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Industrial photochemistry XXIV. Relations between light flux and polymerized depth in laser stereophotolithography

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Abstract

The stereophotolithography process allows a three-dimensional object to be built by layer-by-layer, space-resolved, light-induced polymerization of a liquid monomer into a solid polymer. The relationship between the light penetration depth in the photoreacting medium, the scanning speed of the laser beam on the surface of the resin and the laser power has been studied. Experimental measurements have been performed and compared with a kinetic model. Empirical laws of evolution of the polymerized depth vs. macroscopic parameters have also been determined allowing the optimal operating conditions in stereophotolithography to be defined. © 1997 Elsevier Science S.A.

Keywords: Laser stereophotolithography; Light flux; Polymerization; Polymerized depth

1. Introduction

In the laser stereophotolithography process, a model of the object to be built, stored in the memory of a computer, is virtually sliced in layers of a chosen thickness. Thus, layer-by-layer coordinates of contour lines or surfaces are obtained. The use of light-induced polymerization of a liquid resin allows three-dimensional objects to be built without tooling or moulding. Some manufacturing processes have been patented [1,2] and developed industrially. These processes have some common points with two-dimensional photolithography, but involve the third dimension of space; as a result, they have been named stereophotolithography (SPL) processes [3,4].

In these processes, the different layers of the virtually sliced computer model are successively manufactured by space-resolved, light-induced polymerization of a liquid monomer into a solid polymer. The deflection of a UV laser beam, obtained using two low-inertia galvanometric mirrors, induces the phototransformation. Thus, every layer of the object to be built is obtained vector by vector. When a slice of the object is finished, the addition of a new layer of thephotoreactive medium on the already polymerized part enables the manufacturing process to be continued. The stacking of the layers leads to a three-dimensional physical part.

One of the main interests in the SPL technique comes from the use of networking resins photopolymerizing in long chains leading to a cross-linked network polymer. A photoinitiating product or system is added to the reactive medium to produce free radicals (in the case of acrylate monomers) or cations (in the case of epoxy resins), and induces the polymerization reaction [5]. The power of the lasers used to initiate such photopolymerization processes is rather low, typically between 10 mW and 1 W, which makes the SPL technique economically attractive.

Nevertheless, this process suffers from the shrinkage of the polymer during the photopolymerization reaction, and from poor coupling between the use of photons and the phototransformation, which may result in deformations in the objects or layers which do not adhere to others.

In this paper, we define the relationship between the light penetration depth in the photoreactive medium, the scanning speed of the laser beam on the surface of the resin and the

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laser power. Experimental measurements are performed and compared with a theoretical model.

2. Theoretical basis

In the standard operating conditions, a laser beam does not possess a homogeneous light flux density over its cross-section. A gaussian distribution and circular symmetry are observed, which induce polymerization ratios and profiles showing variations in both time and space. This is particularly prejudicial to a correct resolution of the manufactured objects.

2.1. Light absorption phenomena

The resolution of the layer-by-layer manufactured parts is expected to depend only on the thickness of the layers; the surface roughness is expected to depend essentially on the geometry of the object to be built (Fig. 1).

The surface roughness should be linked directly to the angle between the surface and the vertical direction; however, the situation is more complex due to optical and photochemical phenomena which are difficult to control precisely. If thin polymerized layers can be obtained, we must be aware that the local polymerized depth depends on the local flux of active photons and on the irradiation time. Therefore, in a first approximation, a laser-induced photopolymerized point (obtained without scanning) has a shape defined by the gaussian energetic distribution of the light beam. A bidimensional model allows a good representation of this volume because of the circular symmetry of the problem.

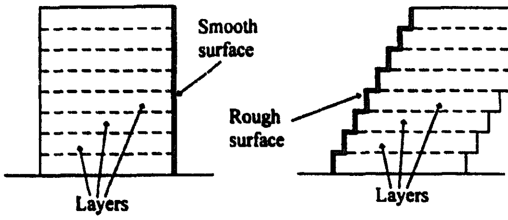

Fig. 1. Influence of the geometry of the object on the surface roughness.

