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Photopolymer characterization by high frequency pulsed laser

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ABSTRACT

Maximizing phase modulation in photopolymers remains a challenge in order to use these materials to fabricate photonics devices. Different material compositions and irradiation conditions have been studied in order to achieve it. One of the main conclusions has been that with continuous laser exposure better results are achieved. However, our results show that higher phase modulation can be achieved using pulsed laser. The study has been done with crosslinked acrylamide-based photopolymers (AA/PVA), Biophotopol and Holographic Polymer-Dispersed Liquid Crystals (H-PDLC) exposed with a pulsed laser (532 nm). Thus, phase modulation increases of 8-15% have been achieved between pulsed laser and continuous laser exposure, with a maximum phase depth of 3π radians in AA/PVA, $\sim 3\pi/2$ in Biophotopol and $\sim \pi$ in H-PDLC. This opens the door to the use of this photopolymer in large-scale manufacturing, such as H-PDLC photopolymers to fabricate tunable lenses using the laser-induced direct transfer (LIFT) technique.

Keywords: Polymers; Tunable lenses; Optical storage materials; Diffractive Optics; Holography

1. INTRODUCTION

The use of photopolymers to fabricate lens [1,2] or recording elements such as holographic [3,4] and diffractive devices [5,6] has been a field in constant development in recent decades. The good experimental performance of photopolymers with continuous wave (CW) laser irradiation for the fabrication of engraving elements has led to the use of these lasers over pulsed lasers [7,8,9]. The recording mechanisms with CW laser have been studied for a wide group of photopolymer compositions and irradiation conditions [10,11]. However, there are not many studies about pulsed laser interactions in photo-materials for recording elements. For example, the effect of energy, pulse duration, wavelength at different photo-materials has been studied [7, 10] as well as different irradiation techniques [12,13,14]. The investigations with pulsed laser made in photopolymers based on PVA/AA show gratings with diffraction efficiencies of 60%, [15,16], achieving higher values (85%) by adding monomer crosslinker to the material [17]. However, in both studies the diffraction efficiency and index modulation are lower than in continuous laser irradiations for similar layer thicknesses. Meanwhile, the use of pulsed lasers has been consolidated for the fabrication of other photopolymer-based devices [18,19,20] and have become industrially used tools for polymer processing due to advances in energies and repetition rates of pulsed lasers. Therefore, further study of the processes that induce photopolymerization in the fabrication of recording elements with pulsed lasers is needed to try to achieve diffraction efficiency and index modulation values like those achieved with continuous wave lasers.

It is known that the photopolymerization process is initiated by the generation of free radicals, which reacts with the monomer initiating the polymer chain growth (radical growing) [5,7,9]. The next step in the reaction process with CW laser is the bimolecular combination, where two growing macroradicals come together and finish the process [13]. However, for a low repetition rate pulsed laser such as the one used by *Garcia* and *Gallego* (up to 10 Hz and a pulse duration of 8 ns) [15,16,17], the initiation of the polymer chain growth is produced during the off-time between consecutive pulses. When the next pulse comes, new free radicals are created that can react with the polymer chains which are growing and cause an earlier end to the process. This premature process termination causes the formation of a broad molecular-weight distribution that increases the polymer chain length, which is biggest as the frequency (or pulse repetition rate) decreases, and that reduce the diffraction efficiencies. Conversely, when the repetition frequency of the laser pulse increases, the rate of free radical generation also increases. This leads to an increase in the number of

reactions with the monomer molecules, and thus to a higher polymerization rate and energy sensitivity. This lead one to believe that at high repetition rates it will be possible to achieve at least the same diffraction efficiencies, polymerization rate, energy sensitivity and refractive index modulation as with continuous lasers.

