Research on the resolution of micro stereo lithography

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Micro stereo lithography is a kind of technology utilizing the solidified effect that photo curable polymer will appear under ultraviolet (UV) laser exposure. It is widely used in three-dimensional (3D) micro fabrication. We get the experimental values of a pair of UV laser curing coefficients, absorption coefficient and critical curing energy, of curable resin by fitting the calculation results of the Gaussian beam theory and experimental curing results. The theoretical relation between the curing unit's shape and the exposure features of time and intensity of convergent Gaussian beam is presented. The calculation and experimental results of curing unit under different conditions agree well with each other. This research offers a steady base for further research about the improvement of resolution.

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Micro stereo lithography (MSL) is a method derived from the technology of rapid prototyping (RP) in the field of laser-based micro fabrication. The basic principle is that, under an ultraviolet (UV) exposure, some kinds of polymers can absorb photons and cause a photochemical reaction, leading to photo polymerization[1]. MSL is attracting global concern for its three-dimensional (3D) micro fabrication ability. Kobayashi *et al.* researched the polymerization of freely movable 3D microstructure using conductive photo curable resin[2]. Zhang *et al.* used a solution consisting of curable resin and ceramic suspension to lead a layer-by-layer polymerization on silicon substrate[3]. Products of microstructure using the technology of UV polymerization of liquid resin and lithography with mask are being provided by Micro-TEC-D company[4]. It is now one of the most important researching realms in 3D micro fabrication[5,6].

MSL uses scanning UV beam to focus on the UV curable resin, leads to the polymerization, and then forming points, lines, planes, and finally the layer-by-layer 3D microstructure. In this letter, we analyze the resolution of MSL through researching the relation between the characteristics of single curing unit and focal spot by the principle of micro photo polymerization. A mathematical model is constructed based on the experimental data. This will offer a steady base for the future 3D micro fabrication study.

According to the photon absorption theory, after exposure, the molecules will turn into excited state and energy will be transmitted or reflected in compound system. With the interaction of chromophore (chemical bonds or groups that can absorb photons), polymerization and cross linking reaction will happen, resulting in phase transformation and photo curing[7]. Photo curing is a kind of photochemical reaction resulting from the absorption of photon by photo-curable compound. When the absorption happens, if the absorbed photons' energy lets the molecules reach the critical value of excitation, the liquid resin's photo curing can appear. Generally, the main properties to evaluate the liquid photo curable resin include physical properties, optical properties in a specific wavelength, and mechanical properties. Analysis of influences on photo polymerization is mainly about its optical performance parameter. Photo sensitive resin used in MSL research is mainly UV curable resin. And the principal coefficients reflecting the curing property contains critical curing energy and absorption coefficient. The feature value of a particular kind of resin is different when the wavelength of UV exposure is different, so only through the curing experiments and theoretical calculation can the feature parameters be fixed.

The experimental system is schematically shown in Fig. 1. The process of experiment is as follows. The UV laser exits from quartz fiber, passes through the cover slip, reaches the container full of liquid resin, and reacts with resin, while single point curing unit is produced. In the experiment, the fiber has a numerical aperture (NA) of 0.37 and a radius of 0.6 mm. Its working distance (from the tip face of the fiber to the liquid level of resin including the depth of cover slip) WL = 0.38 mm and the exposure spot radius on liquid level is 0.9 mm. The intensity of exposure spot can be measured by UV intensity meter (UV-A type Developed by Beijing Normal University, whose measurable peak value of wavelength is 365 nm, minimum resolution is 0.1 μW/cm^2, and accuracy is $\pm$5%). Usually, the photo polymerization of UV curable resin obeys the Beer-Lambert law of absorption which can be expressed as[8,9]

$$I = I_0 \exp(-\alpha z), \quad (1)$$

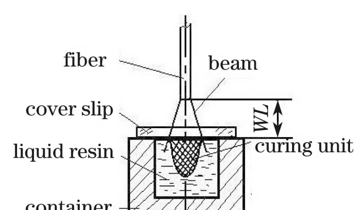


Fig. 1. Principle of experimental system.

where I is the transmission intensity of light, I_0 is the central incident intensity, α is the absorption coefficient of resin[10], and z is the transmission depth.