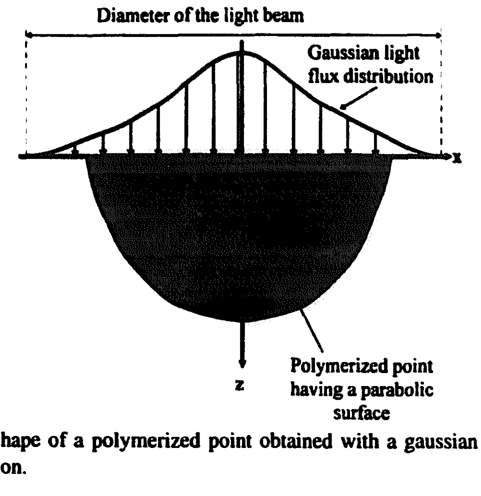

Fig. 2. Shape of a polymerized point obtained with a gaussian light flux distribution.

In the following calculation, Oz is the laser beam axis, with the origin point O fixed on the surface of the monomer, and Ox is an axis orthogonal to Oz, allowing the local spatial light flux distribution to be defined (Fig. 2). $\Phi_{\min}$ is the minimum light flux density needed to achieve the liquid–solid phototransformation of the resin when the irradiation time lasts for Δt. Two laws then rule the photopolymerization phenomenon:

- the Beer–Lambert law

$$\Phi(z,X)=\Phi(0,X)10^{-\epsilon cz} \tag{1}$$

- the gaussian light flux distribution

$$\Phi(0,X)=\Phi_{\max}10^{-X^2} \tag{2}$$

where c is the concentration of the photoinitiator in the resin, ϵ is the absorption coefficient at the irradiation wavelength and $X=x/(1.51\sigma)$ where x is the distance from the point O and σ is the width of the light beam.

The local light flux distribution is obtained by combining these two relations

$$\Phi(z,X)=\Phi_{\max}10^{-X^2}10^{-\epsilon cz} \tag{3}$$

The equation of the boundary surface between the liquid and the solid is given by

$$\Phi(z,X)=\Phi_{\min} \tag{4}$$

which is equivalent to

$$z=\frac{1}{\epsilon c}\left[\log\left(\frac{\Phi_{\max}}{\Phi_{\min}}\right)-X^2\right]=\mu\left[\log\left(\frac{\Phi_{\max}}{\Phi_{\min}}\right)-X^2\right] \tag{5}$$

where $\mu=1/(\epsilon c)$ is the optical thickness.

In a more simple way, Eq. (5) can be written as

$$z=a_1-a_2X^2 \tag{6}$$

where a_1 is a parameter which depends on the resin and on the irradiation time and a_2 is a parameter which depends only on the resin.

The polymerized volume is then a paraboloid. Since a_2 only depends on the characteristics of the photopolymerizable resin, the polymerized volume has a paraboloidal shape irrespective of the irradiation time.

We recently demonstrated that secondary effects due to variations in the refractive index during the photopolymerization process can exist, which also induce variations in the polymerized depth [6]. In the case of low optical thicknesses and photoinitiators which do not photobleach, the refractive index effects, resulting in the confining of the active radiation, are negligible [7].

2.2. Consequences on the resolution of manufactured parts

An evident consequence of the paraboloidal shape of every polymerized point, which has been observed qualitatively by Kodama [8], is that, even in the case of a favourable geometry of the object (such as a vertical column), smooth sur-

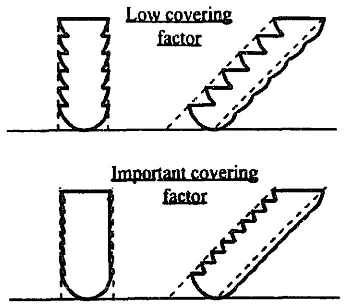

Fig. 3. Defects in the manufactured objects induced by a gaussian light flux distribution.

faces cannot be obtained. To control the resolution as well as possible, the covering factor (equal to the ratio between the polymerized depth and the layer thickness) must be chosen accurately (Fig. 3). Precise focusing of the laser beam on the liquid surface helps to obtain better resolution. Nevertheless, even if the loss of resolution is reduced, the paraboloidal shape of every polymerized point remains present and must be taken into account.

To face, as well as possible, all geometries encountered in the manufacture of three-dimensional objects, a compromise must be made when choosing the covering factor. A process in which the covering factor is optimized point by point cannot be considered, since it would be too complex and would need prohibitory calculation times. Nevertheless, a more precise experimental knowledge of the polymerization phenomena involved in the SPL technique will allow computational adjustments which may lead simultaneously to a better resolution of the dimensional specifications and to a low surface roughness, without any local modification of the thickness of the layers. As the ratio between the price and speed of computers is constantly decreasing, this type of solution will soon be economically advantageous.