For this reason, in this work we study the refractive index modulation in three photopolymers, PVA/AA, Biophotopol and Holographic Polymer-Dispersed Liquid Crystals (H-PDLC), using high repetition rate irradiations (10-500 kHz). We demonstrate that for the three photopolymers, under specific conditions of pulsed irradiation (pulse duration and periodicity), phase depths greater than those achieved in continuous irradiation (CW) are achieved. Thus PVA/AA achieves a phase depth of up to a maximum of 3π radians, which is 15% more phase modulation than continuous laser irradiations, whereas in Biophotopol the maximum phase depth is $\sim 3\pi/2$ radians, which is 15% more than CW, and H-PDLC show a maximum phase depth is $\sim \pi$ radians, which is 8% more than CW.

2. MATERIALS AND METHODS:

The experimental setup used to measure the phase depth is formed by a real-time interferometric system. This system employs a He-Ne continuous laser to generate the two beams with a grating of 5 lines/mm (Fig. 1). Then, The two first-order diffraction beams are then focused by a lens that produces the spatial overlap of the two beams after passing through the photopolymer sample, with one beam crossing the irradiated area of the photopolymer and the other beam crossing the non-irradiated area. Finally, a microscope objective (M-20X, AN = 0.4, and $f = 9.0$ mm) is used to form a magnified image of the interference plane onto the CCD camera (PCO-1600, high dynamic 14-bit cooled camera). The camera software allows controlling the exposure time, to adjust the saturation level, and the delay between consecutives images. Thus, we can register in real-time the complete growth of phase shift depth. In the measures have been used an exposure time of 6-8 ms and a delay of 250 ms.

The irradiation pulses are obtained from a CW Diode-Pumped Solid-State Lasers (Coherent Verdi V5, wavelength of 532 nm and maximum power of 5 Watts) by means of an acousto-optic chopper, which generates a train of pulses with a minimum period of $2 \mu\text{s}$ (500 kHz) and pulse duration of $1 \mu\text{s}$ where the period and pulse duration can be controlled independently. The pulse parameters are controlled by a pulse generator (Quantum Composers 9200 series), which sends an electric signal to the acousto-optic modulator (AOM) of the chopper.

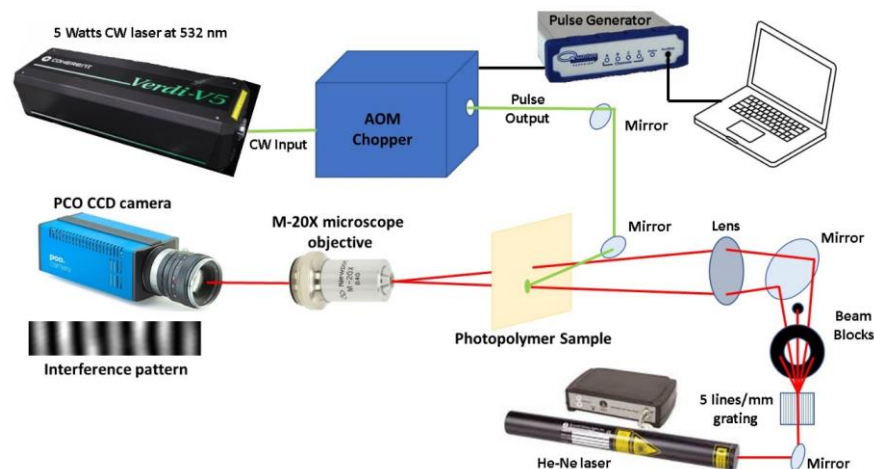


Figure 1. Experimental setup of the irradiations system.

It is important to indicate that since a CW laser is used to generate the pulse train, the maxima fluence per second is achieved in continuous mode, whereas the fluence per second decreases as the laser time off increases. Moreover, the fluence per pulse is also affected by this fact, as it decreases when the pulse width decreases. This means that, unlike pulsed lasers, this way of generating pulse trains does not concentrate all the energy in a pulse but maintains the average energy level in the on times and zeroes the energy in the off times. The beam diameter is $\varnothing = 5.5$ mm and the pulse fluence is 55 mJ/cm^2 . The material is exposed around 240 second until achieving the maximum phase modulation.

