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Study of the spatial resolution of a new 3D microfabrication process: the microstereophotolithography using a dynamic mask-generator technique

A. Bertsch *, J.Y. Jézéquel, J.C. André

DCPR (GRAPP) URA 328 and GdR 1080 CNRS, ENSIC-INPL, B.P. 451, F-54001 Nancy Cedex, France

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Abstract

In order to manufacture new micromechanical components, a new 3D microfabrication technique called the 'microstereophotolithography using a dynamic mask-generator' process has been developed. This technique is based on the use of a liquid crystal display as dynamic mask-generator. It obliged us to choose photopolymerizable chemical mixtures, specifically designed for microfabrication, that react to visible wavelengths. The chemical resin we used showed a main disadvantage. It contains an organic dye that undergoes photochemical bleaching. A precise control of the spatial resolution of the physico-chemical processes happening during the photoreaction is required in order to manufacture small components. Then, the influence of photobleaching on the photopolymerization resolution has thus been investigated. An experimental study has been compared with a mathematical model describing the phenomenon and allowed to optimize the operating conditions of the microstereophotolithography device we built, and to manufacture small three-dimensional objects made of a large number of complex layers with a resolution better than 5 μm. © 1997 Elsevier Science S.A.

Keywords: LCD; Microtechniques; Rapid prototyping; Acrylates; Photopolymerization

1. Introduction

The development of microsystems and microrobots requires the manufacture of adapted microcomponents [1]. The microfabrication techniques based on silicon machining can produce planar microparts or objects composed of a very small number of layers, but the manufacture of three-dimensional structures having curved surfaces is still impossible. In order to obtain three-dimensional micro objects made of a large number of layers and having a complex geometry in the three space directions, processes derived from the rapid prototyping industry have been developed.

Among them are two main microstereophotolithography (μSPL) processes. The first one is based on a vectorial tracing of every layer of the object to be built, and has many disadvantages, indeed, the manufacture process is slow and consequently the objects that can be manufactured in a reasonable time are very simple, each layer being composed of a very small number of vectors. Moreover, this process cannot easily evolve into a collective manufacturing technique [2,3].

The second microstereophotolithography process, described in the present paper, is based on the use of a dynamic mask-generator, which allows the manufacture of a complete layer by one irradiation only [4] and presents more interest to manufacture quickly complex micro objects.

2. Microstereophotolithography using a dynamic mask-generator

2.1. Principle of the process

The part is manufactured layer by layer (Fig. 1). Only one irradiation is necessary to manufacture a complete layer what-

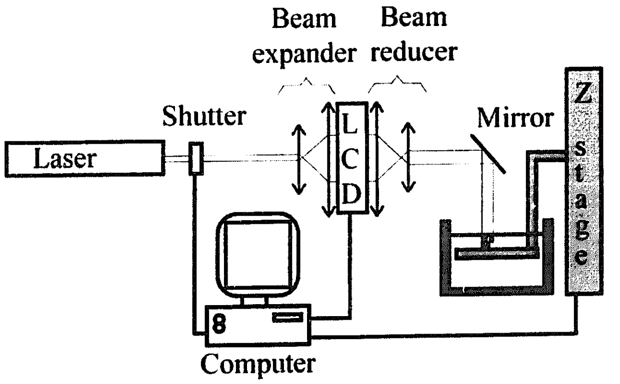

Fig. 1. μSPL device using a dynamic mask-generator.

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* Corresponding author. Tel.: +33 3 83175006.

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ever its shape may be. Its pattern appears on a computer controlled liquid crystal display (LCD) that is used as a dynamic mask-generator. The pixels in their opaque state stop the light, in contrast to those which are in their transparent state, so, when the beam has passed through the liquid crystal display, it contains the pattern of the layer. The light beam then passes through a beam reducer and is focused on the surface of the photopolymerizable medium, which allows the selective polymerization of the irradiated areas corresponding to the transparent pixels of the LCD.

