Effect of Concentration of DYE on the Storage Life of Plane Wave Gratings on Photopolymer Film

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ABSTRACT: Holographic grating with good storage life in poly(vinyl alcohol) based photopolymer film, prepared by gravity settling method, with reduced concentration of the dye was found to give good diffraction efficiency without crosslinking. The material was found to show good diffraction efficiency and sensitivity (75% diffraction efficiency at exposure energy of 80 mJ/cm^2). The shelf life of the photopolymer solution could be improved by storage at a temperature $\sim$ 4°C in refrigerator. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1238–1243, 2012

Key words: PVA-AA photopolymer film; methylene blue; sensitivity; storage life; shelf life

INTRODUCTION

Photopolymers were first introduced as holographic recording material by Close et al. in 1969.[1] This system generally comprise of one or more monomers, initiator, and sensitizer. The dry photopolymers consist of an additional polymeric binder. Other components are added to control a variety of properties such as pre-exposure shelf life, and viscosity of the recording medium. Vinyl monomers, such as acrylate and methacrylate are used in most photopolymer systems. Binders are included to modify the viscosity of the formulation, to aid sample preparation, and to enhance holographic exposure. In 1980s Calixto reported acrylamide incorporated poly(vinyl alcohol) (PVA), triethanol amine (TEA), and methylene blue (MB) were used as photo initiating system.[2] Acrylamide-based poly(vinyl alcohol) films constitute a low cost organic material, and a great deal of attention has been given to this photopolymeric system in recent years.[3–8] Addition of each component is found to contribute to the performance the performance of the film.

In this work, acrylamide incorporated poly(vinyl alcohol) photopolymer film was used. Previously our research group has successfully recorded holographic gratings in acrylamide incorporated poly (vinyl alcohol) film with a diffraction efficiency (DE) of 70% with an exposure energy of 125 mJ/cm^2, having a dye concentration of 2.09 $\times$ 10^{-4}M, but a gradual decrease in diffraction efficiency was observed on storage.[9] The reason for the decrease may be due to the diffusion of residual dye molecules from destructive region to constructive region and by the instability of leuco form of the dye molecule.[8] Doping with ammonium dichromate and copper chloride, resulted in good storage life with low diffraction efficiency. But Pramitha et al. has reported that by using silver ion as a crosslinker, a diffraction efficiency of 75% could be achieved with an exposure energy of 80 mJ/cm^2 and it remained as 50% even after 1 year.[9] In order to study the storage life of the material in the absence of metal ions, the dye concentration was reduced from 2.09 $\times$ 10^{-4}M and concentration was optimized by recording gratings at different exposure energies. Surprisingly, good diffraction efficiency and storage life was obtained for a dye concentration of 1.4 $\times$ 10^{-4}M. From this result, the role of dye molecules on the material's storage life was clear. The sensitivity of the material also improved. It is clear from the result that, without the addition of any metal ion, storage life of the material could be improved at low dye concentration.

EXPERIMENTAL

All the materials used in this work were analar grade and were used without further purification.

TABLE I
Concentration of Different Constituents

PVA	10% by weight
Acrylamide	$0.38M$
Triethanolamine	$0.05M$
Methylene blue	$2.09 \times 10^{-4}M$ to $0.7 \times 10^{-5}M$

Photopolymer solution was prepared by dissolving 10 g poly(vinyl alcohol), in 100 mL cold distilled water. (SD-Fine, molecular weight; 1,25,000 and degree of hydrolysis, 86–90%). To this, acrylamide, AA (Merck), Triethanolamine, TEA (Merck), and methylene blue, MB (Merck) were added and the solution was stirred well to get a homogeneous solution. The polymer film was prepared by gravity settling method under normal laboratory conditions (RH-55–65%, temperature-28–32°C) and 48 h of drying was required. The concentration of each component is given in Table I. The dried film showed a thickness of 130 μm measured using Dektak 6 m Stylus profiler. The optical characterization was done using Jasco V-570 spectrophotometer and the modulation in refractive index (RI) was calculated using Kogelink's coupled wave theory;

$$\Delta n = \text{Sin}^{-1}(\eta^{1/2}) \times \lambda \cos \theta / \pi \times d \quad (1)$$

where, Δn, RI modulation; η, DE; λ, wavelength of reading beam; θ, angle inside the material measured from the normal to the surface; and d, thickness of the film.