As exposure beam follows Gaussian distribution, the exposure plane is defined as x-y plane, and the direction along the optical axis of exposure beam and starting from the exposure plane is defined as the positive direction of z axis. Therefore, the curing depth of resin can be expressed as

$$z = \frac{1}{\alpha}\ln\frac{I_0 T}{E_c} - \frac{2}{\alpha}\frac{x^2+y^2}{w^2}, \tag{2}$$

where T is the exposure time of a single point unit, E_c is the critical curing energy of resin, and w is the spot radius of exposure.

By Eq. (2), the maximum curing depth along the optical axis ($x = 0$, $y = 0$) can be expressed as

$$z_{\max} = \frac{1}{\alpha}\ln\frac{I_0 T}{E_c} = \frac{1}{\alpha}\ln\frac{E}{E_c}. \tag{3}$$

By Eq. (3), the critical curing energy and absorption coefficient of resin under this experimental system can be fitted from experimental data of different maximum curing depths.

The exposure amount can be influenced by exposure intensity and exposure time, so we get the experimental data by changing these two coefficients orthogonally. The central intensity of exposure spot has been calculated from UV intensity meter's value using $I_0 = 2P/\pi w^2$ with P being the exposure power. For different exposure intensity and exposure time, the corresponding curing depth values are shown in Table 1.

The exposure amount is defined as the normalized product of central exposure intensity and respective exposure time. Through a series of experimental data of curing exposure, the maximum curing depths at different exposure intensity and time values are measured by a microscope with the resolution of 1 μm. The relation between exposure amount and curing depth is shown in Fig. 2, where the intersection of fitting line and transversal axis means the critical curing energy $E_c = 0.2879$ mJ/mm^2. The absorption coefficient obtained from the average value of different exposure amounts and the maximum curing depths is $\alpha = 1.9576$ mm^{-1}.

As the most efficient way to increase the fabrication resolution in MSL is to minimize the exposure spot, in our experimental system, the micro UV laser spot is obtained from an objective lens, and the liquid level plane of resin is made overlap with the focal plane, as shown in Fig. 3.

Table 1. Curing Depths (mm) for Different Exposure Intensity and Time

Exposure Intensity (mW/mm^2)	Exposure Time (s)				
	1	2	3	4	5
1.04	0.745	0.988	1.203	1.342	1.442
1.63	0.908	1.222	1.426	1.553	1.678
1.96	0.992	1.322	1.519	1.651	1.770
2.34	0.974	1.450	1.610	1.810	1.927
2.80	1.184	1.548	1.736	1.912	2.052

If the Gaussian distribution is satisfied, the power density function of exposure beam at the focal plane can be expressed as

$$I(x,y) = I_0\exp(-\frac{2(x^2+y^2)}{w^2(x)}). \tag{4}$$

By Beer-Lambert law, the energy field in a single curing point whose exposure time is T can be described as

$$E = \frac{2PT}{\pi w^2(z)}\exp(-\frac{2(x^2+y^2)}{w^2(z)})\exp(-\alpha z), \tag{5}$$

where P is the exposure beam's power, $w(z)$ is the respective exposure radius in the z axial position of resin.