To obtain a high resolution, it is necessary to illuminate the largest possible surface of the liquid crystal display. To do so, a beam expander is used. A specially designed device is also added to this apparatus in order to eliminate, to a certain extent, the energy density gradient of the laser beam as well as the 'speckle' effects resulting from the use of a coherent light source.

Between two irradiation steps, an electromechanical shutter occults the laser beam in order to execute all the tasks required to spread a new layer of fresh resin on the already polymerized part of the object being manufactured.

In this apparatus, the only remaining mobile element is the motorized z positioning stage.

2.2. *Advantages of the process*

In this process, the time required to manufacture a layer is independent of its pattern, and very short in comparison of the time needed to manufacture a layer with a vectorial microstereophotolithography apparatus, even in the case of simple layers.

To have a good resolution in such processes, the number of mobile operating elements has to be as small as possible, and in particular, the optical elements have to remain fixed during the manufacturing process. In this μSPL apparatus, there is only one mobile mechanical part: the vertical translation stage which allows a good manufacturing accuracy.

Another advantage of this process is that the light flux density on the surface of the resin is low compared to that in the vectorial tracing process. As a result, there are no problems of unwanted thermal initiation of the photopolymerization reaction during the manufacturing process of the layers.

Moreover, this system can be the starting point of a collective fabrication process.

2.3. *Limitations of the process*

The major problem of this apparatus comes from the low resolution and low contrast of the liquid crystal display. Its usable surface is a circle containing too small a number of pixels, which does not allow the manufacture of parts requiring a very high precision. Its contrast level is poor: the pixels in their opaque state let some 20% of the light pass. To overcome this problem, a chemical reactive medium having a polymerization threshold has to be used.

Moreover, the liquid crystal matrix is inserted between four glass windows which are opaque to ultraviolet light. This implies the use of a light source emitting in the visible spectrum and a photochemical mixture reactive to these wavelengths.

No scraper can be used to add a layer of reactive medium on the surface of the part being manufactured, because such a kind of device could damage or destroy the micro objects during their manufacture. So, the time necessary to obtain a horizontal fresh layer depends on the rheological properties of the resin. As a result, low viscosity reactive resins have to be used, as often as possible.

2.4. *Description of the chemical medium to be photopolymerized*

To make this process work, a chemical photopolymerizable resin having an adapted polymerization threshold, a low viscosity, and initiated by visible wavelengths is required. This chemical medium has to be highly absorbing, indeed, the less the light will propagate in the reactive medium, the better the vertical resolution will be. Most reactive media used in stereophotolithography or microstereophotolithography are initiated by ultraviolet radiations, and are not adapted to the microstereophotolithography apparatus that uses a liquid crystal display as dynamic mask-generator [5,6]. So, an important part of the work that has been done to develop this process concerns the search for new reactive media, and the study of their physico-chemical properties.

The chemical resin we used initiates the polymerization reaction by a photosensitizing process. Indeed, at wavelengths larger than 400 nm, less energetic than ultraviolet radiations, there are very few photoinitiators able to initiate by themselves polymerization processes, and multicomponent chemical media have to be used [7]. To produce the initiating radicals, the combination of a photosensitizer and of a coinitiator molecule is required. In the case of the microstereophotolithopgraphy apparatus we designed, the use of Eosin Y as photosensitizer with *N*-methyldiethanolamine (MDEA) as coinitiator, which allows the initiation of an acrylate monomer. As we need to dissolve important quantities of Eosin Y in the resin to obtain a highly absorbing reactive medium, we chose the pentaerythritol triacrylate (PETIA) as acrylate monomer.

This photopolymerizable resin fulfils most of the conditions required in the apparatus designed by us. Nevertheless, it has a main drawback that could lead to loss of resolution. During the photoinitiation process of the polymerization reaction, a photobleaching of the dye is observed. This increases the light penetration depth in the resin [8]. As a consequence, the polymer formation is no longer constrained to a thin film near the surface, but propagates more and more deeply in the chemical medium as the dye is bleached.

