J Mater Sci: Mater Electron
DOI 10.1007/s10854-007-9544-6

Effect of chromium doping on the diffraction efficiency of methylene blue sensitized PVA/acrylamide films

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Received: 19 July 2007 / Accepted: 13 December 2007

Abstract The effect of chromium doping on methylene blue sensitized Poly (vinyl alcohol)/Acrylamide was carried out by varying the ratios of Ammonium dichromate and methylene blue. In the case of films without ammonium dichromate, the diffraction efficiency was found to decrease on storage. On chromium doping the storage life was improved. Interestingly, a self-enhancement in efficiency was observed for a particular ratio of methylene blue and ammonium dichromate.

1 Introduction

Holography breaks through the density limits of conventional storage by going beyond recording only on the surface, to recording through the full depth of the medium. The flexibility of the technology allows for the development of a wide variety of holographic storage products that range from handheld devices for consumers to storage products for the enterprise. In this context, development of inexpensive photopolymer systems that satisfies the media requirements for holographic data storage is of great importance.

Methylene blue sensitized Poly (vinyl alcohol)/acrylamide films [1] are promising candidates for holography on account of its high efficiency, sensitivity and easiness of fabrication. But the efficiency was found to decrease on storage unless a post-exposure or UV curing is provided. The efficiency drop is mainly due to the reconversion of dye molecule from leuco form. The efficiency was stabilized by copper doping [2] where a stable leuco form exists on storage. As dichromated polymers have made significant impact in holography, as an attempt to improve the storage life of the gratings, copper ions were replaced by chromium ions [3]. In the present paper the effect of chromium doping on the diffraction efficiency of MBPVA/Acrylamide films are discussed.

2 Methodology

The films were fabricated using gravity settling method at room temperature ($\cong$30 °C). The film constituents are 10% PVA, acrylamide (0.381 mol/L), triethanolamine (.05 mol/L), methylene blue (MB) and ammonium dichromate (ADC). MB concentration was varied from 0.7×10^{-4} to 4.16×10^{-4} mol/L and ADC concentration was varied from 0 to 2.106×10^{-3} M. The concentration of ADC was selected such that the product of the concentrations of MB and ADC should be less than the solubility product 2×10^{-2} $(\text{mol/L})^2$. It is reported that, if this value exceeds the solubility product, methylene blue will separate in the film [4].

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Gratings were recorded on the films using standard holographic technique using a 15 mW, CW, polarized He–Ne laser (Melles Griot-632.8 nm). The beam intensity ratio was 1:1 and the spatial frequency was 1,100 lines/mm. The diffracted beam intensity was measured by illuminating the grating with a 1 μw He–Ne laser beam 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. The sensitivity of the material was studied by measuring the real time transmittance. The absorption spectra were recorded using JASCO V-570 spectrophotometer.

3 Results and discussion

3.1 Diffraction efficiency measurements

Gratings were recorded on films with various combinations of MB and ammonium dichromate at different exposures. In call cases, the efficiency and sensitivity of chromium doped MBPVA/acrylamide films were less than that of undoped films. As an example, the diffraction efficiency of films having 2.096×10^{-4} M methylene blue doped with ammonium dichromate is plotted in Fig. 1. But an anomalous behavior in diffraction efficiency was observed in the case of films with 2.79×10^{-4} M methylene blue. The diffraction efficiency of films having 2.79×10^{-4} M methylene blue doped with dichromate is plotted in Fig. 2. From the graph it is evident that, the diffraction efficiency and sensitivity is the least for films with 1.59×10^{-3} M ADC. In this particular case, both efficiency and sensitivity were improved for higher concentration of ADC.

