

Copper Doped Methylene Blue Sensitized Poly(vinyl alcohol)–Acrylamide Films for Stable Diffraction Efficiency

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Copper doped methylene blue sensitized poly(vinyl alcohol) (MBPVA)–acrylamide films were fabricated to improve the storage life of recorded gratings. The films were fabricated using gravity settling method and the copper chloride concentration was optimized as 3.18×10^{-3} mol/l for a dye concentration of 6.2×10^{-4} mol/l. The gratings recorded on the optimized film constitution could be stored for months with stable diffraction efficiency (24%) without any chemical or thermal fixing techniques. The resolution of the material is found to be unaffected with the addition of copper chloride.

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1. Introduction

Volume phase holograms in photopolymers have found many potential applications in optical data storage, optical data processing and the production of holographic optical elements. Compared with other holographic materials such as dichromated gelatin and silver halide emulsions, photopolymers have the great advantage of recording and reading holograms in real time and the spectral sensitivity could be easily shifted to the type of recording laser used by simply changing the sensitizing dye. Also these materials possess characteristics such as good light sensitivity, real time image development, large dynamic range, good optical properties, format flexibility, and low cost. Generally a photopolymerizable material consists of a photoinitiator [photosensitizing dye, an electron donor (generally an amine)], one or two monomers and an inert polymer matrix (acts as binder). The photopolymerization begins by absorption of light by the photoinitiator, which results in the formation of primary free amine radicals. In the second step of the initiation, the primary radicals react with a monomer unit to form a growing radical of one repeat unit in length. In the second stage (propagation), a monomer is added, following a chain-reaction process, to the growing polymer radical. Two separate paths exist for termination. The first is the normal bimolecular combination, in which two growing macro radicals come together and terminate. The second path for termination is disproportionate, in which a labile atom (usually hydrogen) is transferred from one polymer radical to another.¹⁾ As the monomer in the constructive interference region gets polymerized, diffusion of monomer occurs from the destructive interference region. This causes a refractive index modulation and results in grating formation. Here the absorbance modulation that occurs during exposure also contributes to the grating formation. Polymeric materials such as poly(methyl methacrylate) (PMMA), poly(diacetylene) (PDA), poly(vinyl carbazole) (PVK), poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), polythiophene, poly(vinyl chloride) (PVC), etc. have been widely investigated for holographic applications.^{2–7)} Of these, PVA based films are of interest on account of its easiness of fabrication

and economy of materials. Compared to the dye sensitized PVA based recording media like PVA/vinyl acetate⁸⁾ and PVA/PAA⁹⁾ blend, PVA/acrylamide films have high diffraction efficiency (DE), high sensitivity and high resolution.^{1,10,11)}

The major drawbacks of dye sensitized PVA/acrylamide is the decrease in diffraction efficiency (DE) on storage.^{11–13)} Therefore only short-term storage is possible in this material. The decrease in DE is due to the diffusion of monomer from the region of destructive interference to that of the constructive interference. As a result the grating become blurred and the DE decreases. The reconversion of dye molecule from leucoform to the original state is another reason. Due to the reconversion of dye molecule, during reconstruction, the dye molecules absorb major portion of the incident energy and as a result, the efficiency decreases. In certain conditions the efficiency decreases to a fraction of its original value in a matter of hours due the humidity. The high moisture makes the PVA layer more permeable to migrating species and this induces a decrease in diffraction efficiency.

If a crosslinker is added to the system, it can inhibit further diffusion of molecules and as a result, the recorded grating becomes undisturbed and hence constant diffraction efficiency can be obtained. But in the case of dye sensitized films the addition of organic crosslinkers like methylene dimethylacrylamide were reported to be not successful as the efficiency decreased.¹¹⁾ In this study efforts were made to crosslink the matrix with a metal ion as there are reports that in metal ion (Cr^{+6} and Fe^{+3}) doped PVA, on absorbing suitable energy, the metal ions crosslinks with PVA matrix.^{14,15)} Since the absorption spectrum of copper chloride well matches with that of methylene blue, to maintain the spectral sensitivity of the material unaffected, copper chloride was selected as the crosslinker. In the present study, MBPVA/acrylamide films were fabricated by varying the cupric chloride concentration using gravity settling method. Experiments were performed to analyze how cupric chloride influences the diffraction efficiency of MBPVA/acrylamide films.

