

Methylene blue doped polymers: efficient media for optical recording

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(Received 7 July 2003; revised version 20 October 2003)

Abstract. Polymer materials find application in optical storage technology, namely in the development of high information density and fast access type memories. A new polymer blend of methylene blue sensitized polyvinyl alcohol (PVA) and polyacrylic acid (PAA) in methanol is prepared and characterized and its comparison with methylene blue sensitized PVA in methanol and complexed methylene blue sensitized polyvinyl chloride (CMBPVC) is presented. The optical absorption spectra of the thin films of these polymers showed a strong and broad absorption region at 670–650 nm, matching the wavelength of the laser used. A very slow recovery of the dye on irradiation was observed when a 7:3 blend of polyvinyl alcohol/polyacrylic acid at a pH of 3.8 and a sensitizer concentration of $4.67 \cdot 10^{-5}$ g/ml were used. A diffraction efficiency of up to 20% was observed for the MBPVA/alcohol system and an energetic sensitivity of 2000 mJ/cm² was obtained in the photosensitive films with a spatial frequency of 588 lines/mm.

1. Introduction

Holography promises to be a technology that overcomes two approaching physical barriers to data storage through a powerful combination of high storage densities and fast data transfer rates. And interest in holographic applications has in recent years generated a new optimism in the holographic community. Success in hologram recording depends both on the selection of lasers and on the production of the necessary recording medium.

The currently available materials for hologram recording such as the widely available inexpensive He-Ne lasers are unstable in time, require large hologram development and fixation process, are affected by the atmosphere and show insufficient sensitivity.

Among the great number of photosensitive hologram media, photopolymers that combine considerable sensitivity, high diffraction efficiency and ease of preparation are of interest [1].

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Methylene blue is a common sensitizing dye for polymer matrices like polyvinylalcohol [2], gelatin [3], polymethymethacrylate [4], and acrylimide [5] based polymers, because it has absorption maxima similar to those of the wavelength of inexpensive laser diodes and He-Ne lasers used. Moreover the spectral region can be extended to 700 nm.

Studies on methylene blue sensitized gelatin and polyvinyl alcohol (in water medium) have highlighted shortcomings such as shorter storage life, lack of environmental stability, long drying time before hologram registration, susceptibility to high humid conditions, the need for a fixing process etc.

Acryl amide based polyvinyl alcohol films constitute low cost organic materials and a great deal of attention has been devoted to the composition of an acryl amide-polyvinyl alcohol system initiated by methylene blue in recent years [6–8]. In this matrix a diffraction efficiency of 80% and an energetic exposure of 40 mJ/cm^2 recorded with a He-Ne laser with a power of 4 mW/cm^2 and spatial frequency of 1000 lines/mm have been reported [9].

The mechanism of hologram formation includes two processes, radical polymerization and diffusive mass transfer. A polymer molecule is assumed to be formed through the sequential addition of monomer chains, i.e. only the chain propagation step can be taken into account. The polymerization of a medium in an interference field causes spatial modulation of the refractive index. The magnitude of the refractive index change is determined by the modulation of the density and polarizability of a polymer and the modulation of its composition, which is caused by diffusive redistribution of components between exposed and unexposed areas of the recording layer. In most cases, one of the components capable of polymerization is replaced by a neutral component that does not enter into chemical reaction with other ingredients of the medium. When the material is exposed to an interference fringe pattern there are more monomers being polymerized in the bright region than in the dark region. This non-uniform irradiance distribution sets up monomer concentration gradients and hence results in the diffusion of monomers from dark regions to the neighbouring bright regions. Thus, a polymer density spatial distribution is formed which results in a refractive index distribution of a similar form. The refractive index modulation resulting from this segregation can be greatly amplified by various physical and chemical treatments [10–14].

Therefore it is tempting both scientifically and technically to try to develop and study new polymer blends for hologram information recording that would possess both the advantages of laser photopolymerizable systems (such as acrylic acid) and the specific positive properties of polyvinyl alcohol.

We have conducted a comparative study on the holographic characteristics of methylene blue sensitized polymer films fabricated in our laboratory, namely polyvinyl alcohol (PVA) in methanol, polyvinyl alcohol/polyacrylic acid blend in methanol and polyvinyl chloride, using a 10 mW He-Ne laser as the laser source.

2. Experimental

2.1. Preparation of methylene blue sensitized polyvinyl alcohol/polyacrylic acid blend (MBPVA/PAA)

A 10% polyacrylic acid (PAA) was prepared by refluxing acrylic acid (10 ml), water (90 g) and potassium persulphate (0.2 g) at 90°C in a three necked flask fitted with an additional funnel, a reflux condenser, a thermometer and a stirrer. The

heating is applied for 4 h. The 10% PAA thus obtained was mixed with 10% PVA in the ratio 3:7 in methanol (20 ml). This mixture was then sensitized with methylene blue solution. An optimum dye concentration of $4.67 \cdot 10^{-5}$ g/ml was employed.