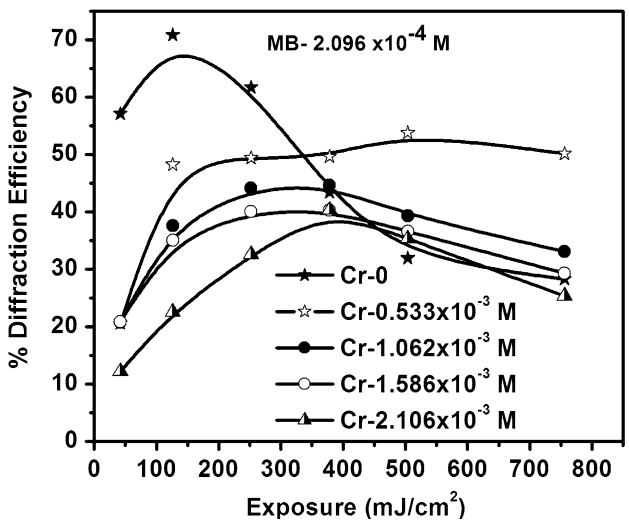

Fig. 1 Diffraction efficiency of films having 2.096×10^{-4} M methylene blue

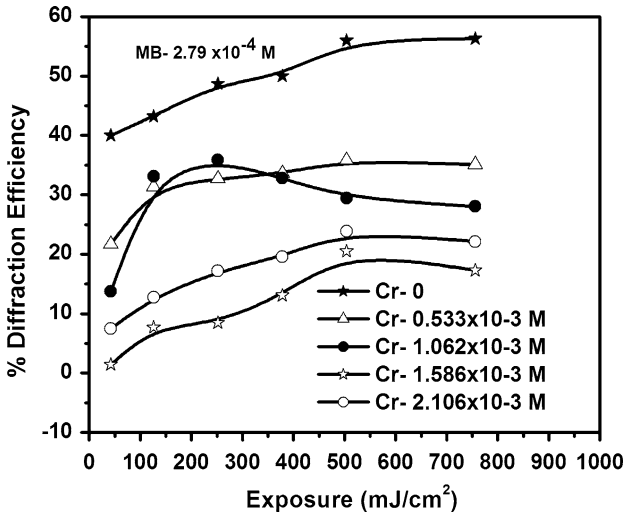

Fig. 2 Diffraction efficiency of films having 2.79×10^{-4} M methylene blue

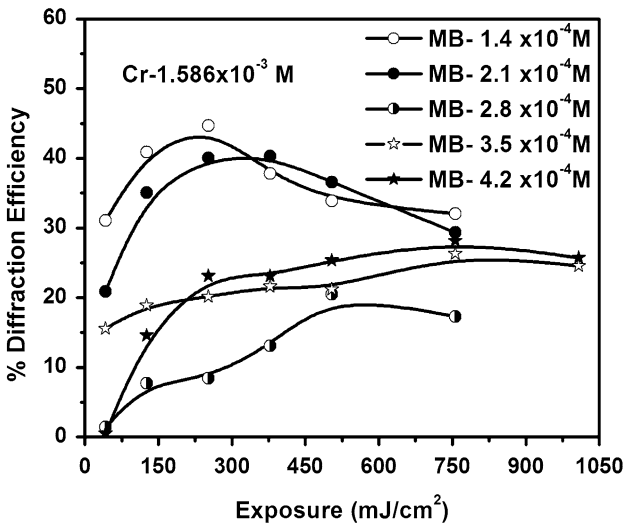

Fig. 3 Diffraction efficiency of films having 1.586×10^{-3} M ammonium dichromate

The diffraction efficiency of polymer films having different dye concentration and 1.59×10^{-3} M ammonium dichromate is determined by varying exposure and is shown in Fig. 3. In that case also, the efficiency of films with 2.79×10^{-4} M MB and 1.59×10^{-3} M ADC is lesser than other dye concentration. For other dichromate concentrations, the efficiency and sensitivity were decreased with methylene blue

3.2 Diffraction efficiency on storage

Diffraction efficiencies of both undoped films and dichromated films were monitored on storage. The efficiency was

found to decrease on storage except for two combinations of ammonium dichromate and methylene blue. Unlike other films, films with 2.79×10^{-4} M methylene blue and 2.106×10^{-3} M ammonium dichromate showed stable efficiency on storage. Whereas the films with 2.79×10^{-4} M methylene blue and 1.59×10^{-3} M ammonium dichromate showed a self-enhancement of diffraction efficiency on storage. These samples (just after recording) showed highest efficiency of 20% at 500 mJ/cm^2 without any pre exposure and chemical fixing. The diffraction efficiency was found to slowly increase to 40% by 3 months. It remains the same for months and then the efficiency gradually decreases and reaches the initial efficiency of 20%. The diffraction efficiency on storage is plotted in Fig. 4.

The self-enhancement of a hologram is the increase in its diffraction efficiency after the recording over time under light illumination or in the dark. Self-enhancement both during and after the recording can together be regarded as a two stage holographic recording method, which is profitable when the recording energy or the exposure time is limited at the first stage. Such a recording method has the advantage of large vibration stability at the second stage. Though self-enhancement of diffraction efficiency was reported in $LiNbO_3$: Fe crystals [5], KBr crystals with F centers [6], amorphous AS_2S_3 films [7], thionine-PVA layers [8], Dichromated PVA (DCPVA) [9, 10] and Dichromated Gelatin (after chemical fixing) [11], this is the first observation of self-enhancement in acrylamide films. In Dichromated PVA the self-enhancement increases with pH, but it decreases with dichromate concentration and exposure energy [12]. In Dichromated PVA, it was reported that the efficiency increases within 1–3 days depending on the pH and then it decrease [10]. But in this case it takes around four months to complete the self-enhancement. A slight self-enhancement at low energy was observed in acrylic acid-Cr^{+6} solutions kept in dark due to the formation of Cr^{+3} [12].