3. Theoretical study of the influence of photobleaching on spatial resolution

The microstereophotolithography device using a dynamic mask-generator has been designed to attenuate the spatial resolution losses resulting from the mobile mechanical elements and from unwanted polymerizations due to thermal effect. Nevertheless, the chemical medium that seems the most suitable for this application undergoes photobleaching. The influence of this phenomenon on spatial resolution has to be evaluated in order to find the optimal operating conditions of the microstereophotolithography apparatus.

3.1. Theoretical photobleaching model

In order to evaluate the influence of photobleaching on the spatial resolution of the process, a theoretical model has been developed. In this model we consider that the incident photons penetrate in an orthogonal way into the chemical medium, and that the photobleaching phenomenon has no influence on the direction of the incident photons, which means that only the vertical resolution of the photopolymerization phenomenon is influenced by the photobleaching of the chemical resin. Moreover, the photosensitization reaction is considered to be of first order with regard to the absorbed light intensity.

The photochemical reaction is described by the following over-simplified mechanism:

$$A \xrightarrow{h\nu} B \rightarrow P$$

where A is the photosensitizer. Its napierian absorption coefficient is α_A. B is the transformed molecule that initiates the reaction. Its napierian absorption coefficient is α_B. P is the polymer chain.

The polymerization reaction with or without photobleaching can be described by this mechanism, by choosing adapted values of α_A and α_B.

The temporal evolution of the concentrations of A and B is related to the absorbed light intensity by the following relation:

$$\frac{\mathrm{d}C_A(z,t)}{\mathrm{d}t} = -\frac{\mathrm{d}C_B(z,t)}{\mathrm{d}t} = -\varphi I_a(z,t) \qquad (1)$$

where C_A is the concentration of A (mol m^{-3}), C_B the concentration of B (mol m^{-3}), φ a proportionality coefficient that coincides with the efficient photoinitiation quantum yield (mol Einstein^{-1}), I_a the absorbed light intensity (Einstein m^{-3} s^{-1}).

φ is defined by:

$$\varphi = \varphi_0 \frac{\alpha_A C_A(z,t)}{\alpha_A C_A(z,t) + \alpha_B C_B(z,t)} \qquad (2)$$

I_a is defined by:

$$I_a = \frac{\mathrm{d}F(z,t)}{\mathrm{d}z} \qquad (3)$$

where φ_0 is the initial value of the efficient photoinitiation quantum yield, F the light flux density in the reactive medium (Einstein m^{-2} s^{-1}), F_0 the incident light flux density (Einstein m^{-2} s^{-1}).

$$F(z,t) = F_0 \exp[-\int_0^z (\alpha_A C_A(z,t) + \alpha_B C_B(z,t))\,\mathrm{d}z] \qquad (4)$$

The polymerization process can be approximated by a threshold system. A threshold quantity of photons by volume unit T has to be absorbed before the photopolymerization begins:

$$\int_0^t \frac{\alpha_A C_A(z,t)}{\alpha_A C_A(z,t) + \alpha_B C_B(z,t)} \frac{\mathrm{d}F(z,t)}{\mathrm{d}z}\,\mathrm{d}t \geq T \qquad (5)$$

These equations can be numerically resolved. The results obtained by giving to α_A and α_B equal values correspond to a photopolymerization without photobleaching, while the ones obtained by choosing $\alpha_B = 0$ correspond to a complete photobleaching of the photosensitizing dye during the initiating reaction. When the quotient α_B/α_A takes values between 0 and 1, the photosensitizer is partly bleached, which means that the obtained polymer still absorbs the incident light, but with less efficiency than the photosensitizer.

All the units on the figures obtained with this theoretical model are arbitrary (au).

3.2. Evolution of the light flux in the chemical medium.

Figs. 2 and 3 show the temporal evolution of the light flux in the chemical medium. Fig. 2 corresponds to a total bleaching of the photosensitizer whereas Fig. 3 corresponds to a partly photobleached compound.

