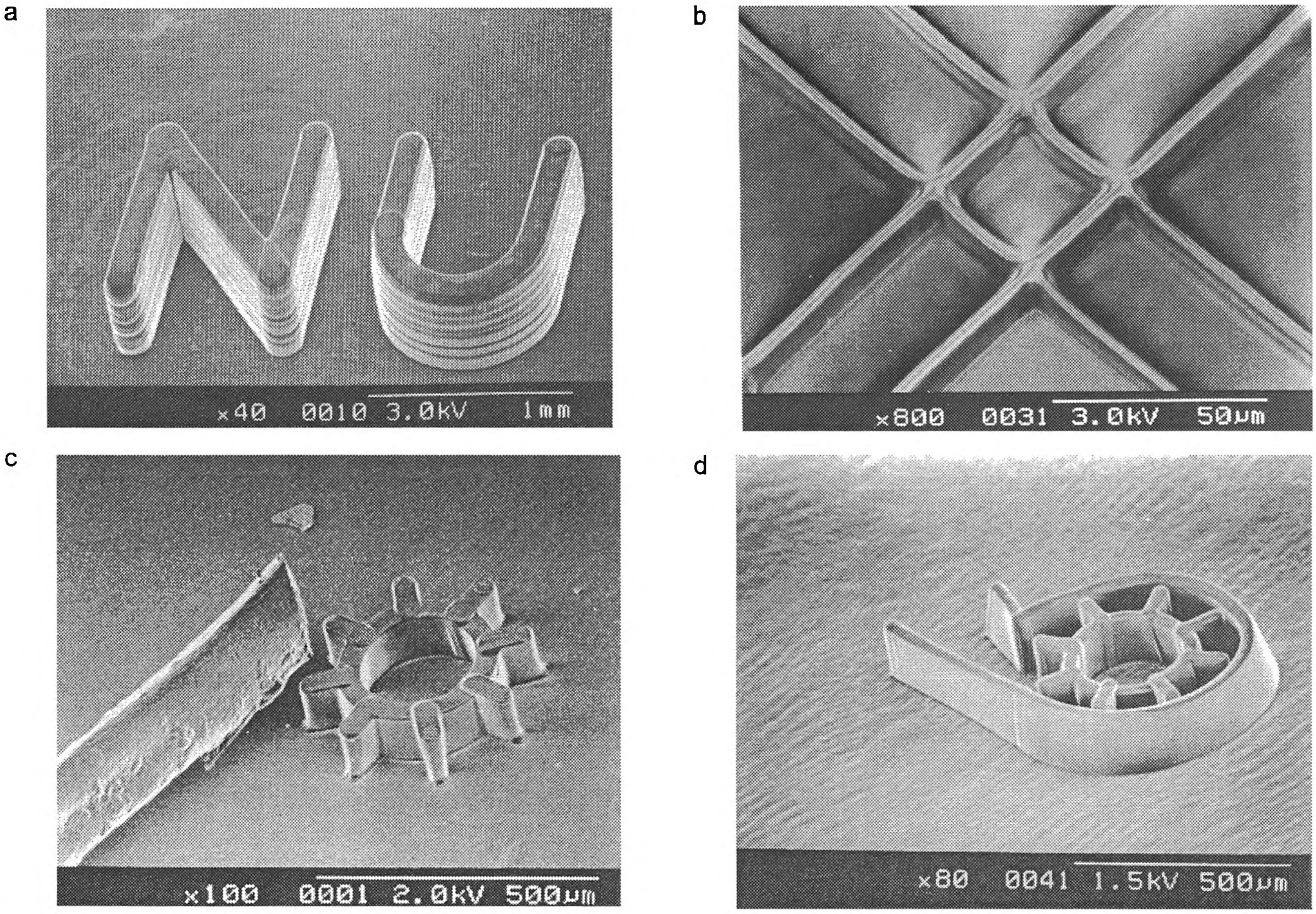

Fig. 17. Polymer microstructures produced by direct focused beam writing: (a) letter pattern, (b) microcell, (c) micro gear and (d) micro pump [25, 26] (provided by Prof. K Yamaguchi, Department of Mechanical Engineering, School of Engineering, Nagoya University, Nagoya, Japan)

method" (Fig. 13), can easier control the resin surface with a higher forming resolution and accuracy. The theoretical models and basic equations to shape the solidified polymer have been given elsewhere [23—29].