The self-enhancement process can be characterized by the self-enhancement coefficient, $\xi = \eta_t/\eta_0$ and by the self-enhancement rate, $\beta = d\xi/dt$. Where η_0 is the initial DE immediately after the recording and η_t is the DE after time t. Highest value of self-enhancement coefficient, $\xi = 1.984$ was observed on 120th day after recording. The self-enhancement rate with time is determined and plotted in Fig. 5. A noticeable change in the self-enhancement rate is observed during the first month after preparation. It is nearly zero during second to ninth month after recording.

This self-enhancement observed in this case may be due to the dark reaction, diffusion, polymerization and internal stresses as observed in Dichromated PVA [9]. Cr^{+6} is consumed slowly during photochemical reaction induced during the exposure. All the Cr^{+5} (produced by the reduction of Cr^{+6}) are not reduced to Cr^{+3} during exposure and this reduction continue in the dark. This reduction is large in the more exposed regions than in the less exposed region. The number of crosslinkage between Cr^{+3} and the PVA increases and thus the index modulation also increases which induces an increase in DE. This dark reaction may be the major reason for the self-enhancement. Cr^{+3} or unreacted Cr^{+5} may diffuse from the less exposed regions to the more exposed regions. Diffusion of Cr^{+3} ions is possible only if all the Cr^{+3} ions are not bound in the crosslinkage. The polymerization was not finished during the recording period. Polymerization continues bringing new crosslinkages together with Cr^{+3} ions, which is responsible for the grating formation. The internal stress in the coating increases during drying and exposure times. But when the coating expands by absorbing moisture at

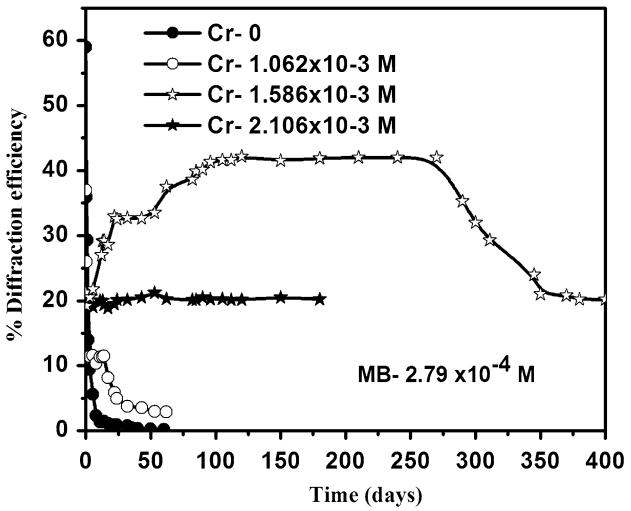

Fig. 4 Diffraction efficiency of both undoped and chromium doped films on storage (methylene blue concentration—2.79×10^{-4} M)

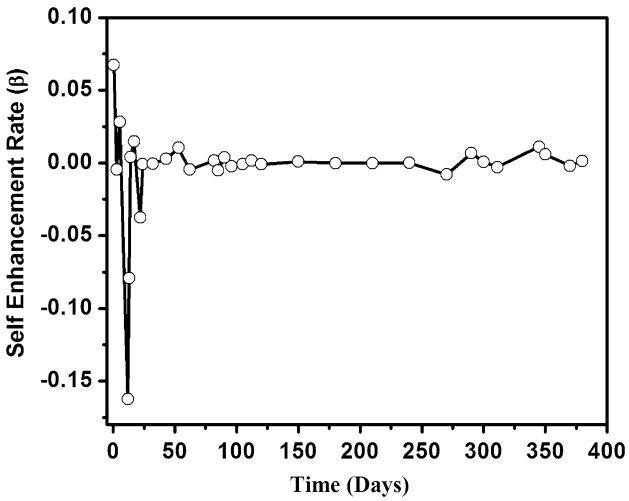

Fig. 5 Self-enhancement rate with time

room temperature, the internal strain is relaxed and this also contributes to the increase in diffraction efficiency.

3.3 Behavior of Dye

The films were exposed to an expanded laser beam of intensity 5 mW/cm^2 for 10 minutes and the relative transmittance of both Cr doped and undoped samples were measured. The relative transmittance of films having 2.79×10^{-4} M dye with different dichromate concentration is plotted in Fig. 6. From the graph it is evident that on Cr doping, the MBPVA/acrylamide films became less sensitive to laser and the energy requirement is high. This is because of the photocrosslinking caused by the dichromate. Figures 7 and 8 show the absorption spectrum of undoped and Cr doped sample (2.79×10^{-4} M dye and 1.59×10^{-3} M ammonium dichromate), respectively. In undoped samples, the recovery of the dye molecule from the leucoform is very fast. It is almost fully recovered within two weeks. But in the case of Cr doped samples, the recovery is very slow and it remains the same leucoform on storage. In this case, the leuco MB formed is crosslinked in the PVA matrix and so further oxidation of leuco dye is not possible as observed in the dye sensitized polymers.