The material composition has been selected following the recommendations given by the Gallego and Fernandez studies [21,22]. So, the PVA/AA photopolymer is composed of AA as polymerizable monomer (AA, 0.84 gr), triethanolamine

(TEA, 1.2 ml) as coinitiator and plasticizer, yellowish eosin (YE, 0.7 ml) as dye, PVA as binder and a small proportion of water as additional plasticizer (25 ml of 8% w/v PVA), and N,N'-methylene-bis-acrylamide (BMA, 0.25 gr) as crosslinking monomer. The solution was deposited using the force of gravity, and distributed with a thickness controller rod of 500 μm on a glass substrate, and left 24 hours in the dark to evaporate part of the water, which allows generating a layer with enough mechanical resistance to be cut without deforming. Such as is indicated in Ref [22], for this photopolymer composition a 2π radians phase shift can be achieved for a thickness layer of 68 μm . In our case, the final layer has a thickness of $95 \pm 5 \mu\text{m}$, which enables a higher phase depth. The refractive index of the pre-exposed photopolymer is 1.477, measured with a refractometer in previous works [23]. In order to avoid the surface diffusion once the irradiation starts, which induces an incorrect fitting of the monomer diffusion, an index matching method proposed in Ref. [5,21] is used. This enables to decouple the surface and internal changes. To obtain an accurate index matching we have used commercial baby oil proposed in reference [24], 98% composed of glycerine, with refractive index of 1.484 very close to the mean of the polymer. This index matching method includes a coverplate (microscope slide) to cover the liquid oil and to improve the conservation.

Since AA and BMA are toxic monomers, we use also a green photopolymer called Biophotopol [25], where AA is replaced by sodium acrylate (NaAO), which is less toxic than AA, and BMA is not used. Thus, the final composition of Biophotopol is as follows: NaAO as polymerizable monomer (0.4 ml), triethanolamine (TEA, 0.05 ml) as coinitiator and plasticizer, yellowish eosin (YE, 0.11 ml) as dye, PVA as binder and a small proportion of water as additional plasticizer (5 ml of 8% w/v PVA). The reference [22] indicate that for this biophotopolymer composition a π radians phase shift is achieved for a thickness layer of 90 μm . In our case, the final layer has a thickness of $55 \pm 5 \mu\text{m}$, which should lead to a smaller phase depth.

The last photopolymer used is Holographic Polymer-Dispersed Liquid Crystals (H-PDLC), which is composed for the dipentaerythritol penta/hexa-acrylate monomer (DPHPA, 1.1 gr) with a refractive index $n = 1.490$. We use the nematic liquid crystal, licristal BL036 from Merck, with a concentration of at 28 wt%. It has an ordinary refractive index $n_0 = 1.5270$, and a difference between extraordinary and ordinary index $\Delta n = 0.2670$ [26]. There is a difference of 0.037 between the ordinary refractive index of the liquid crystal and that of the monomer. N-Methyl-2-pyrrolidone (NMP, 0.47 ml) was used as crosslinker, N-phenyl glicine (NPG, 0.01 gr) as radical generator and octanoic acid (OA, 0.145 ml) as cosolvent [26], and ethyl eosin (Yet, 1 mgr) as dye. The solution is deposited between two glass slide that are separated using glass microspheres with a thickness of 40 μm . For this polymer the reference [22] indicates that the phase depth of 2π can be achieved using a sample of 30 μm .

3. EXPERIMENTAL RESULTS

We have measured the phase modulation using the experimental setup described in the figure 1 under different irradiation conditions: fluence per pulse, fluence per second, pulse period and pulse width. Table 1 summarizes the polymer phase depth values achieved in PVA/AA with these different irradiation conditions. As described in the reference [27], no relationship is observed between fluence per pulse and phase depth, nor between fluence per second and phase depth, because the same fluence per pulse and fluence per second lead at different values of phase depth. This leads us to believe that the greatest influence on phase modulation is given by the period and pulse width.