Polymeric reaction of resin will happen when $E(x,y,z) \geq E_c$. Equation (5) can be described using the radius of single curing point as

$$r = \frac{w(z)}{\sqrt{2}}\sqrt{\ln(\frac{2PT}{E_c\pi w^2(z)}) - \alpha z}. \tag{6}$$

When $r = 0$, the maximum curing depth is

$$z_{\max} = \frac{1}{\alpha}\ln\frac{2PT}{E_c\pi w^2(z)}. \tag{7}$$

By Eq. (7), when the convergent beam exposes a divergent fashion inside the resin, exposure amounts at different curing depths are defined not only by logarithmic absorption obeying Beer-Lambert law, but also by the microscope's NA and the liquid resin's refractive index to UV laser, which can be written as

$$w(z) = w_0 + z\tan\theta, \tag{8}$$

where w_0 is the exposure radius at liquid resin level, θ is the divergence angle of exposure beam inside resin. In

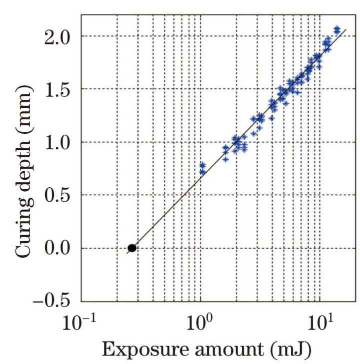


Fig. 2. Relation between curing depth and exposure amount.

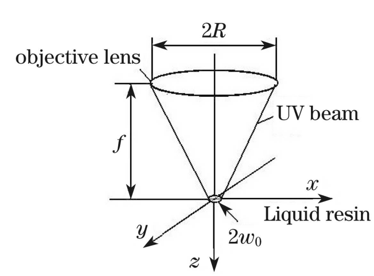


Fig. 3. Principle of micro photo polymerization.

a certain experimental system, the shape and size of a single curing point can be calculated from Eqs. (7) and (8). Moreover, the resolution of curing can be analyzed through theoretical calculation and optimization of processing parameters.

The objective lens used in this experimental system is UV fluorescent objective lens (25×, NA = 0.65, $WL = 0.6$). There is a circular diaphragm, with its radius $R = 100$ μm, setting in the optical path, and the exposure spot radius after the objective lens is $w_0 \approx 5$ μm (measured value).

Before the experiment of producing curing unit, the working distance must be fixed. The experimental devices are almost the same with those shown in Fig. 1, but the fiber is changed into micro objective lens. The influences on single curing point exerted by different working distances and different positions of focal plane are expressed in Fig. 4. The WL values were gained from observing the shape of curing unit.

Scanning electron microscope (SEM) photos of experimental results are shown in Fig. 5 for the exposure time of 2 min. The working distances in Fig. 5(a) are 650, 680, 715, 740, 780, 800, 820, and 860 μm respectively from left to right (the second one on the right has been turned over in the process of cleaning). By actual experimental measurement, when the working distance was $WL =$ 750 μm, the focal plane overlapped the liquid level. Figures 5(b) and (c) are the curing units' SEM photos at the working distances of 680 and 820 μm, respectively.

Because of the differences of working distance between the experimentally measured result and the system's nominal value, the exposure beam's divergence angle inside resin was affected. Relations between working distance WL, NA, and clear aperture D are[11]

$$\text{NA} = \sin U = \arctan\left(\frac{D}{2WL}\right), \tag{9}$$

where U is the aperture angle of the objective lens.

Moreover, there will be refraction at the exposure plane because of the different medium[12], and the divergence angle inside resin will also be affected as

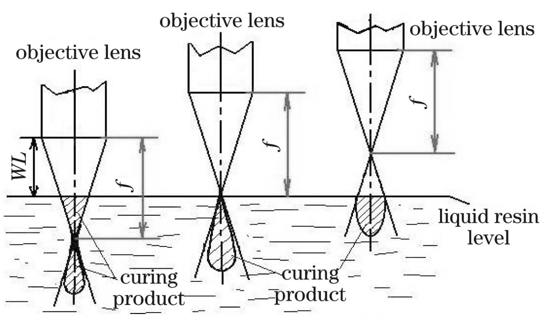
$$\theta = \arcsin\left(\frac{\sin U}{n}\right), \tag{10}$$

where n is the refractive index of resin. Methods to get the polymer material's refractive index include experimental measurement[13] and mathematical calculation method. For most of polymer resin used recently, the refractive index used is around 1.4−1.6[14]. We take $n =$ 1.5.