Another way to improve the resolution of objects manufactured by the SPL process is to decrease the layer thickness. Nevertheless, the time needed to build the object will then increase strongly.

3. Experimental results

3.1. Simplified model of evolution of the polymerized depth

The polymerized depth and width can be deduced from Eq. (5)

$$z_{\max}=\frac{1}{\epsilon c}\log\left(\frac{\Phi_{\max}}{\Phi_{\min}}\right)\ \text{(depth)} \tag{7}$$

$$x_{\max}=\left[\log\left(\frac{\Phi_{\max}}{\Phi_{\min}}\right)\right]^{1/2}\ \text{(half-width)} \tag{8}$$

Many experiments were performed with a single scanning of the laser beam on the surface of the resin. The depth and width of the polymerized threads thus obtained were measured. The influence of three parameters was studied:

P, the power of the laser beam (50, 100, 150 and 200 mW);
s, the scanning speed (10–150 mm s^{-1});
c, the concentration of the photoinitiator in the resin (1, 2, 3 and 4 wt.%).

The photoinitiator used was 2,2′-dimethoxy-2-phenylacetophenone (DMPA, Aldrich) and the monomer was Diacyl 101 (Akzo Chemicals).

Theoretically, the curves showing the evolution of the maximum polymerized depth vs. the square of the half-width (X) are straight lines. Their slopes are given by

$$\frac{z_{\max}}{X}=\frac{1}{\epsilon c}=\mu \tag{9}$$

In a first approximation, the experimental measurements are straight lines as shown in Fig. 4. The evaluation of the slopes (Table 1) confirms the linear evolution of the polymerized depth with the square of the half-width. Nevertheless, Fig. 4 clearly shows that the points corresponding to low-power irradiation (100 mW) are positioned above the average curve, whereas those corresponding to high-power irradiation (150 and 200 mW) are clearly under this curve. This indicates that the ratio between the polymerized depth and the square of the half-width mainly depends on the con-

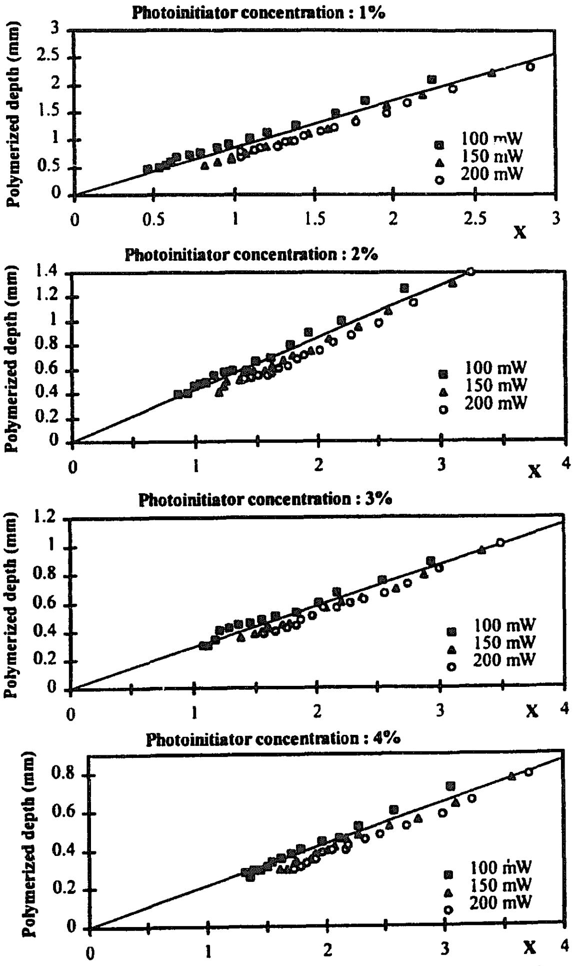

Fig. 4. Polymerized depth vs. X (the square of the half-width).

Table 1
Experimental verification of Eq. (9)

Concentration of photoinitiator (wt.%)	Measured slope	Product of slope × concentration
1	0.87	0.87
2	0.42	0.84
3	0.27	0.81
4	0.21	0.84

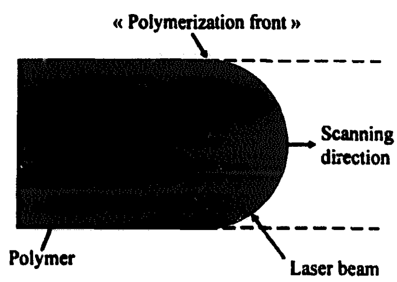

Fig. 5. Diagram of linear scanning.

centration of the photoinitiator in the reactive medium, but as the irradiation power increases, the value of this ratio decreases slightly.