Using this equation a RI modulation of 1.52×10^{-3} was obtained.

To find the diffraction efficiency of transmission hologram, plane wave gratings were recorded on the film, using He-Ne laser (632.8 nm) by standard double beam method [Fig. 1(a)]. The laser beam was split in to two using a beam splitter (B) with R/T ratio 50/50 and these beams were directed to the film using front silvered mirrors (C). These beams were expanded using spatial frequency filter (D) and collimated (E, collimating lens). The collimated laser beams are allowed to interfere inside the film (F). The exposure time was controlled by an electronic shutter (A) placed in front of the laser. For measuring the DE, unexpanded laser beam was used. This unexpanded laser beam was allowed to fall on the grating recoded film placed at Bragg's angle. The diffracted beam was observed on the screen at Bragg angle and its intensity was measured using Ophir 200 power meter. The intensity of the laser beam was reduced to 1 μW using neutral density filters (ND filter). The intensity of incident beam (I_i) and diffracted beam (I_d) was measured. The percentage diffraction efficiency (η) of the recorded grating was measured as a ratio of intensity of the diffracted beam to intensity of the incident beam [Fig. 1(b)].

The diffraction efficiency (DE) was calculated as the ratio of intensity of diffracted beam to the intensity of the incident beam.

RESULTS AND DISCUSSION

Optimization of concentration of dye

For optimizing the concentration of the dye, samples were prepared by varying concentration of the dye from $2.09 \times 10^{-4}M$ to $0.7 \times 10^{-5}M$ (films were named as C_{20}, ..., $C_{0.007}$, respectively) by keeping the concentration of the other components same as shown in the Table I. Gratings were recorded on these films at different exposure energies by keeping the recording angle as 40° and power at the recording position as 4 mW. Variation in DE with exposure energy for different concentration of the dye was plotted (Fig. 2). It was clear from the graph that, only for a particular dye concentration, maximum DE was obtained. When the concentration of the dye increased further, the bleaching was not perfect and this causes scattering and reduction in DE. When the concentration of the dye was reduced further from this particular concentration, again a reduction in DE could be observed because the free radical formation in this case is by the reduction of the dye molecules and if there is no enough molecules, the formation of free radicals and hence DE also get reduced.[10,11] Regarding the exposure energy, it is clear from the graph that for all dye concentrations,
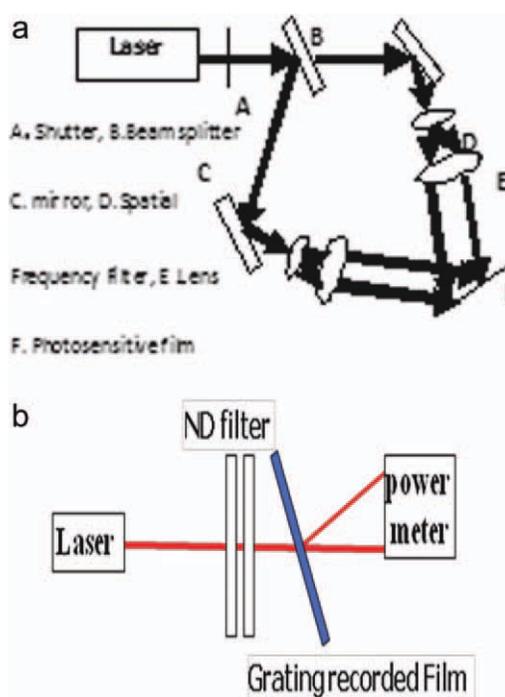
Figure 1 (a) Double beam setup for recording grating. (b) Experimental setup for diffraction efficiency measurement. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
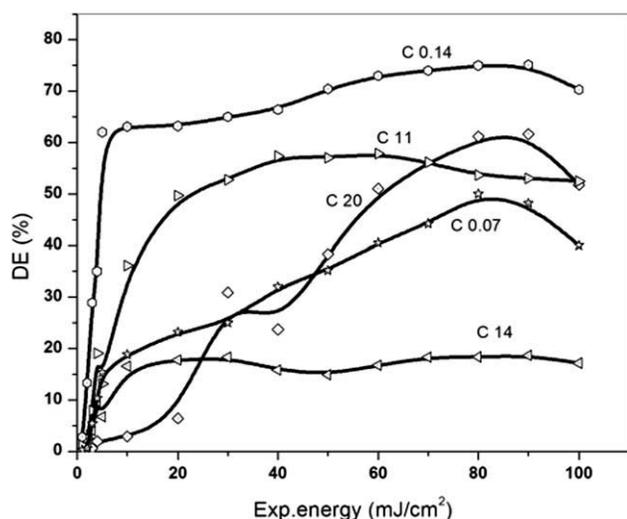
Figure 2 Exp. energy versus % DE of the films with different dye concentration.