The micromachining process equipped with the CAD system allows to design small micro-mechanical parts within several hours [22—27]. The schemes employed to produce a micromechanical part such as a gear, by the photomask and the scanning methods, are shown in Fig. 14 and Fig. 15, respectively. The desired product

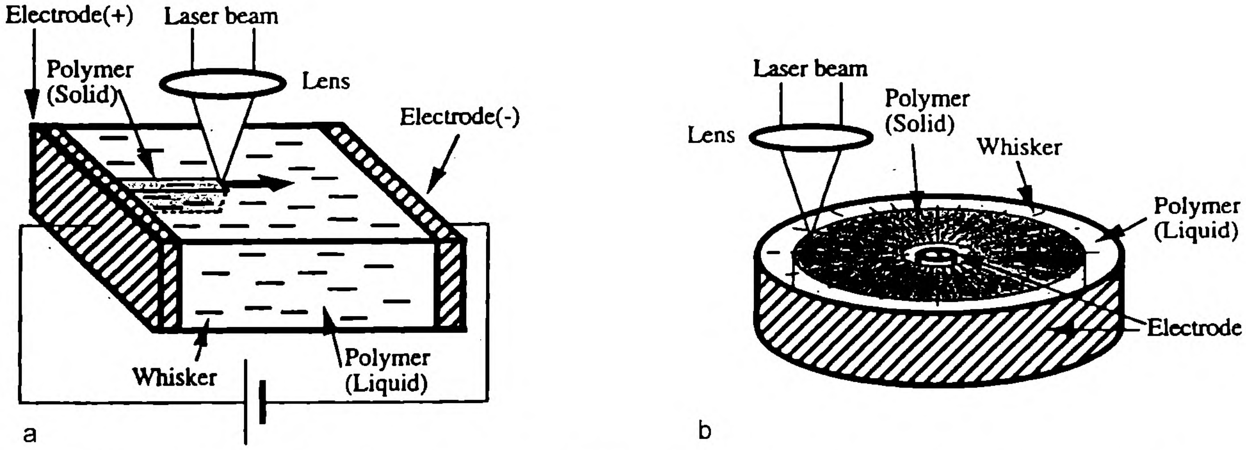

Fig. 18. Schematic diagram for manufacturing unidirectional whisker reinforced micro-parts: (a) straight line whisker alignment; (b) radial whisker alignment [27]

shape is obtained by scanning the entire area by using controlled exposure. Direct laser writing along the contour produces a micro-gear as shown in Fig. 14c. When writing on the outer side of the contour, a mold is obtained as shown in Fig.14d. Further mold filling processors yield products made of metals, plastics and ceramics [23, 25]. The most common process is electroforming, in which nickel or copper material is deposited into a polymer mold. In Fig. 16 and in Fig. 17 are shown polymer microstructures produced by direct beam writing.

Addition of the TiC whisker to the photopolymerizing resin has reinforced micro-mechanical parts [27]. The TiC whiskers have a small diameter (0.5—2 μm), and a high strength (10.5 GPa) [27]. In this method, TiC whiskers are added to a liquid monomer fomulation. The mixture is put into a vessel which has electrodes (Fig. 18). By applying direct current (200 V/mm DC) to the electrodes, the axis of the whisker is aligned along the direction of the line of the electric force in the monomer mixture with TiC. Polymerization occurs under the UV laser irradiation while the direct current is being applied. The irradiation is carried out by a direct focused beam writing along the contour micrographs of the solidified polymer. The direction of the whisker is perpendicular or radial to the beam writing direction. The shrinkage is restrained by the whisker and the strength of the final micro-mechanical parts is increased.