At the beginning ($t = 0$), the penetration of the light flux in the medium is the same as in the case of a medium that does not undergo photobleaching. As time passes by, the light propagates more and more deeply in the medium. For an infinite value of time, the concentration of A in the medium falls to zero, and Eq. (4) can be simplified:

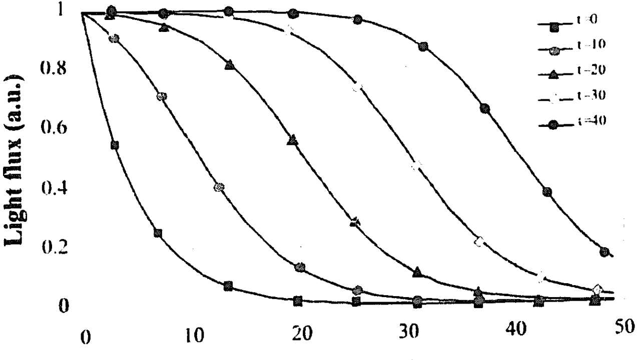

Fig. 2. Evolution of the light flux in the chemical medium with the depth and time, in the case of a complete photobleaching of the photosensitizer.

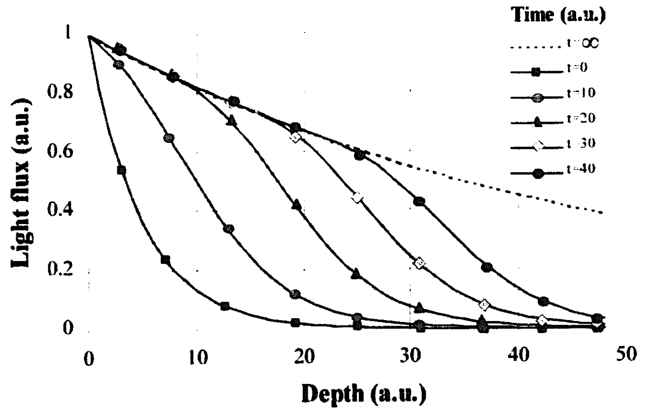

Fig. 3. Evolution of the light flux in the chemical medium with the depth and time, in the case of a partly bleached photosensitizer ($\alpha_B/\alpha_A = 0.1$).

$$F = F_0 \exp(-\alpha_A C_A z) \qquad (6)$$

This indicates the light flux evolution profile in the medium after the total transformation of A in B. When the photobleaching is total ($\alpha_B = 0$), the medium has become completely transparent, and no attenuation of the light flux can be observed.

3.3. Evolution of the absorbed light intensity in the medium

Fig. 4 shows the evolution of the absorbed light intensity I_a with the depth and time in the case of complete photobleaching of the photosensitizer.

At the very first moment, the photobleaching has not started, and the evolution of the absorbed light intensity in the medium looks the same as if there was no bleaching.

At long times, the light flux is absorbed deep into the medium, and the shape of the curve of evolution of the light flux intensity is the same whatever the moment of observation, this curve only shifting more and more into the medium as time passes by. In this case we have a stationary light absorption rate in the chemical medium.

At short times, a transitional period can be seen, during which the absorbed light intensity evolves from the shape of the curve without bleaching, to the stationary light absorption rate curve.

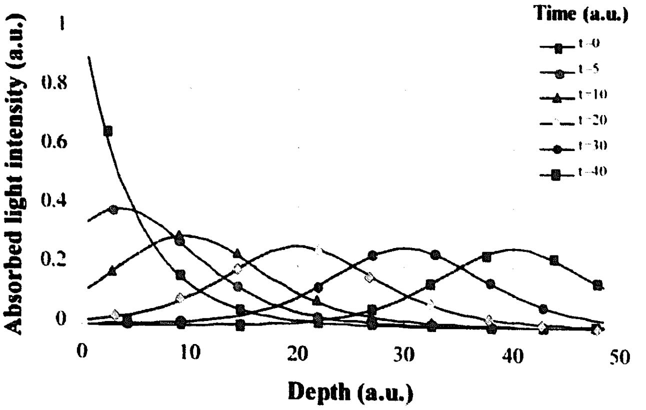

Fig. 4. Evolution of the absorbed light intensity in the chemical medium with the depth and time, in the case of a complete photobleaching of the photosensitizer ($\alpha_B/\alpha_A = 0$).