with increase in exposure energy, DE also increased, reached a maximum value and then decreased. At high exposure, decrease in DE might be caused by cross talk of holograms.[12] The polymer film C 0.14 (dye concentration: $1.4 \times 10^{-5}M$) showed a maximum diffraction efficiency of 75% with exposure energy of 80 mJ/cm².

Sensitivity and response time of the optimized film

For studying the sensitivity of the optimized film (C 0.14), optical absorption spectrum was taken (Fig. 3). The hologram formation in the photopolymer film has been discussed by several researchers[13,14] and Lawrence et al.[15] has studied the mechanism in acrylamide photopolymer in which gratings were recorded by photopolymerization of acrylamide.

It consists of photophysical and photochemical processes.

Photophysical process

When the dye molecule D, is exposed to laser, it absorbs a photon and is promoted into a singlet excited state $^1D^*$

$$D + h\upsilon \ \rightarrow \ ^1D^* \tag{2}$$

The singlet excited state dye can return to the ground state by fluorescence

$$^1D^* \ \rightarrow \ D + h\upsilon \tag{3}$$

or by radiationless transfer to another molecule and here it is the electron donor (ED).

$$^1D^* + ED \ \rightarrow \ D + ED^* \tag{4}$$

The singlet state can also undergo intersystem crossing into more stable and longer lived triplet state

$$^1D^* \ \rightarrow \ ^3D^* \tag{5}$$
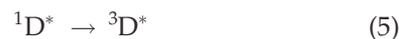
Here the excited dye molecule can undergo a reaction with the electron donor by abstracting two hydrogens to get converted to leuco form. Here the electon donor is triethanolamine and it donates an electron to the excited triplet state of the dye, leaving the dye with one unpaired electron and an overall negative charge

$$^3D^* + (OHCH_2CH_2)_3N : \ \rightarrow \ D^{\cdot -} + (OHCH_2CH_2)_3N^{\cdot +} \tag{6}$$
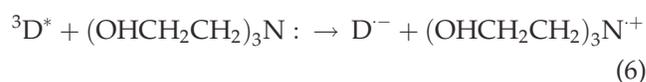
The radical cation of the electron donor loses a proton and becomes a free radical.

$$\begin{aligned}(OHCH_2CH_2)_3N^{\cdot +} \\ \rightarrow (OHCH_2CH_2)_2NC^{\cdot}HCH_2OH + H^+\end{aligned} \tag{7}$$
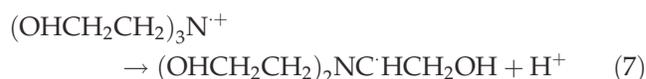
The radical anion of the dye molecule abstracts hydrogen from the free radical of the electron donor.

$$\begin{aligned}(OHCH_2CH_2)_2NC^{\cdot}HCH_2OH + H^+ + D^{\cdot -} \\ \rightarrow (OHCH_2CH_2)_2NCH{=}CHOH + H_2D\end{aligned} \tag{8}$$
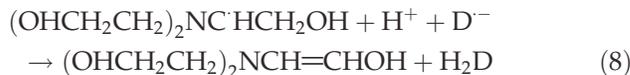
Photochemical process

The photochemical process involves free radical polymerization. It consists of three steps, initiation, propagation and termination.

