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New Non-Toxic Holographic Photopolymer Material

Dervil Cody
Technological University Dublin, dervil.cody@tudublin.ie

Izabela Naydenova
Technological University of Dublin, izabela.naydenova@tudublin.ie

Emilia Mihaylova
Technological University of Dublin, emilia.mihaylova@tudublin.ie

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D Cody[1, 2], I Naydenova[1, 2] and E Mihaylova[1, 2, 3, *]

[1]Centre for Industrial and Engineering Optics, Dublin Institute of Technology, Dublin 8, Ireland
[2]School of Physics, College of Sciences and Health, Dublin Institute of Technology, Dublin 8, Ireland
[3]Department of Mathematics and Physics, Agricultural University, Plovdiv, Bulgaria
*corresponding author e-mail: emilia.mihaylova@dit.ie

There is an increasing need for environmentally friendly holographic recording materials which can be produced in bulk with little risk to the health of workers in manufacturing. This is why the development of non-toxic photopolymer materials is crucial, and has attracted attention in recent years. Composition and preliminary characterization of a new non-toxic photopolymer material are presented. It operates well at a range of spatial frequencies, and achieves diffraction efficiencies and refractive index modulation comparable to the known acrylamide-based photopolymers.

1. Introduction

Acrylamide-based photopolymers are fast becoming one of the most popular recording media for different holographic applications. Their high sensitivity, wide dynamic range and self processing nature, together with their low cost of production, make them an excellent candidate for applications such as holographic sensors, diffractive optics and data storage. However acrylamide (AA) is a toxic chemical [1-3] and has been classified by the World Health Organization as probably carcinogenic to humans, following studies conducted by the International Agency for Research on Cancer [4].

In this paper, the design and testing of a new non-toxic and environmentally-compatible photopolymer material is described. The improved photopolymer is shown to have holographic recording features similar to those of the standard AA-based photopolymer [5]. It has already been shown to surpass the holographic recording capabilities of other reported low toxicity photopolymer alternatives [6-8].

Any new non-toxic monomer must   be compatible with the other components of the photopolymer composition. It must be hydrophilic, and it must react through a radical chain mechanism. A detailed description of the radical chain steps and reaction equations is given elsewhere [9].

In the work presented here, AA is replaced by Diacetone Acrylamide (DA) as the main monomer in the photopolymer composition. DA is a crystalline solid and contains only 0.1 wt % AA, and is not a probable carcinogen, according to research reported by the IARC [10]. It is classified as a category 4 material in terms of acute toxicity, compared to AA which is a high risk category 3 material [11,12]. Aside from its low toxicity, DA is highly hydrophilic, and it readily polymerizes via a radical chain mechanism with a variety of co-monomers [13].

2. Experimental

2.1 Layer Preparation

The DA photopolymer layers were prepared by mixing 1.0g DA, 0.2g N, N-methylene-bisacrylamide (BA), 2ml triethanolamine (TEA) and 4ml Erythrosin B 0.11% wt/vol dye solution (EB) to 20ml of 10% wt/vol polyvinyl alcohol (PVA). The photopolymer solution was then deposited on to glass slides (76 x 26mm) and allowed to dry for 12-24 hours in darkness under normal laboratory conditions (20-25ºC, 40-60% RH). Layer thickness was measured using a white-light surface profiler (Micro XAM S/N 8038). The preparation of the acrylamide containing layers, is described elsewhere [10] for comparison purposes.

2.2 Experimental Set-up

A two-beam holographic optical setup (figure 1) with an angle of 30º between the beams was used to record unslanted transmission gratings using a 532nm Nd:YVO$_4$ laser. Gratings were recorded in the layers with an exposure of 200mJ/cm^2 at a spatial frequency of 1000 lines/mm. The recording intensity was controlled by a variable neutral density filter. The absorption of the photopolymer at 633nm is negligible, so a 633nm He-Ne laser was used as a probe beam at the Bragg angle to enable the diffracted beam intensity to be monitored in real time. The angular selectivity of the gratings was measured after holographic recording was finished. In order to measure the diffracted intensity dependence on the incident angle of the probe beam, the grating was placed on a rotational stage (Newport, ESP 300). An optical power meter (Newport 1830-C) recorded the intensity of the diffracted beam and the data was transferred to a computer.
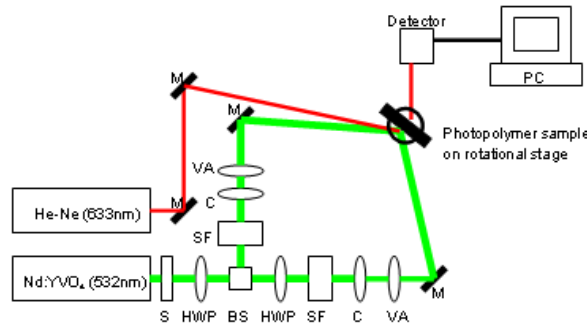