When a chemical medium, that is partly photobleached during photopolymerization, is taken into consideration, no stationary light absorption rate can be observed (Fig. 5). At the very first moment, when the photobleaching phenomenon has not started, the evolution of the absorbed light intensity in the medium looks the same as if there was no bleaching, because only A is present. For an infinite value of time, the concentration of A in the medium falls to zero and the evolution curve of the absorbed light intensity is due to the absorption of B only.

3.4. Evolution of the polymerized depth

When the photosensitizer is completely bleached during the photopolymerization process, the evolution of the polymerized depth can be easily divided into three main zones (Fig. 6).

At the very first moment, the photobleaching has not started, and the evolution of the polymerized depth is the same as if there was no bleaching.

At long times, corresponding to the stationary light absorption rate in the chemical medium, the polymerized depth

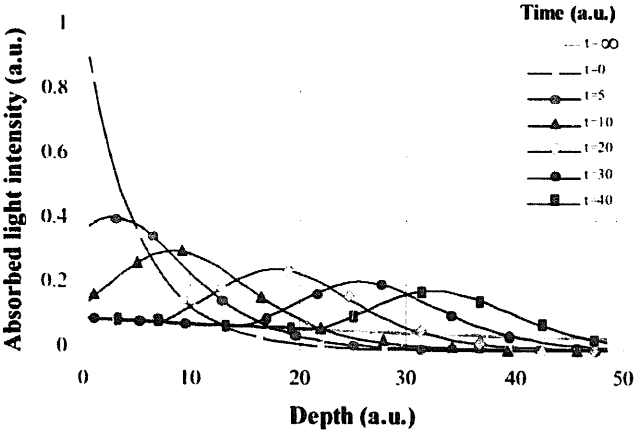

Fig. 5. Evolution of the absorbed light intensity in the chemical medium with the depth and time, in the case of a partly photobleached photosensitizer ($\alpha_B/\alpha_A = 0.1$).

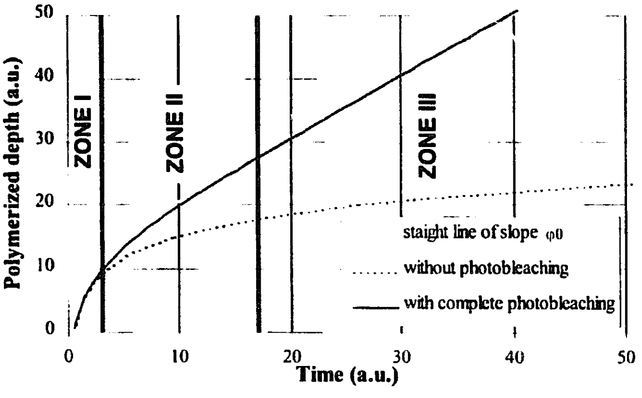

Fig. 6. Evolution of the polymerized depth in the chemical medium vs. time, in the case of a complete photobleaching of the photosensitizer ($\alpha_B/\alpha_A = 0$).

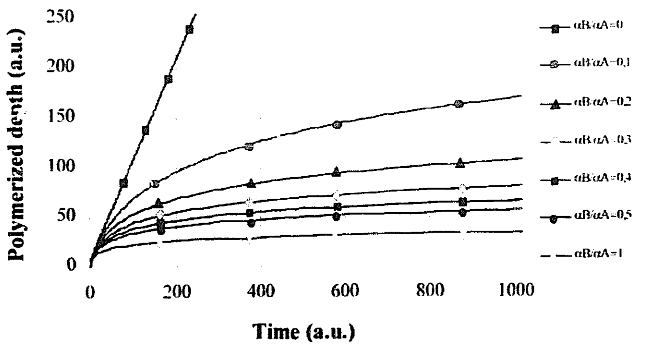

Fig. 7. Evolution of the polymerized depth in the chemical medium vs. time, in the case of different photobleaching conditions.

shows a linear evolution vs. time. This evolution can be approximated by a straight line of slope φ_0.