Analysing the influence of the pulse time parameters on the phase modulation, the first fact to highlight is that the maximum phase modulation of 3π radians (553° , irradiation 9) is achieved in the pulsed irradiation regime, being greater than in the CW laser case (2.63π radians or 473° , irradiation 1) for almost all conditions of pulsed irradiation. Just one pulsed irradiation achieves a phase depth lower (458° , irradiation 2) than CW irradiations (473°). This show that even for high pulse rates (10 kHz) lower phase depth than the CW irradiations can be produced. This result together with those obtained in references [16, **Error! Marcador no definido.**], with 10 Hz frequency and 8 ns pulse duration, leads us to think that when the pulse off time is long, at least more than 30 μs , the phase depth (polymerization rate) is lower than in CW irradiations because between consecutive pulses the concentration of free radicals decreases to near zero, which leads to stop the radical-monomer reaction, so that the growing polymer chain reacts with new free radicals generated by the following pulses and causes an earlier end of the process.

The second point of interest is the three irradiation conditions (3, 5 and 6) with a phase depth slightly higher than CW irradiation (473°). When the ratios between pulse width and pulse period are higher than 80% (5 and 6), the material behaviour is like CW irradiations because the free-radical rate remains almost continuous between consecutive pulses. Whereas for irradiations 3 the long pulse off time (10 μs) can explain the similar behaviour to CW irradiations.

The third fact to highlight is the two irradiations groups with a medium (8, 10 and 11) and high (4, 7 and 9) increment of phase depth regarding of CW irradiations. The common points between them are a pulses off time lower than 10 μs (≤ 7 μs), and ratios between pulse width and pulse period lowers than 80% (70%-30%), whereas the main difference is that for high increment of phase depth the pulses off time is between 5 μs and 7 μs , and for medium increment of phase depth the pulses off time is between 1 μs and 2 μs .

Irradiation number	Fluence per pulse (J/cm^2)	Fluence per second (mJ/cm^2)	Pulse Period (μs)	Pulse Width (μs)	Phase Depth (degrees)
1	55×10^{-3}	55	CW	CW	473
2	3.48×10^{-6}	35	100	70	458
3	0.52×10^{-6}	26	20	10	495
4	0.51×10^{-6}	34	15	10	533
5	0.52×10^{-6}	43	12	10	500
6	0.48×10^{-6}	48	10	9	494
7	0.27×10^{-6}	27	10	5	530
8	0.26×10^{-6}	37	7	5	515
9	0.15×10^{-6}	15	10	3	553
10	0.10×10^{-6}	25	4	2	522
11	0.05×10^{-6}	25	2	1	517

Table 1. Polymer phase depth of PVA/AA after CW irradiations and after pulsed irradiations as a function of pulse period, pulse width and pulse fluence.

Classical explanations of the photopolymerization process (*Shelkovnikov* [13], *Garcia* [16] and *Gallego* [**Error! Marcador no definido.**]), do not give an answer both to the medium and to the high increase in phase modulation for pulsed irradiation compared to CW irradiation. However, *Decker* gives us a possible explanation for this behaviour in the reference [28]. They observe a saturation effect, in which a partial recombination of the excited photoinitiator occurs to produce the starting dye again, once the concentration of the excited photoinitiator reaches a certain high value. A continuous exposure with the CW laser does not favour partial recombination of the excited photoinitiator because there is no pulse off time to stimulate this recombination, which reduces regeneration of the starting dye and thus results in fewer total free radicals. However, in pulsed lasers, when the pulse off-time is greater than 1 μs (our maximum time resolution) and the ratio of pulse width to pulse period is less than 80%, recombination of the excited photoinitiator is favored and thus high regeneration of the starting dye. This leads to higher total free radical formation and thus higher polymerization rates. However, for a large pulse off time (≥ 10 μs), although the number of initial dye regenerated also increases, the long pulse off time allows for radical-monomer reaction and polymer chain growth, resulting in an early end of the process.

To check if this behaviour is common in other photopolymers, we have reproduced the same irradiation conditions but using Biophotopol (1, 2, 3 and 4) and H-PDLC (5, 6 and 7). Table 2 summarizes the phase depth values achieved in both photopolymers with the main irradiation conditions observed in PVA/AA.