2. Experimental Procedure

MBPVA acrylamide solution was prepared by dissolving

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acrylamide crystals (SRL) in 10% PVA solution (molecular weight 1,25,000: MERCK) and this solution was sensitized with methylene blue (6.2×10^{-4} mol/l) and triethanolamine (0.05 mol/l). The acrylamide concentration was varied from 0.095 to 0.475 mol/l. To this homogeneous solution with optimum acrylamide, copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) solution prepared in water was added. Copper chloride concentration was varied from 0.8×10^{-3} to 7.75×10^{-3} mol/l. This homogeneous solution was casted on micro slides using gravity settling method.¹⁶ The drying period was 48 h. In all the cases, films with good optical clarity were obtained.

Gratings were recorded on these films using standard holographic technique by keeping the beam intensity ratio as 1 : 1. For this a 15 mW, CW, polarized He-Ne laser (Melles Griot) having emission at 632.8 nm was used. The diffracted beam intensity was measured by illuminating the grating with a He-Ne laser beam of low intensity and it was monitored using an Ophir power meter positioned at Bragg's angle. The diffraction efficiency was calculated as the ratio of diffracted beam intensity to that of incident beam intensity. Though the same wavelength was used for both recording and reconstruction, real time DE measurements were not carried out. The sensitivity of the material was studied by measuring the real time transmittance by exposing to an expanded laser beam of intensity 5 mW/cm² for 10 min. The refractive index before and after exposure was measured using an Atago DR-M2 refractometer and change in refractive index was calculated.⁸ The absorption spectra of the samples were recorded using JASCO V-570 spectrophotometer and the change in absorbance was calculated the same way as reported earlier.¹⁷

3. Results and Discussion

3.1 Optimization of acrylamide concentration

To optimize the acrylamide concentration, the acrylamide concentration was varied from 0.095 to 0.475 mol/l and gratings were recorded (685 lines/mm) on these samples at 700 mJ/cm². The variation of diffraction efficiency with acrylamide concentration is plotted in Fig. 1. As the acrylamide concentration increases, the DE increases and reaches a maximum of 36% at an acrylamide concentration of 0.381 mol/l. This is because, as the monomer concentration increases, the number of monomers getting polymer-

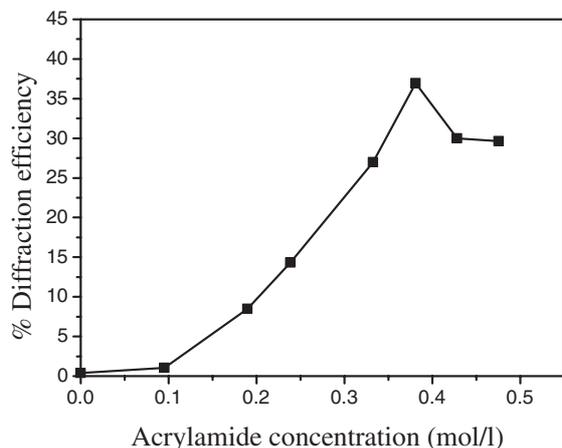


Fig. 1. Variation of diffraction efficiency with acrylamide concentration.