Initiation. Initiation takes place when the free radical initiator attaches to the monomer by addition across the C—C double bond.

While bond formation, to attach itself to the monomer, the free radical uses its own unpaired electron and a π electron from C—C bond. This leaves one of
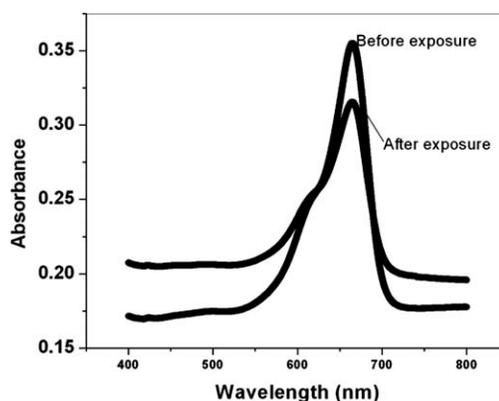

Figure 3 Optical absorption spectrum of the film C 0.14.

the carbons with an unpaired electron therefore the monomer becomes free radical [Eq. (9)].

$$H_2C{=}CH + I^\bullet \longrightarrow I{-}CH{-}CH_2^\bullet \qquad (9)$$

with the carbonyl (C=O) and amide (NH_2) substituents shown on the structures.
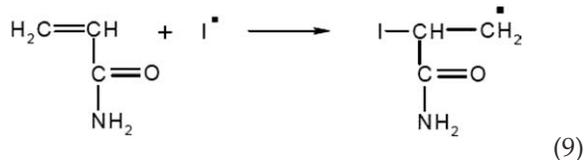
Propagation. Propagation occurs when the new radical attaches itself to another monomer by addition across the double bond by the same method as above. The second monomer now becomes a radical and in this way a polymer grows [Eq. (10)].

$$(10)$$
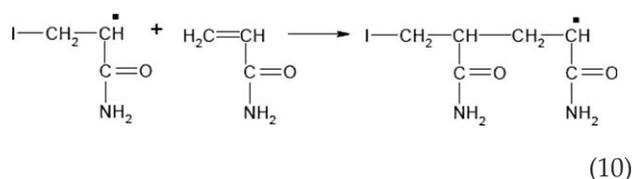
Termination. After initiation and propagation, the newly formed chain will continue to grow until it is stopped by a termination reaction. This process can arise by two reactions known as disproponation or combination.[15] Disproponation takes place when hydrogen is abstracted from one propagating chain by another. The hydrogen reacts with the free radical and the original double bond is reformed. This process results in two separate chains [Eq. (11)].

$$(11)$$
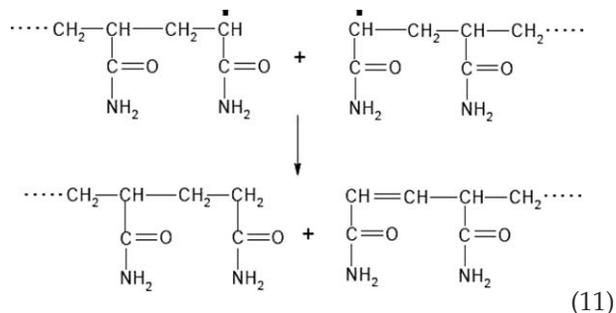
The second method of termination is combination, this consist when the radicals at the ends of two propagating react forming one long chain [Eq. (12)].