Figure 1. Experimental setup: S: shutter, HWP: half wave plate, BS: beam splitter, SF: spatial filter, C: collimator, VA: variable aperture, M: mirror.

3. Composition Optimization

3.1 DA monomer optimization

First, the concentration of the DA monomer in the photopolymer composition was optimized. Concentrations of DA monomer varying from 25 - 75 mg/ml were tested, without addition of cross-linking monomer BA. Transmission gratings were then recorded using with these layers. The diffraction efficiency of the gratings recorded in the layers was calculated using the formula

$$\eta = \frac{I_d}{I_{in}} \times 100$$

where Id = diffracted beam intensity, Iin = incident intensity and _ = diffraction efficiency.

As can be seen from figure 2, there is steep increase in the diffraction efficiency with increasing concentration of DA. However above ~60 mg/ml, the quality of the layers begins to deteriorate as saturation of the amount of monomer that can be dispersed in the binder has been reached, and the diffraction efficiency falls off due to the poor optical quality of the layers.
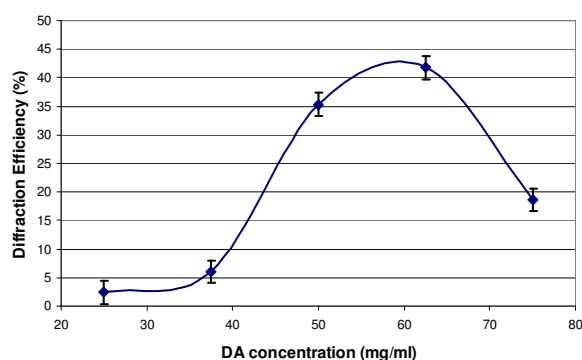
Figure 2. Graph of diffraction efficiency vs. diacetone acrylamide concentration.

3.2 Cross-linker optimization

Cross-linking monomer BA (N, N'-Methylenebisacrylamide) was then added to the photopolymer solution. The function of the cross-linker is to hold the polymer chains together in the grating once it is formed, preventing polymer diffusion. The presence of the cross linker prohibits post-recording decay of diffraction gratings. This is shown in figure 3. The total amount of monomer was kept constant at 1.25 g (= 62.5 mg/ml) and the ratio of the DA: BA was varied. The different compositions tested are shown in Table 1. Photopolymer layers prepared with composition B were the most stable. The other solutions produced layers from which BA precipitated out of the layers, as the saturation point of the solution had been reached. This effect was not initially observed in layers of composition B, but occurred 24 hours after holographic recording. To prevent this and improve the material's shelf-life, the amount of BA was reduced by 0.05g (20% of the initial value) without a significant decrease in diffraction efficiency. The final composition is shown in Table 1.
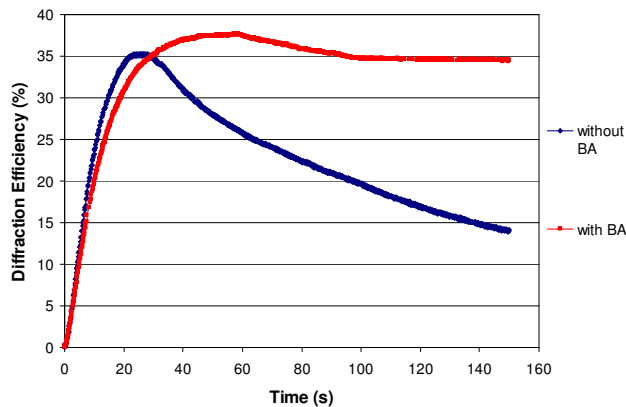

Figure 3. Graph of real-time diffraction efficiency growth curves for DA photopolymers without and with bisacrylamide (final composition in Table 1).