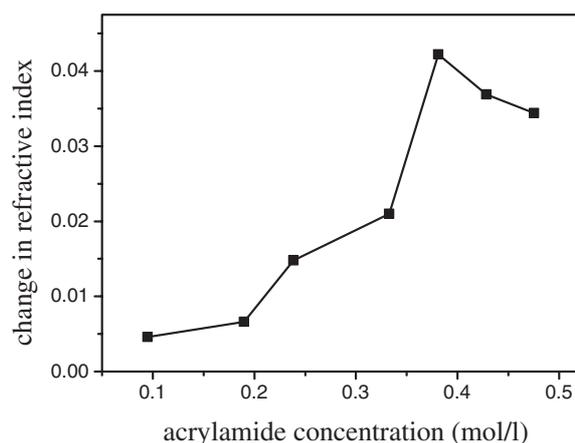


Fig. 2. Variation of change in refractive index with acrylamide concentration.

ized increases, which results in a large refractive index modulation and the DE increases. At high acrylamide concentrations, acrylamide crystallizes and loses the film properties. Change in refractive index with acrylamide concentration is plotted in Fig. 2. The change in refractive index also is found to be highest (0.042) for the sample with acrylamide concentration of 0.381 mol/l. There can be slight decrease in refractive index modulation due to diffusion of monomers when illuminated with fine fringes.

Gratings were recorded on the films at different fluences for a spatial frequency of 685 lines/mm. 36% DE was obtained for exposures ranging from 350 to 800 mJ/cm² and above this the DE decreased. The DE and sensitivity depends on the dye concentration and preparation techniques also. Blaya *et al.*¹ reported 50% DE in the films prepared by coating 7.4% PVA sensitized with 2.6×10^{-4} mol/l MB, 0.2 M triethanolamine and 0.45 M acrylamide using TLC coater. They used 441 nm wavelengths for reconstruction where the material has no absorption. In the present case for both construction and reconstruction He-Ne laser is used and since the material has absorption at 632.8 nm the maximum efficiency we could obtain been only 36%. The efficiency was decreased from 36 to 0.2% within 48 hours and it remained the same for weeks. Therefore only short-term storage was possible in this material. To improve the storage life of the gratings recorded, copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) solution prepared in water was added to the MBPVA solution. The Copper chloride concentration was varied from 0.8×10^{-3} to 7.75×10^{-3} mol/l.

3.2 Effect of copper chloride as crosslinker

3.2.1 Material sensitivity with the incorporation of copper chloride

To find out the material sensitivity on Cu doping the real time transmittance measurements were carried out as in our earlier work.¹⁷ The relative transmittance T/T_0 was determined; where T is the real time transmittance of the sample on laser exposure and T_0 is the transmittance of the PVA/acrylamide films without dye and CuCl_2 . The relative transmittance of both undoped (Cu-0 or samples without CuCl_2) and Cu doped samples are plotted in Fig. 3. Here the sensitivity is defined as the increase in transmittance on laser

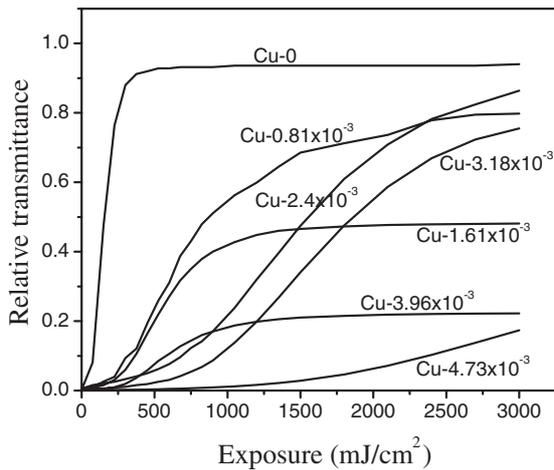


Fig. 3. Relative transmittance of undoped and Cu doped films at different exposures.

exposure. As the material sensitivity increases the transmittance increases at low exposures. This is because even at low exposure, the dye molecules were getting excited and initiate the photochemical reaction and then it is converted to the leucoform. Here the relative transmittance of the undoped sample is much higher than that of the Cu doped samples and it remains constant after an exposure of 400 mJ/cm². The relative transmittance of Cu doped samples increases slowly and high energy is required to bleach the sample. So the sensitivity of the undoped sample is much higher than that of Cu doped samples. As the copper concentration increases, the material sensitivity decreases. Samples with copper concentration above 6×10^{-3} mol/l were almost insensitive to laser. This is because, on laser exposure, Cu⁺² ions in the cupric chloride get reduced to Cu⁺¹ resulting in ionic crosslink between PVA chains. The methylene blue molecules may be trapped inside this crosslinked chain and it prevent the further reaction of the dye molecules that results in decrease of material sensitivity. Thus it was observed that in general adding copper chloride the sensitivity of the material decreases or higher exposures are needed.