REFERENCES

1. Jakubiak J., Rabek J. F.: *Polimery* 2000, **45**, 759.
2. Castle P. M., Sadhir R. K. in: "Lasers in Polymer Science and Technology: Applications", Vol III (Eds. Fouassier J. P., Rabek J. F.), CRC, Boca Raton, Florida 1990, p. 37.
3. Jacobs P. F. in: [18], p. 79.
4. André J. C., Corbel S.: "Stereophotolithographie Laser", Polytechnica, Paris, 1994.
5. Jacobs P. F. (Ed.): "Stereolithography and Other RP&M Technologies: from Rapid Prototyping to Rapid Tooling", Society Manufacturing Engineers, Deaborn 1996.
6. Stenson P. H., McLean C. H.: *Proc RadTech'92 North America*, Northbrook, Illinois, USA 1992, p. 62.
7. Rabek J. F.: "Experimental Methods in Photochemistry and Photophysics", Vol. II, Wiley, Chichester 1982.
8. Clerc M., Mialocq J. C. in: "Lasers in Polymer Science and Technology", Vol. I (Eds., Fouassier J. P., Rabek J. F.), CRC Press, Boca Raton, Florida, 1990, p. 1.
9. Murphy E. J., Sullivan M. G.: *Proc. RadTech'92 North America*, Northbrook, Illinois, USA, 1992, p. 68.
10. Hug W. F. in: [18], p. 59.
11. Flach L., Chartoff R. P.: *Proc. RadTech'90 North America*, Chicago, Illinois, USA 1990, p. 52.
12. Flach L., Chartoff R. P.:"A Computer Model for Laser Photopolymerization in Solid Freeform Fabrication Proceedings" (Ed., Beaman J. J.), University of Texas, Austin, Texas, USA 1990, p. 155.
13. Chartoff R. P., Flach L., Lightman A.: *Proc. RadTech'91, Europe*, Edinburgh 1991, p. 471.
14. Anderson R. E., Lightman A. J.: Proc. 2nd Intern. Conf. on Rapid Prototyping, University of Dayton, Dayton, USA 1991, p. 33.
15. Cabrera M., Jézéquel J. Y., André J. C. in: "Lasers in Polymer Science and Technology", Vol. III (Eds., Fouassier J. P., Rabek J. F.), CRC Press, Boca Raton, Florida 1990, p. 73.
16. Manners C. R. in: [5], p. 119.
17. Bernhard P., Hofmann M., Hunziker M., Klingert B., Schulthess A., Steinmann B. in: "Radiation Curing in Polymer Science and Technology", Vol. IV "Practical Aspects and Applications" (Eds., Fouassier J. P., Rabek J. F.), Elsevier Applied Science, London 1993, p. 195.
18. Jacobs P. F. (Ed.): "Rapid Prototyping & Technology: Fundamentals of Stereolithography", Society of Manufacturing Engineers, Deaborn 1992.
19. Deitz D.: *Mech. Eng.* 1990 (Feb.), 34.
20. Murphy E. J., Sullivan M. G.: *Radiation Curing* 1989 (Feb/March), 3.
21. Ashley S.: *Mech. Eng.* 1991 (April), 34.
22. Takagi T., Nakajima N.: *Proc. RadTech'93 Asia*, Tokyo, Japan 1993, p. 451.
23. Yamaguchi K., Nakamoto T., Abbay P. A., Mibu S.: *Trans. ASME* 1994, **116**, 370.
24. Abraha P. A., Nakamoto T., Yamaguchi K., Karyawan Y. in: "Advancement of Intelligent Production" (Ed., Usui E.), Elsevier Science, London 1994, p. 564.
25. Nakamoto T., Yamaguchi K., Abraha P. A., Mishima K.: *J. Micromech. Microeng.* 1966, **6**, 240.
26. Yamaguchi K., Nakamoto T., Abraha P.: *JSME Intern. J.* 1996, **39**, 387.
27. Yamaguchi K., Nakamoto T.: "Rapid Product Development" (Eds., Ikawa N., Kishinami T., Kimura F.), Chapman & Hall, London 1997, p. 159.
28. Cabrera M., Bertsch A., Chassaing J., Jézéquel J. Y., André J. C.: *Mol. Cryst. Liq. Cryst.* 1988, **315**, 223.
29. Schwarzel R. E., Wood E., McGinniss V. D., Weber C. M.: *Appl. Lasers Ind. Chem.* 1984, **90**, 548.

Received 2 III 2000.