$$(12)$$
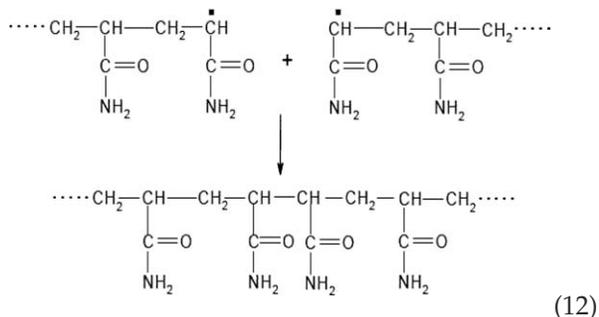
Here, in order to study the response time of the C 0.14 film, gratings were recorded on the film by
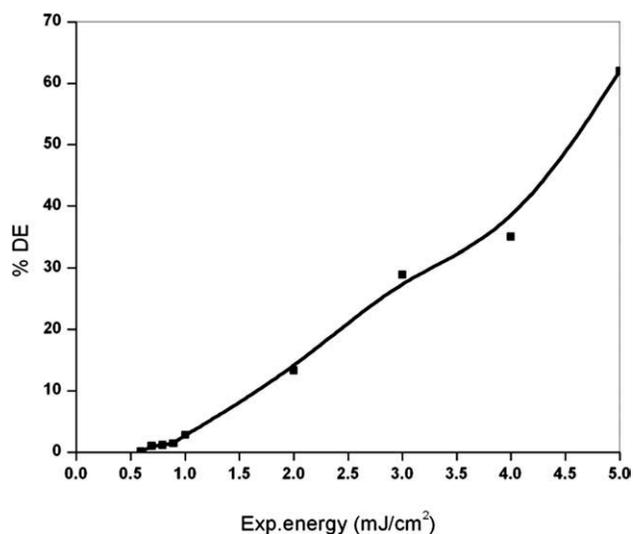
Figure 4 Variation in DE with Exposure Energy of C 0.14.

varying the exposure energy by keeping the power at the recording position as 4 mW and the spatial frequency as 1080 lines/mm. The variation in % DE with exposure energy was plotted (Fig. 4). The minimum exposure energy needed to record the grating was 590 J/cm^2 and for this a DE of 0.05% was obtained when a high power laser was used for reconstruction. As the exposure energy increased to 5 mJ/cm^2, DE also increased to 62% for reconstruction with 1 W He-Ne laser (Fig. 4). Diffraction efficiency reached a maximum of 75% with 80 mJ/cm^2 for 1 W He-Ne laser reconstruction (Fig. 2, for C 0.14).

Resolution

For studying the resolution of the material, gratings were recorded on the optimum sample (C 0.14) at different interbeam angles (30°–80°) and spatial frequency was calculated using Bragg's equation;

$$2d\sin\theta = n\lambda \qquad (13)$$

$$\text{Number of lines, } N = 1/d \qquad (14)$$

(spatial frequency, 818–2032 lines/mm, respectively) with the optimum exposure energy of 80 mJ/cm^2. A maximum diffraction efficiency of 75% could be achieved with spatial frequency of 1080 lines/mm. With 2032 lines/mm also, a diffraction efficiency of 65% could be achieved (Fig. 5).

Variation of beam ratio

For studying the effect of beam ratio on the diffraction efficiency of the film C 0.14, ratio between the two beams were varied by keeping the angle of recording and exposure energy same as 40° and
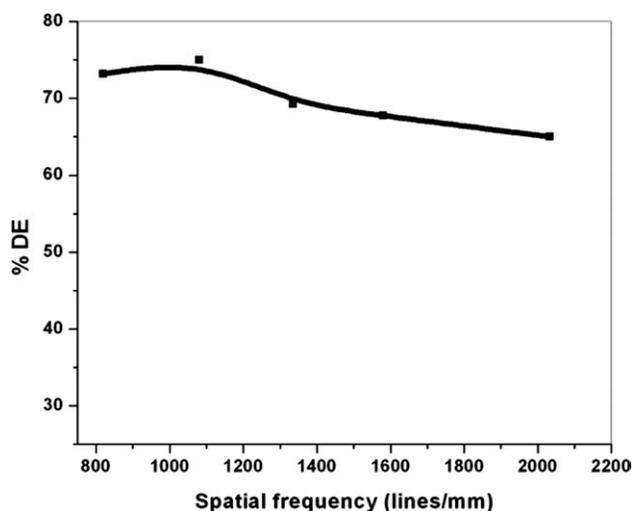
Figure 5   Variation in DE with spatial frequency of C 0.14 film.