At short times, a transitional period can be seen, during which the polymerized depth evolves between these two limits.

When the photosensitizer is partly bleached (Fig. 7), the curves of the polymerized depth vs. time cannot be as easily described as in the cases of a complete photobleaching ($\alpha_B=0$) or when there is no bleaching ($\alpha_B=\alpha_A$). At the very first moment, the polymerized depth is the same as in a medium that undergoes no bleaching, but then, neither by straight lines, nor by logarithmic curves can the evolution curves be approximated.

3.5. Conclusion

The numerical resolution of the equations used to indicate the influence of the photobleaching phenomenon, on photopolymerization vertical resolution of the kind of chemical media that can be advantageously used in microstereophotolithography using a dynamic mask-generator apparatuses, shows clearly that the polymerized depth increases much faster with time in chemical media undergoing photobleaching than in those not subjected to this phenomenon. The loss in vertical resolution is the most important for the chemical resins being the most subjected to photobleaching (when α_B/α_A is almost zero). This effect is amplified by the use of resins having high efficient photoinitiation quantum yields.

In stereophotolithography or microstereophotolithography apparatuses based on a vectorial tracing process and using ultraviolet resins that do not undergo photobleaching, it is easy to choose operating conditions in which the evolution of the polymerized depth in time is low. Those conditions can be obtained for important irradiation times of every elementary volume element, and the polymerized depth can be fixed by chemical means (choosing an adapted concentration of photoinitiator and eventually adding photoinhibitors or non-reactive highly-absorbing chemicals in the medium).

In the microstereophotolithography device using a dynamic mask-generator, it is not possible to control the polymerization depth by chemical means only, because of the photobleaching phenomenon. Indeed, the increase of the polymerized depth does not slow down with time. Nevertheless, for microfabrication applications, it is necessary to use highly absorbing resins to have low penetration of light in the medium. To control accurately the polymerization depth, a precise control of the irradiation time of every elementary polymerized volume has to be achieved. If this cannot be done easily in microstereophotolithography processes based on a vectorial tracing of every layer, it is quite simple by manufacturing a complete layer of the object by one irradiation only. So, the use of a photosensitizer that undergoes photobleaching is compatible with the microstereophotolithography apparatus using a dynamic mask-generator, but the irradiation times have to be well controlled.

4. Experimental

4.1. Resolution measurement principle

Vertical and transverse resolution have been evaluated by measuring the dimensions of a polymerized thread manufactured with the microstereophotolithography apparatus using a dynamic mask-generator, at the surface of the chemical resin in the real operating conditions. In a stereophotolithography apparatus, the polymerized depth does not correspond to the mechanically imposed depth of the positioning system superimposing the layers. The polymerization depth has to be more important in order to allow a partial interpenetration of the layers so that they could be joined together.

To experimentally manufacture such a polymerized thread and distinguish easily its vertical and transverse sides, this latter has been inserted in a simple object having a 'U' shape (Fig. 8). Moreover, such an object can be manipulated without fear of breaking the polymerized thread.