The mechanism of grating formation can be explained as follows. On exposing to the interference pattern, the MB molecules get excited and electron transfer takes place between MB and triethanolamine. This reaction produce leuco MB and the amine radical and this radical initiates the polymerization reaction. Polymerization takes place at the region of constructive interference and as a result a monomer concentration gradient occurs which allows the diffusion of monomer from the unexposed to the exposed region. At the same time, the Cr^{+3} ions obtained by the reduction of Cr^{+6} ions crosslink with PVA. Both polymerization and crosslinking contribute to the refractive index modulation, which leads to the grating formation. The absorbance modulation occurs during exposure also contribute to the grating formation.

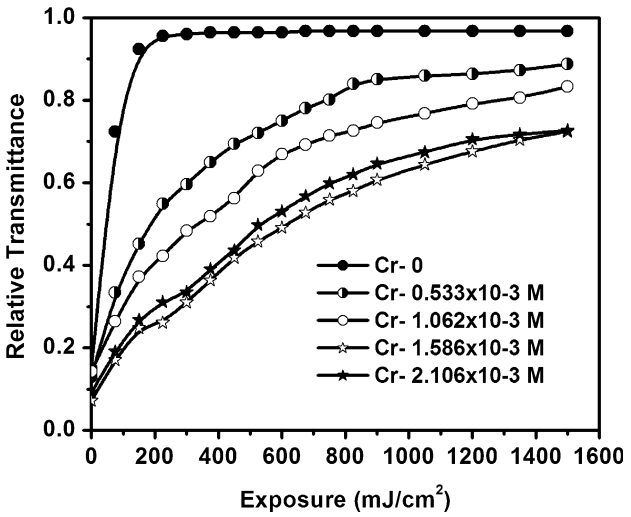

Fig. 6 Relative transmittance of both undoped and chromium doped films (methylene blue concentration is 2.79×10^{-4} M)

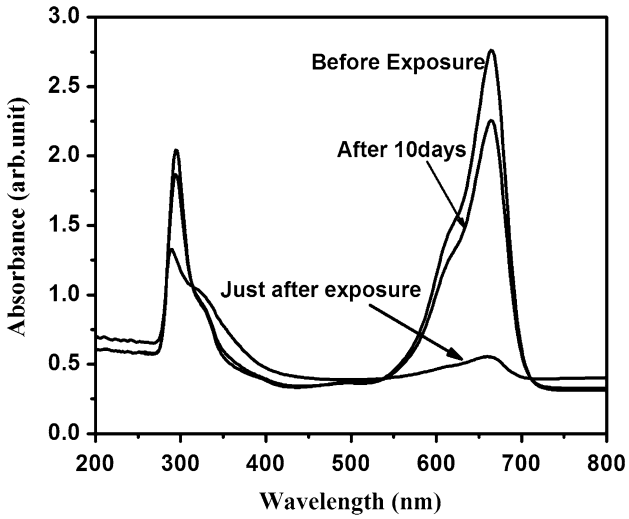

Fig. 7 Absorption spectrum of the undoped sample

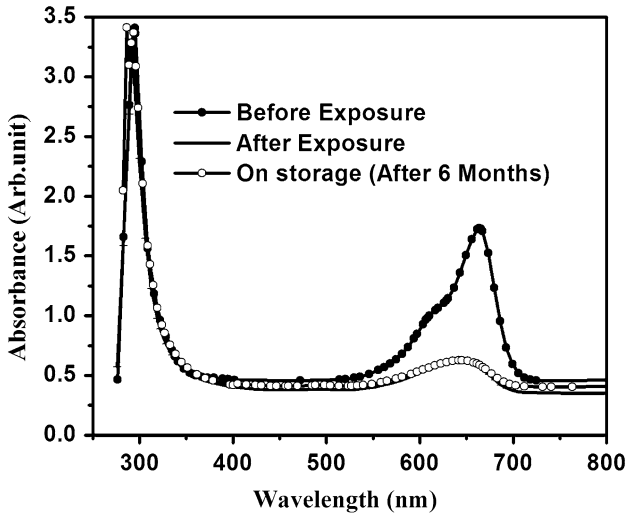

Fig. 8 Absorption spectrum of the dichromated sample

4 Conclusion

Addition of Ammonium dichromate makes the MBPVA/acrylamide films more stable and helps in storage. Even though there is a decrease in DE on incorporating the crosslinker, the self-enhancement observed makes the system regain the diffraction efficiency and helps in maintaining the efficiency constant for several months.

Acknowledgements The authors acknowledge DRDO and DST for the financial support to carry out this work.

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