Figure 7   The DE of grating on C 0.14 film on storage.

80 mJ/cm^2, respectively. Figure 6 shows the variation in DE with beam ratio and from the Figure 6; maximum diffraction efficiency of 75% was obtained when the beam ratio was 1 : 1.

Storage life of the film

Photopolymer films are WORM materials and therefore, storage life has great importance. To study the material storage life, gratings were recorded and the diffraction efficiency was measured on successive days. Initially the material has a diffraction efficiency of 75% and after 2 months, it remained as 73% and after 5 months, the efficiency was 67% and after 1 year it was 43% (Fig. 7). The decrease was observed only when the relative humidity was above 75%. The DE of 43% remained as such for the next 6 months and again a decrease was observed. The decrease in DE in the highly humid condition

can be explained as: when the relative humidity is high, the high moisture makes the PVA layer more permeable to migrating species and this induces a decrease in diffraction efficiency.[16] The major drawbacks of dye sensitized PVA/acrylamide is the decrease in diffraction efficiency on storage without crosslinker as reported in literatures. The reason for decrease in the diffraction efficiency may be due to the diffusion of dye molecules from destructive region to constructive region. But in our case, the concentration of dye molecules was very low and no more dye molecules may remain in the destructive region and comparatively good storage life could be achieved without any crosslinker.

Shelf life of the film

Shelf life of the material was studied by recording gratings on C 0.14 film at different time interval

Figure 6   Dependence of DE on beam ratio for C 0.14.
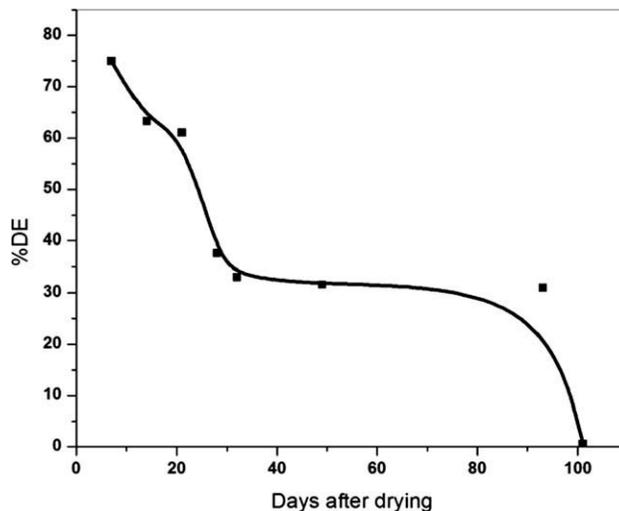
Figure 8   Shelf life of C 0.14 film.

after drying the sample. In all cases, gratings were recorded with an energy sensitivity of 80 mJ/cm^2 at an angle of 40° and reconstructed with low power laser. Figure 8 is the plot of variation in DE versus days after drying. From the Figure 8, it could be seen that grating with DE of 60% could be achieved up to 2 weeks and after 1 month; gratings could be recorded on the film with a DE of 30% only. After 3 months, gratings could be recorded on this sample with low diffraction efficiency and after 100 days, no gratings could be recorded (Fig. 8).

Trials were done to improve the shelf life of the material and for that the photopolymer mixture was kept in the solution form and stored in refrigerator at a temperature of 5°C ± 3°C. The same diffraction efficiency of 75% could be achieved after 5 months of solution preparation. This may be because when the material is in the dried form, the moisture may get trapped and this reduces the film performance.

CONCLUSIONS

The concentration of dye in the polymer system plays an important role on the storage life and sensitivity of the material. A DE of 62% with an energetic sensitivity of 5 mJ/cm^2 was obtained without using any additional component. This material has good storage life also, and it could be used as a permanent recording material. Shelf life of the material could be improved by keeping the solution under controlled condition like low temperature, free from oxygen atmosphere etc.

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