4.2. Vertical resolution measurements

The manufacture of polymerized threads has been performed with various photosensitizer concentrations in the

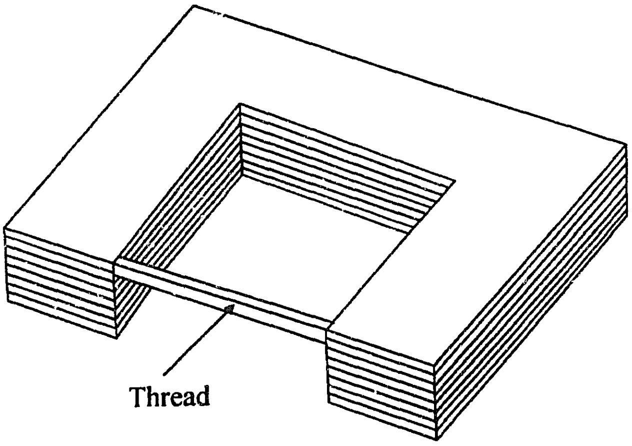

Fig. 8. Object manufactured to measure the vertical and transverse resolution of the photopolymerization process.

chemical medium. When the irradiations have been provided with an important light flux density, the polymerized thread is caught in a polymerized film that covers the whole irradiated surface. This originates from the bad contrast of the liquid crystal display used as dynamic mask-generator. The liquid crystals let light pass partly, even in their opaque state. So, the manufacture of objects can performed in small intervals only, limited on one side by the poor contrast of the liquid crystal display, and on the other side by the threshold of the polymerization phenomenon.

To compare the experimental results and the numerical model of photobleaching, different parameters have to be evaluated. Among them, are the napierian absorption coefficient of the chemical medium before (α_A) and after (α_B) photobleaching, the efficient photoinitiation quantum yield (φ), and the threshold energy per volume unit (T) needed to start the polymerization process. The values of these parameters have been set to: $\alpha_A = 115\,000$ l mol^{-1} cm^{-1}; $\alpha_B = 7600$ l mol^{-1} cm^{-1}; $\varphi = 0.4$ radical photon^{-1}; $T = 1$ J cm^{-1}.

The experimental measurements have been compared to the numerical model for different values of the photosensitizer concentration. One example of this vertical resolution measurement is presented on Fig. 9. The dots correspond to the experimental measurements and the lines to the numerical model.

4.3. *Transverse resolution measurements*

In order to make resolution measurements, the width of the polymerized threads has been fixed to 3 pixels on the liquid crystal display in order to manipulate them without destroying. Moreover, the microstereophotolithography apparatus was not used in its ultimate operating conditions, because the object supporting the thread would have been too small to be easily manipulated. So, the width of the threads is not the smallest that can be obtained with this apparatus and gives only an indication on the reliability of the process. The incident light flux can be considered in first approximation as orthogonal to the photopolymerizable reactive medium, as a result, the polymerized width should be independent of any parameter. Fig. 10 shows the experimental measurements obtained for different photosensitizer concentrations. A dispersion of the experimental results can be observed. The washing operations, using solvents, needed before the measurement of the width of the thread can damage it or cause deformations, and is probably the main reason for the dispersion of the values.

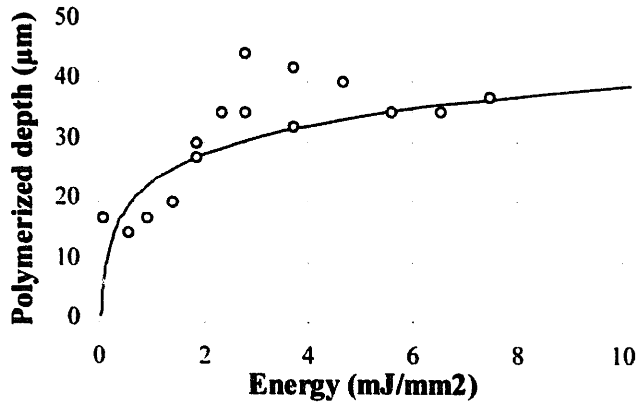

Fig. 9. Depth of a polymer thread for a photosensitizer concentration of 1.26×10^{-2} mol l^{-1}.