It is rather surprising that such a simplified model is in accordance with the experimental data; nevertheless, we only compared the relative values of the slopes, and did not prove that the absolute value is the optical thickness $\mu = 1/(\epsilon c)$.

In the simple model presented above, an important consideration has not been taken into account: the polymerized volume is calculated in the case of a spatial light flux distribution stable in time, but the experimental polymerizations are obtained by scanning the laser beam on the surface of the resin. In the measured samples, the polymerized volume is therefore the result of the combination of many instantaneous light fluxes, as the scanning is performed. At each moment, the light flux distribution corresponds to the intersection of the cylindrical light beam, with a gaussian energetic distribution, with the plane surface of the liquid resin (Fig. 5). Since the previous model is in good agreement with the experimental results, the light flux distribution resulting from straight scanning must be close to a gaussian distribution, the irradiation time being proportional to the ratio between the light beam diameter and the scanning speed.

3.2. Empirical laws of evolution of the spatial resolution

As shown previously, the experimental data exhibit general tendencies which can be expressed by empirical laws taking into account the influences of both the incident light flux and the photoinitiator concentration.

In Eq. (7), Φ_{max} is related to the laser beam power and Φ_{min} depends, for a given monomer, on the quantity of photoinitiator added in the photopolymerizable resin and on the scanning speed s (equivalent to the inverse of the irradiation time $1/\Delta t$). If both the incident light flux and the irradiation time are fixed, the polymerized depth is given by

$$z_{max} = k_1 - k_2 \log(\Phi_{min}(s)) \tag{10}$$

Consequently, we represented the experimental results by tracing log s vs. the polymerized depth (Fig. 6). The curves obtained for the given concentrations of photoinitiator are very close to straight lines. These lines are almost parallel when the laser beam irradiation power is modified. We propose an empirical law of variation of the polymerized depth

$$z_{max} = \frac{1}{b_2(c)}(b_1(P,c) - \log s) \tag{11}$$

where z_{max} is the polymerized depth (mm), P is the power of the laser beam (mW) and s is the scanning speed (mm s^{-1}). It was not possible to find correlation relations for the different values of $b_1(P,c)$, but the average values of $b_2(c)$ are summarized in Table 2.

In the transverse direction, and referring to Eq. (9), the curve showing the evolution of log s vs. X is theoretically a straight line. The experimental curves are very close to straight lines (Fig. 7), but their slopes (obtained by exponential smoothing) show irregular variations between two values (-0.56 and -0.65). A numerical evolution law of

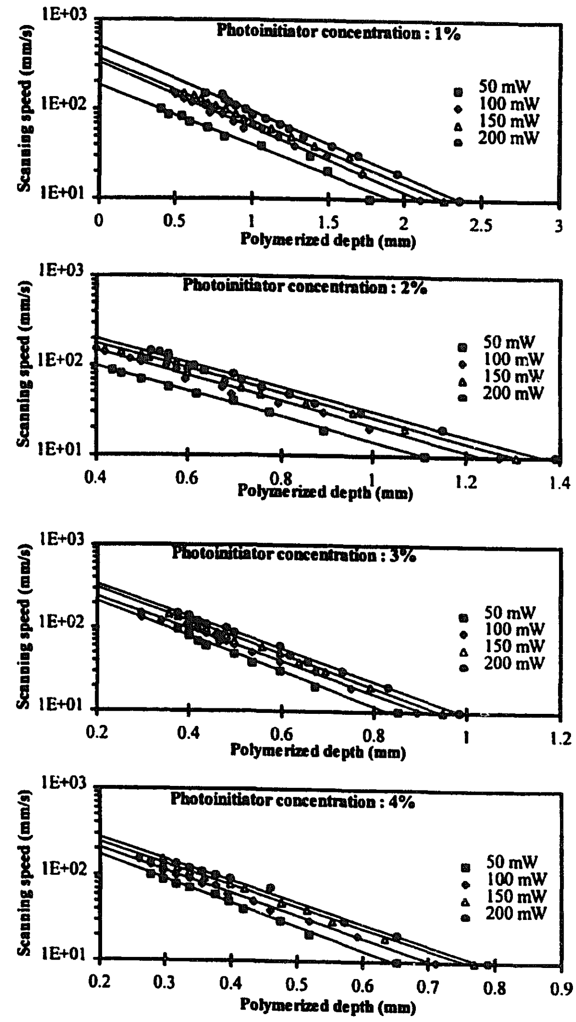

Fig. 6. Scanning speed vs. polymerized depth obtained for different concentrations of the photoinitiator and different values of the incident laser beam power.