Table 1. Compositions for BA Concentration Optimization

Composition	PVA (ml)	TEA (ml)	EB dye (ml)	DA (g)	BA (g)
A	20	2	4	1.125	0.125
B	20	2	4	1.0	0.25
C	20	2	4	0.875	0.375
D	20	2	4	0.75	0.5
E	20	2	4	0.625	0.625
F	20	2	4	0.5	0.5
Final	20	2	4	1.0	0.2

4. Results and Discussion

4.1 Spatial Frequency Dependence of new Photopolymer

Once the composition had been optimized for the new monomer, the spatial frequency dependence of the non-toxic photopolymer was investigated. Transmission gratings were recorded in 55-65 μm thick layers at spatial frequencies of 1000 and 3000 l/mm.

4.1.1 Photopolymer response at 1000 l/mm. The recording intensity was varied in the range 1-5 mW/cm^2. As shown in figure 4, for 1000 l/mm the DA composition reaches a maximum refractive index modulation of ~3.33x10^{-3} after being exposed to an intensity of 2 mW/cm^2 for 55 seconds. The refractive index modulation in the acrylamide based photopolymer composition can reach ~5x10^{-3} after 50 seconds of exposure to 4 mW/cm^2.
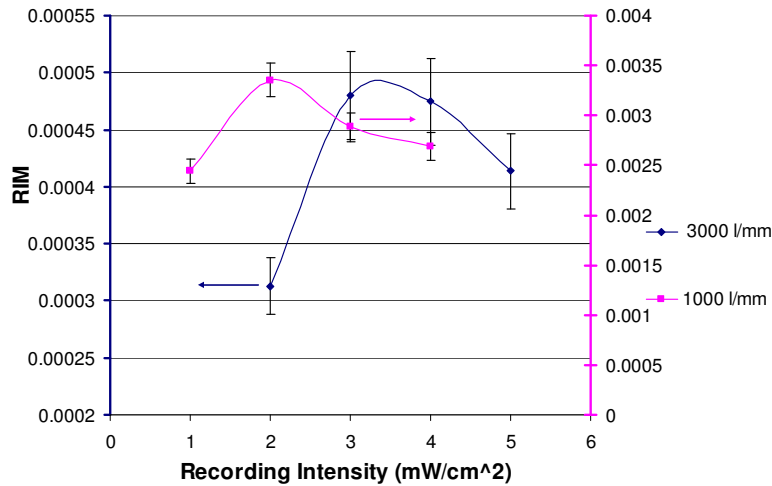

Figure 4. Refractive index modulation vs. recording intensity for 1000 (right hand vertical axis) and 3000 l/mm (left hand vertical axis).

4.1.2 Photopolymer response at 3000 l/mm. At 3000 l/mm the maximum achievable refractive index modulation for DA is 4.7×10^{-4} with an exposure of 3 mW/cm^2 for 32 seconds. The acrylamide photopolymer can reach a refractive index modulation of 8.5×10^{-4} after a relatively low exposure time of 8 seconds at 7 mW/cm^2. The Centre for Industrial and Engineering Optics (IEO) at Dublin Institute of Technology has developed a two-way diffusion model which explains this experimentally observed decrease in refractive index modulation at higher spatial frequencies [14]. Optimisation of the diacetone acrylamide photopolymer will need to be done to further improve its suitability for high spatial frequency recording. One option is to decrease the permeability of the photopolymer matrix, which would prevent the diffusion of short polymer chains [15]. The addition of different types of nanoparticles to the composition will be investigated, as this has previously been shown to improve the sensitivity and refractive index modulation of photopolymer materials [16]. Characterization of the photopolymer for recording in reflection mode is in progress.

5. Conclusion

The development of a new non-toxic holographic photopolymer material has been discussed. The photopolymer composition has been optimized for the non-toxic monomer, and its spatial frequency dependence on the Refractive Index Modulation in transmission mode of recording has been investigated. The new material has been observed to reach refractive index modulation up to 3.3×10^{-3}, and can reach diffraction efficiencies >90% in 70μm thick layers. It is suitable as an environmentally friendly alternative to the known acrylamide photopolymers [17-21] for holographic applications. Further characterization of the materials holographic recording capabilities is currently being carried out. Optimization is also underway to improve this material's high spatial frequency response.

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