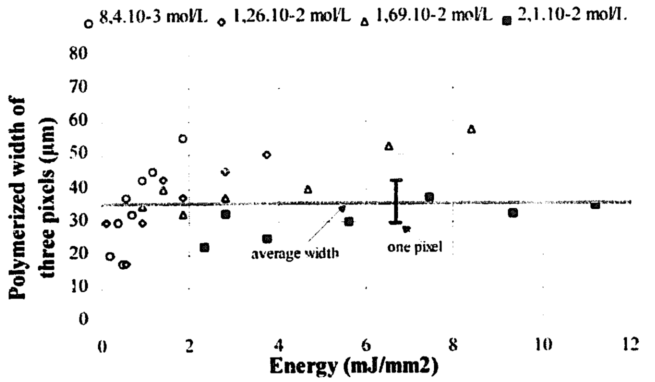

Fig. 10. Experimental measurements of width.

Considering this result, it could seem difficult to really control the transverse resolution of the objects manufactured by microstereophotolithography using a dynamic mask-generator. Nevertheless, a thread made of one layer only and polymerized at the surface of a chemical medium is a very unlikely configuration in the manufacturing of complex-shaped objects having a large number of layers. Moreover, the damage that can be caused by washing operations is strongly reduced when manufacturing complex objects because the interpenetration of the layers gives better mechanical quality to the part.

4.4. *Example of a complex object*

The resolution study allowed us to optimize the operating conditions of the microstereophotolithography device using a dynamic mask-generator we built, and to manufacture different small 3D objects made of a very large number of layers.

The polymer structure presented on Fig. 11 is a prototype of a mechanical structure of a microactuator having a distributed elasticity, made of multiple imbricated springs. It has been made with the microstereophotolithography apparatus using a dynamic mask-generator in 10 h. Its total length is 4 mm and its maximal diameter is 700 µm. It is made of 1040 layers each having a thickness of 5 µm. This structure could be used to manufacture a microactuator by inserting 30 µm in diameter shape memory alloy wires in the clamping areas [9].

The scanning electron microscope (SEM) photograph shows that the objects that can be made with this new microstereophotolithography apparatus have a resolution better than 5 µm in the three space directions, in spite of the limitations of the liquid crystal display, and of the photobleaching of the

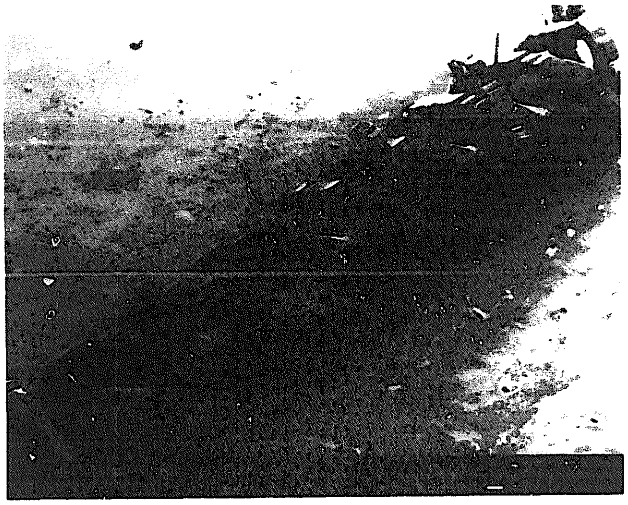

Fig. 11. SEM photograph of a polymer structure of microactuator.

chemical medium used. Moreover, the recent improvements in the manufacture of LCD has given us hope that it should be possible to improve the transverse resolution of the process.

5. Conclusion

The new technique called 'microstereophotolithography using a dynamic mask-generator', is an interesting process that allows to manufacture small, complex in shape objects made of a large number of layers. The liquid crystal display we used as an active component in the apparatus obliged us to use a chemical medium having a polymerization threshold, to attenuate to a certain extent the poor contrast of the liquid crystal display, and reacting to visible wavelengths. Such a medium undergoes photobleaching, however an experimental study and a mathematical model of this phenomenon allowed us to have a correct control of the physico-chemical processes occurring during the photoreaction and to optimize the operating conditions of the apparatus we built. Complex objects have been obtained with this process, with a resolution better than 5 μm in the three directions of space.

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