Table 2
Measured values of the parameter $b_2(c)$ for different values of the incident laser beam power

Power (mW)	$c = 1$ wt.%	$c = 2$ wt.%	$c = 3$ wt.%	$c = 4$ wt.%
50	−0.65	−1.38	−2.06	−2.72
100	−0.71	−1.39	−1.91	−2.58
150	−0.68	−1.36	−1.96	−2.42
200	−0.71	−1.34	−1.90	−2.38
Average	−0.69	−1.37	−1.96	−2.52

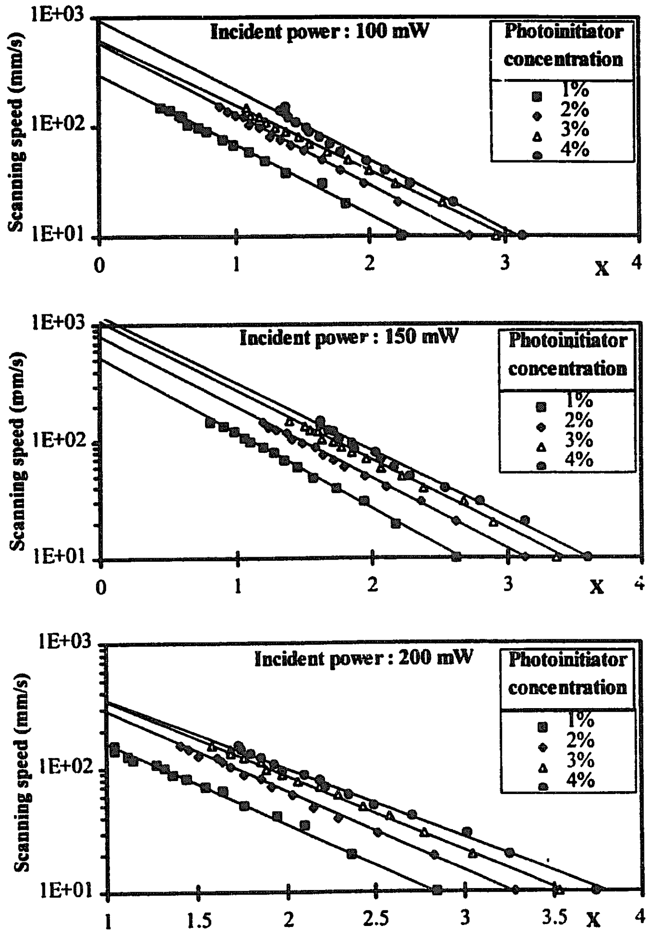

Fig. 7. Evolution of the scanning speed vs. X.

the polymerized width vs. the laser beam power or the initiator concentration cannot be easily obtained.

The photoinitiator concentration is not explicitly present in the theoretical equation of X (the square of the half-width), since the phenomenon described takes place on the surface of the photochemical medium. In this case, the absorption law has no influence. Nevertheless, the value of $\Phi_{\min}$ depends on the photoinitiator concentration. As a consequence, Eq. (8) does not allow a direct interpretation of the experimental results.

However, an approximate empirical law can be used to explain the evolution of the polymerized width w

$$w = 2\left(\frac{a - \log s}{b}\right)^{1/2} \qquad (12)$$

where $b \in [0.56, 0.65]$ and a is a function of the initiator concentration and laser beam power.

3.3. Influence of the focusing of the beam

For practical reasons, the samples which were polymerized to measure the vertical and transverse dimensions were obtained without using any optical focusing device. They were washed with a solvent, and post-polymerized with UV radiation. To evaluate the influence of the focusing of the light beam on the polymerization resolution, some experiments were performed with a focused laser beam. The measurements are similar to those obtained without focusing (Fig. 8).