The exposure focal plane was set to overlap the liquid resin level ($WL = 750$ μm according to the experimental result), and different exposure time (T = 1, 2, 3, 4, and 5 s) and exposure powers (P = 0.1, 0.2, and 0.3 μW) are chosen for obtaining the relation between exposure amount and curing results. According to the experiment, the curing depth and width at the focal plane both increase when the exposure time and power increase. In the following, we take the exposure power of 0.3 μW as an example for the comparison between experiment and simulation results.

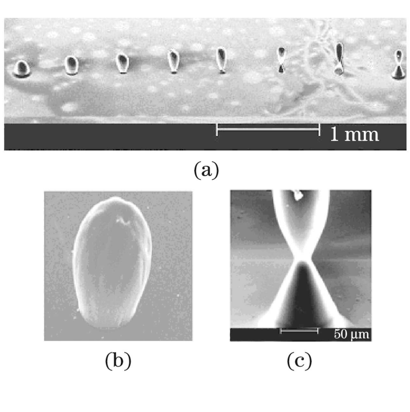
Figure 6(a) shows the single curing units with their exposure time being T = 1, 2, 3, 4, and 5 s from left to right respectively under an exposure power of $P =$ 0.3 μW. Figure 6(b) shows the respective simulation results using the mathematical model of Eq. (6).

The mathematical simulation and experimental results (average value) of curing units' axial size (axial height from the focal plane) and transversal size (diameter at the focal plane) are virtualized in Fig. 7, for the curing power of 0.3 μW. There is a rather good agreement between simulation and experiment results. The experimental heights of curing units change from 55 to



(a) (b) (c)

Fig. 4. Principle of confirming the focal plane.



(a)

(b) (c)

Fig. 5. (a) SEM photos of curing units after 2-min exposure for the working distances of 650, 680, 715, 740, 780, 800, 820, and 860 μm (from left to right); (b) magnified SEM photo of the curing unit for $WL = 680$ μm; (c) $WL = 820$ μm.

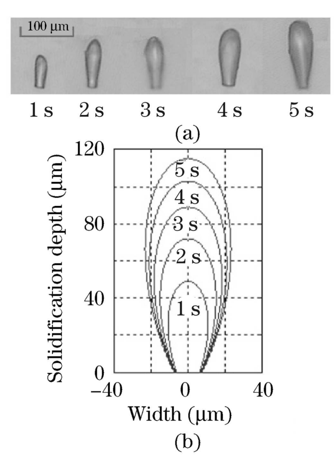


Fig. 6. (a) Experimental and (b) calculated curing results under the exposure power of 0.3 μW after different exposure durations.

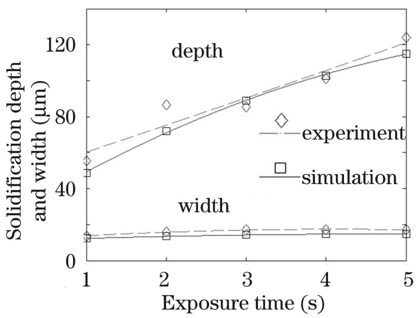


Fig. 7. Relation between curing size and exposure time.

124 nm, while the calculated results change from 49 to 115 nm, the error between them is around 10%. Meanwhile, the experimental diameters of curing units change from 13.8 to 17.2 nm, and the calculated results change from 12.3 to 14.9 nm.

In conclusion, we find that the sizes of curing product grow directly with the exposure amount. The values of two curing coefficients, absorption coefficient and critical curing energy, are obtained in experiments. The shape and size of curing unit produced by MSL are confirmed. These results offer a base for the further improvement in curing resolution.

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