Irradiation number	Fluence per pulse (J/cm^2)	Fluence per second (mJ/cm^2)	Pulse Period (μs)	Pulse Width (μs)	Phase Depth (degrees)
1	55×10^{-3}	55	CW	CW	180
2	0.26×10^{-6}	37	8	5	212
3	0.48×10^{-6}	48	10	9	185

4	3.48×10^{-6}	35	100	80	155
5	55×10^{-3}	55	CW	CW	358
6	0.27×10^{-6}	27	10	5	389
7	0.10×10^{-6}	25	4	2	362

Table 2. Polymer phase depth of Biophotopol (1, 2, 3 and 4) and H-PDLC (5, 6 and 7) after CW irradiations and after pulsed irradiations as a function of pulse period, pulse width and pulse fluence.

From the Biophotopol results, the first fact to note is that the maximum phase modulation of $\sim 3\pi/2$ radians (212° , irradiance 2) is reached in the pulsed irradiance regime, being higher than in the case of the CW laser (π radians or 180° , irradiance 1) and greater than that achieved in the reference [22]. For its part, the phase modulation of irradiation 3 (185°) confirms that when the pulse off time is between $1 \mu\text{s}$ and $2 \mu\text{s}$ there is an average increase in phase depth with respect to CW irradiation. In addition, pulsed irradiation 4 shows a shallower phase depth (155°) than CW irradiations, demonstrating that when the pulse off time is long, at least more than $20 \mu\text{s}$, the phase depth (polymerization rate) is lower than in CW irradiations.

Meanwhile, the H-PDLC results also show that the maximum that the phase modulation of 389° (irradiance 6) for pulsed irradiance meets that the ratio of pulse width to pulse period is less than 80% (70%-30%), and the pulse off time is between $5 \mu\text{s}$ and $7 \mu\text{s}$. This is higher than in the case of the CW laser and equal to that obtained in the reference [22]. For its part, the phase modulation of irradiation 7 (362°) confirms that when the pulse off time is between $1 \mu\text{s}$ and $2 \mu\text{s}$ there is a small increase in phase depth with respect to the CW irradiation (358° , irradiation 5).

Therefore, we can conclude that the minimum irradiation conditions to achieve a higher phase depth than CW irradiations are a ratio between pulse width and pulse period lower than 80% to allow a high regeneration of the starting dye, and a pulse off time between $1 \mu\text{s}$ and $10 \mu\text{s}$ to allow following a chain-reaction process and the polymer radical growing, and avoid an early end of process. That means laser frequencies higher than 20 kHz (period lower of $50 \mu\text{s}$) are necessary to achieve phase modulation higher than CW irradiation because with lower frequencies is not possible to keep these previous conditions. Moreover, the better irradiation conditions to achieve the maximum phase modulation are a pulse off time of between $5 \mu\text{s}$ and $7 \mu\text{s}$ and ratios between pulse width and pulse period lower than 80%.

4. CONCLUSIONS

The irradiation parameters effects in the phase modulation in in three photopolymers, PVA/AA, Biophotopol and Holographic Polymer-Dispersed Liquid Crystals (H-PDLC), have been studied in this paper. In particular, the effect of high frequency irradiation compared with low frequency of previous studies have been checked. The main conclusion is that with high frequencies, more than 20 kHz (period of $50 \mu\text{s}$), higher phase depth values than the CW irradiations can be achieved. PVA/AA show an increment of up to a maximum of 15%, whereas in Biophotopol the maximum phase is 15% more than CW, and H-PDLC of 8%. This is because the pulse off time is long enough to allow a high regeneration of the starting dye but not too long to avoid the reaction between growing polymer-chain and new free-radical, leading to higher polymerization rates. When the ratio between pulse width and pulse period is higher than 80% the phase depth has similar behaviour than CW irradiations. Moreover, when the pulse off time is higher than $20 \mu\text{s}$ the phase depth is lower than CW irradiation. This better behaviour of the three photopolymer with pulsed irradiations will allow its use in holographic copying processes or in the tunable lenses fabrication using the laser-induced direct transfer (LIFT) technique, which improves the perspectives of the utilization of this photopolymer in large-scale industrialized processes.

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