A numerical determination of the values of the different parameters involved in the empirical laws presented above cannot be achieved easily, since it is difficult to quantify properly the focusing of the laser beam. To perform such a numerical determination, a precise measurement of the diameter of the beam on the surface of the resin is required. The

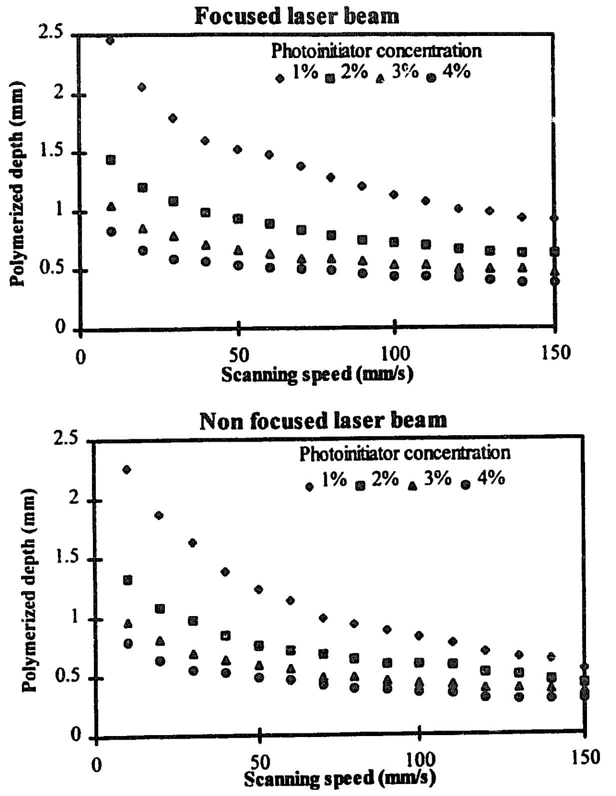

Fig. 8. Influence of the focusing of the light beam on the polymerized depth.

calibration step needed to determine the values of the parameters also depends on the distance between the galvanometric mirrors used in the beam scanning and the surface of the reactive medium. In an industrial SPL apparatus, this distance is fixed, so that these empirical laws can easily lead to a numerical determination.

3.4. *Standardized measurement*

Washing operations and the post-polymerization of the samples may be the source of errors in the vertical and transverse measurements. Moreover, the manufacture of threads polymerized on the surface of the liquid reactive medium is not representative of the real operating conditions. Indeed, the different layers must adhere to one another when an object is being built.

By using the vertical positioning stage in the SPL apparatus, the thickness of the layers can be chosen with an accuracy of 10 μm. To obtain a standardized measurement of the polymerized depth (Fig. 9), an object composed of only a few layers, used as a support, is manufactured. On its top, several rectangles are built with different values of the scanning speed. Only the rectangles having a polymerized depth greater than the thickness of the layer will adhere to the supporting polymerized part. In the experiments performed, rectangles were polymerized for ten different values of the scanning speed, after having built the supporting part and waited for the complete stabilization of the new layer of the liquid reactive resin spread on its surface. The vertical positioning stage was then lowered, and all the rectangles that did not adhere to the supporting part floated on the surface. Therefore an interval was determined whose limits were the scanning speed corresponding to the first floating rectangle and the scanning speed corresponding to the last rectangle adhering to the support. A scanning speed which allows a polymerization depth to be obtained which is exactly equal to the size of the layer belongs to this interval. By gradually reducing the size of this interval, the accuracy of the scanning speed measurement can be increased.

Although the principle of this experiment is very simple, some precautions must be taken in order to obtain a satisfactory reproducibility of the results. If the surface on which the rectangles adhere to the support is too small, the hydrodynamic forces involved when lowering the positioning stage will unstick the rectangles. These hydrodynamic forces depend on the speed and depth at which the object is lowered in the liquid medium, but also on the dimensions of the rectangles and on the width of the supporting object. These parameters were fixed at the following values in our experiments:

- width of the supporting object, 3 mm;
- dimensions of the rectangles, 20 mm × 5 mm;
- translation speed of the vertical positioning stage, 2 cm s^{-1};
- depth to which the object is lowered, 2 cm.

To evaluate the accuracy of the standardized measurements, the same experiment was performed 12 times (with a layer thickness of 1 mm and an incident irradiation power of 100 mW). The zone in which the rectangles do not adhere to the supporting object is centred near a value of 108 mm s^{-1} (Fig. 10). The dispersion of the values probably results from the random evolution of the polymerization reaction (temperature changes, laser flux changes, random growth of the cross-linked polymer network, etc.). This standardized method of measuring the polymerization resolution suffers from an uncertainty of about 10% in the results obtained.