3.2.2 Effect of copper chloride on DE

Gratings were recorded on both undoped and Cu doped samples at 1300 mJ/cm² and DE was determined. The variation of DE with cupric chloride concentration is plotted in Fig. 4. 28% DE was obtained for undoped samples and 32% DE was obtained for the samples with Copper chloride concentration 0.8×10^{-3} mol/l. But the DE decreased with increase in CuCl₂ concentration. Here the grating formation is due to the refractive index modulation produced by both the monomer diffusion resulting from the photopolymerisation and the photocrosslinking. The change in refractive index with copper concentration is plotted in Fig. 5. The refractive index modulation is higher for samples with cupric chloride concentration 2.4×10^{-3} mol/l which showed a diffraction efficiency of 29%. As the CuCl₂ concentration increases, the monomer diffusion decreases and photocrosslinking increases. At low Cu concentration, the refractive index modulation is due to the monomer

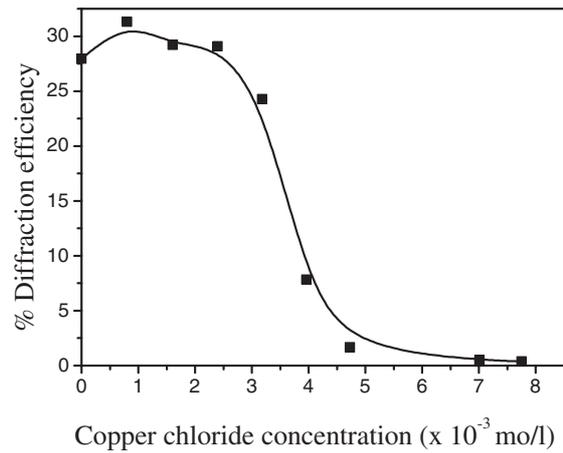


Fig. 4. Variation of diffraction efficiency with copper chloride concentration.

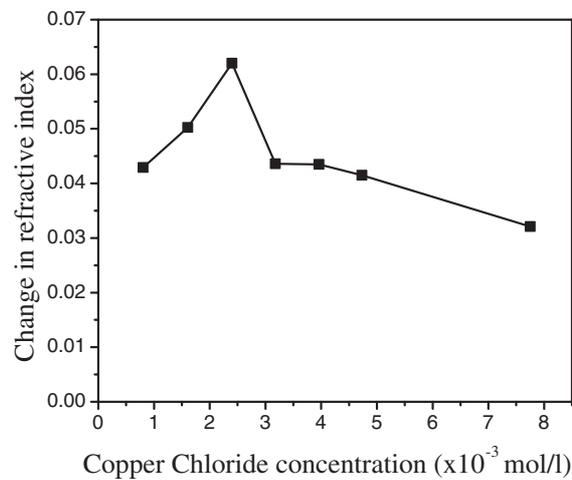


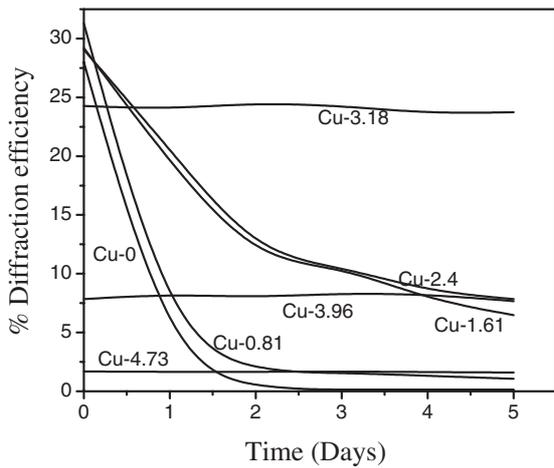
Fig. 5. Change in refractive index for different Cu doped samples.

diffusion and at high concentration it is due to photo-crosslinking.