The resolution measurements performed using the standardized method were repeated more than once to verify the reproducibility of the results. The scanning speeds used to build the rectangles were terms of a geometric series of ratio 1.1. The measurements were performed with layer thicknesses varying from 0.8 to 2.2 mm with a step of 0.1 mm. The incident laser beam powers used were 50, 100, 150 and 200 mW. The liquid reactive medium used in this experiment contained 1 wt.% of photoinitiator.

The results obtained with the standardized test (Fig. 11) show a similar evolution of the polymerized depth as that presented above in which a direct measurement of a polymerized thread was performed (Fig. 6). The polymerized depth shows a linear variation vs. the logarithm of the scanning speed. The straight lines obtained for various incident laser beam powers are parallel, and their slopes are slightly different from those observed in the direct measurements.

Having obtained data for experiments performed with a constant value of the layer thickness, we searched for a correlation between the scanning speed and the irradiation power (Fig. 12). In a first approximation, the values of the poly-

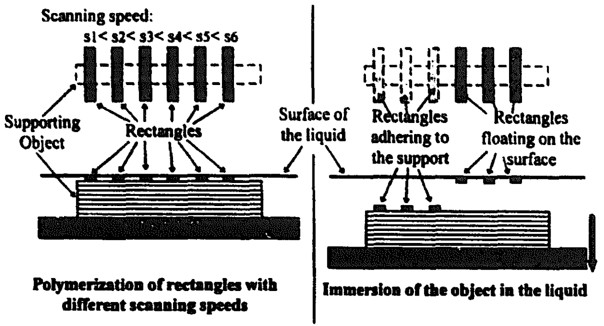

Fig. 9. Diagram of the normalized test.

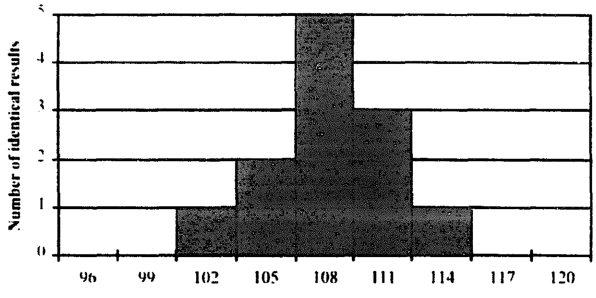

Fig. 10. Variations of the results obtained with the standardized test.

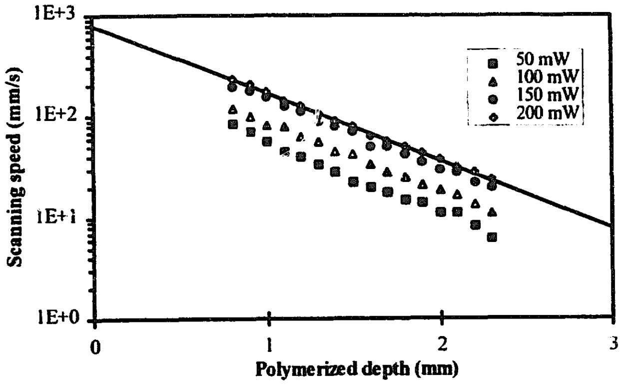

Fig. 11. Evolution of the scanning speed vs. the polymerized depth. Results obtained by the standardized test.

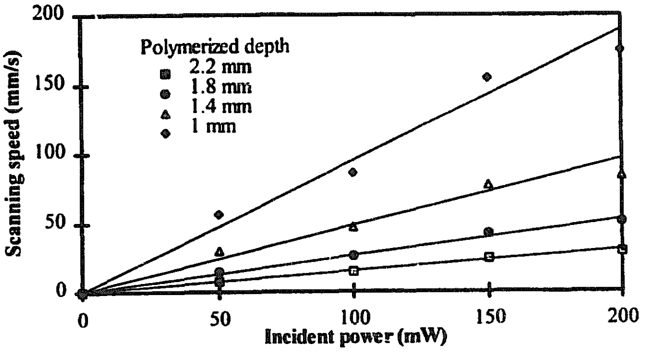

Fig. 12. Correlation between the incident light beam power and the scanning speed for different polymerized depths.

merized depth were linked to the values of the ratio R between the irradiation power and the scanning speed (the unit of R is mJ mm^{-1}) for a given chemical reactive medium. This correlation is well verified in the case of measurements obtained with the standardized test, but not in the case of the direct measurement of polymerized threads where, for a given value of the ratio R, the polymerized depth decreases as the irradiation power increases, as shown in Table 3. It is difficult to explain the differences between these two tests. In the direct measurement of the polymerized threads, the washing operations may damage the objects and result in inaccuracies in the measurements, whereas in the standardized test, the inaccuracies may originate from the adherence phenomenon which is not fully controlled.

The standardized test is very similar to the manufacturing conditions used to fabricate complex shaped objects by the layer-by-layer process in the SPL technique. This test could be used as a calibration method in SPL.

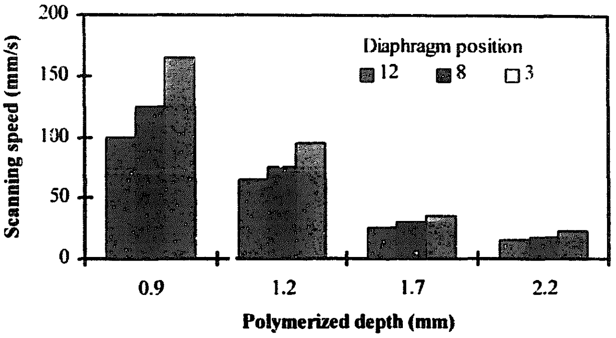

Fig. 13. Influence of the laser mode on the polymerized depth.

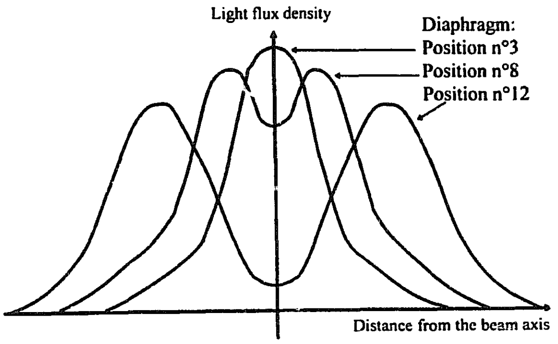

Fig. 14. Light flux distribution in the laser beam cross-section.

3.5. *Influence of the laser mode on the polymerization resolution*

The laser is an optical oscillator. It comprises a resonant amplifier inserted between two mirrors. When an aperture is inserted between the two mirrors, different transverse modes are associated with the spatial light flux distributions of the beam. The gaussian mode is the most confined around the optical axis, and the most difficult to obtain. It requires the use of low diaphragm diameters and suffers from significant energetic losses [9].

The Ar$^+$ laser (Spectra Physics 2020) used has a 12-position diaphragm. Each position is numbered, the smallest diameter corresponding to the smallest number. To evaluate the influence of the laser mode on the polymerized depth, experiments were performed with the diaphragm positions set to 3, 8 and 12. The standardized test was used with a constant incident laser beam power (100 mW) and four different sizes of the layers (0.9, 1.2, 1.7 and 2.2 mm). The standardized measurements show that the larger the diameter of the diaphragm, the slower the scanning speed to obtain a given polymerized depth (Fig. 13). The different laser modes correspond to different light flux distributions (Fig. 14). The

Table 3
Polymerized depths (mm) obtained for different values of R when the dimensions of a polymerized thread are measured

R (mJ mm^{-1})	P = 50 mW	P = 100 mW	P = 150 mW	P = 200 mW
5	1.78	1.72	1.64	1.52
2.5	1.50	1.28	1.12	1.10

gaussian mode (diaphragm position number 3) is the more confined mode and that presenting the most important local energy. Therefore it allows polymerization to be performed quickly at important depths with a correct transverse accuracy. The more open the diaphragm, the more the energy will be distributed in the beam, resulting in large widths of the polymerized threads and low scanning speeds.

4. Conclusions

The laser beam scanning used in SPL generally results in parabolic shapes of the polymerized vectors. This induces many limitations in the resolution of the layer-by-layer manufacturing process: the surfaces of the objects are slightly distorted and it is impossible to fix separately the polymerized depth and width without using specifically designed photopolymerizable media containing a chosen concentration of photoinitiator.

The experimental methods proposed in this paper show different methods of determining the relations between the light absorption of the photoinitiator, the laser beam scanning speed and the coherent light beam power. The experimental results are in fairly good agreement with simple kinetic models allowing the optimal operating conditions in SPL to be defined.

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