The variation in DE of the samples on storage were determined and plotted in Figs. 6(a) and 6(b). DE of the undoped samples decreased from 28 to 0.23% within 48 h. DE of samples with CuCl₂ concentration less than 3.18×10^{-3} mol/l also showed a decrease in diffraction efficiency on storage. But the decrease is slow compared to that of the undoped samples. One of the major observations that could be made is that DE of samples with Copper chloride concentration 3.18×10^{-3} mol/l or above remained the same for 3 months. But there was a decrease in the value of DE on increasing CuCl₂ concentration. So in the present case the CuCl₂ concentration was optimized as 3.18×10^{-3} mol/l, where 24% DE was maintained for more than three months. This constant diffraction efficiency could be obtained due to the absence of monomer diffusion and crosslinking effect of CuCl₂ that makes the leucoform more stable. The stability of grating may also be due to the stability of change of state (leucoform) occurred to the dye molecules.

3.2.3 Stability of leucoform

If the dye molecules remain in the leucoform on storage,



(a)

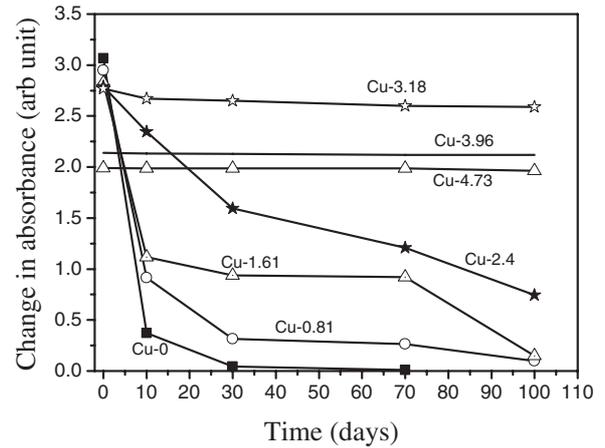
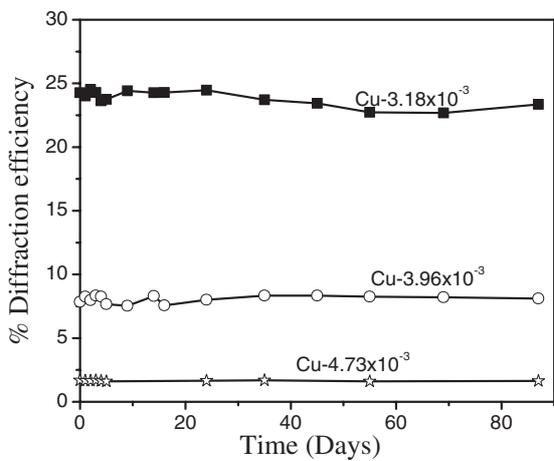


Fig. 7. The change in absorbance on storage.



(b)

Fig. 6. (a) Diffraction efficiency on storage for different Cu doped samples. (b) Stability of diffraction gratings.

there will be less absorption losses during reconstruction. As a result major part of the reconstructing beam gets diffracted and which results in better DE. The reconversion of methylene blue from leucoform to initial state is already reported in the case of MBPVA–acrylamide films.¹⁸⁾ To check the stability of the leucodye in Cu doped films, the absorption spectra of the samples with different copper concentrations were recorded before and after exposing to the laser beam (5 mW/cm^2 for 10 min). The change in absorbance on storage¹⁷⁾ was determined for all samples and it is plotted in Fig. 7.

At low Cu concentrations there is a change in absorbance on storage. But samples with CuCl_2 concentration $3.18 \times 10^{-3} \text{ mol/l}$ or above did not show any decrease of change in absorbance on storage. Since the sensitivity of samples with CuCl_2 concentrations above $3.18 \times 10^{-3} \text{ mol/l}$ is low, bleaching is less for these films and thus the change in absorbance is low compared to that of $3.18 \times 10^{-3} \text{ mol/l}$ films. In the case of samples with Cu concentrations $3.18 \times 10^{-3} \text{ mol/l}$ or above, the dye molecules in the exposed regions remain in the leuco form for months as in CMBPVC films.^{4,16,17)} But unlike CMBPVC, in Cu doped MBPVA/acrylamide films the gratings could be stored for months with stable diffraction efficiency. On Cu doping, the dye

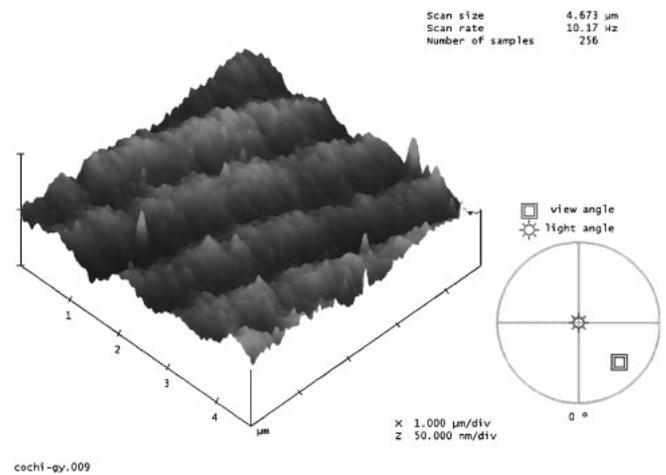


Fig. 8. AFM image of the gratings recorded for a spatial frequency of 1100 lines/mm.

molecules may trap inside the crosslinked PVA and which results in the stability of leucoform. The stability of the leucoform may be the major reason for obtaining a constant DE in Cu doped films.

3.2.4 Resolution

Gratings were recorded on the optimum sample (copper chloride $3.18 \times 10^{-3} \text{ mol/l}$) at different spatial frequencies. Constant diffraction efficiency could be obtained for gratings recorded with 625–1300 lines/mm. The spatial resolution of the undoped MBPVA/acrylamide films was also the same. Thus with the incorporation of cupric chloride the resolution of the material remains unaffected. Figure 8 shows the AFM image of the gratings (1 month after recording) recorded with 1100 lines/mm. The fringe spacing is $0.925 \mu\text{m}$. The thickness of the laser-exposed region is lower than that of the unexposed regions. The relief height (depth) was determined using a Dektak 6m stylus profiler. The depth of the fringes recorded at various spatial frequencies was 4 nm. There were not much differences observed on gratings recorded at various exposure energies. So the contribution of the surface relieves to total diffraction on adding to the refractive index modulation is negligible.

Thus with the incorporation of CuCl_2 the storage life of

the gratings improved without any fixing process. Attempts are being made to improve the material sensitivity and also for increasing diffraction efficiency. If the dye concentration is decreased, the amount of CuCl₂ required for crosslinking may be decreased; accordingly the grating can be recorded at low exposures. This opens the scope for an inexpensive permanent recording medium with considerable DE and sensitivity.

4. Conclusions

Copper chloride acts as a crosslinker in MBPVA/acrylamide films and helps to store gratings recorded on it for longer periods without any fixing process. There is an optimum CuCl₂ concentration required for keeping the diffraction efficiency constant. The Copper chloride concentration was optimized as 3.18×10^{-3} mol/l, for a dye concentration of 6.2×10^{-4} mol/l, which maintained a Diffraction efficiency of 24% for more than 3 months. The resolution of the material is unaffected on incorporation of copper chloride in PVA.

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