2.2. Preparation of methylene blue sensitized polyvinyl alcohol in methanol (MBPVA/alc)

A solution of PVA (10%) was prepared by adding PVA (10 g) in water (100 ml). To this solution methanol (20 ml) was added. The resulting solution was homogeneously stirred with methylene blue solution. An optimum dye concentration of $9.31 \cdot 10^{-5}$ g/ml was employed.

2.3. Preparation of complexed methylene blue sensitized polyvinyl chloride in cyclohexanone (CMBPVC)

The coating solution consists of a polymer (PVC), a sensitizer (M.B), a complexing agent (copper acetate), a solvent for the polymer (cyclohexanone) and a solvent for the dye (glacial acetic acid). PVC was dissolved in cyclohexanone and a few drops of complexed methylene blue in glacial acetic acid were added. The mixture was well stirred to get a homogeneous solution [15].

Coating was achieved by pouring a fixed volume of these solutions over clean glass slides, which were kept on a level surface. The thickness of all these films was maintained at 0.03 mm. The slides were protected from dust and dried at room temperature for 24 h. The optimum concentration and pH of these samples were found as described elsewhere and are given in table 1.

The studies reported in this paper were carried out on these optimized samples.

3. Laser exposure

The laser used was a Coherent Melles Griot He-Ne with emission at 632.8 nm. The laser beam was expanded and filtered using a spatial filter arrangement set up in the laboratory. The samples were placed in an expanded beam. The experimental set up used for the real time transmission study is explained in reference [2]. The transmitted intensity was measured using a power meter (OPHIR model 2000). The transmittance value of the undoped sample was taken as T^0 , that obtained for the dye-doped film was taken as T and their ratio T/T^0 (relative transmittance) was determined for standardization. The effect of the He-Ne laser irradiation on the absorption spectra of the methylene blue sensitized films was studied using a Hitachi 30 UV-VIS-NIR spectrophotometer. For pH measurements, a digital pH meter (Systronics 335) was used. The pH was decreased by adding HCl and increased by adding an ammonia solution. The experimental set up used for diffraction efficiency measurements are shown in figure 1. The expanded laser beam from the He-Ne laser is allowed to fall on a mirror kept at a fixed distance. The laser beam reflected from the front and back

Table 1.

Material	Optimum dye concentration	Optimum pH
MBPVA/PAA	$4.67 \cdot 10^{-5}$ g/ml	3.8
MBPVA/alc	$9.31 \cdot 10^{-5}$ g/ml	5.81
CMBPVC	$4.1 \cdot 10^{-4}$ gm/ml	4.5

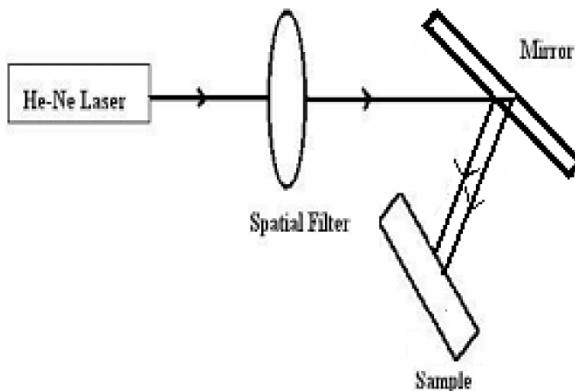


Figure 1. The experimental set up used for diffraction efficiency measurements by the single mirror method.

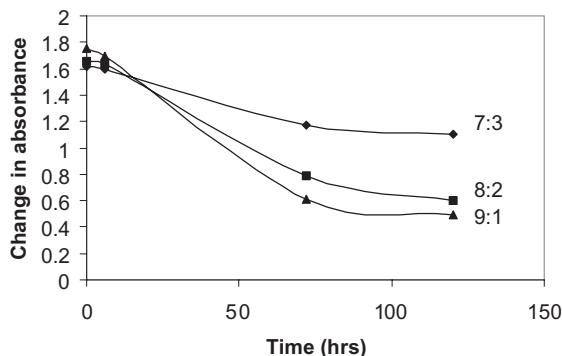


Figure 2. A plot of the recovery by the dye of its original form monitored by noting the change in absorbance with time for three different ratios of PVA/PAA.

surfaces of the mirror will interfere to produce an interference pattern, which is allowed to fall on the sample. The angle between the incident beam and reflected beam from the mirror is taken as θ .

4. Results and discussion

4.1. Optimization of PVA/PAA ratio

A decrease in film clarity and non-uniformity was observed when a ratio 6:4 (PVA/ PAA) or lower was used. Moreover, as the acrylic acid content was increased in the mixture, the film became sticky and less sensitive to the He-Ne laser. So a detailed study was performed for the ratios 7:3, 8:2 and 9:1. These films were exposed to the He-Ne laser (wavelength = 632 nm) and the change in transmittance was monitored for a fixed time interval. The change in transmittance was found to be almost the same in all the three cases. Hence to optimize the ratio, the change in absorbance with time was monitored to determine the recovery by the dye back of its original form. Figure 2 shows the change in absorbance $A^0 - A$ (A^0 is the absorbance of the sample immediately after irradiation and A is the absorbance after a time t) with time for three different ratios of PVA/PAA. It was

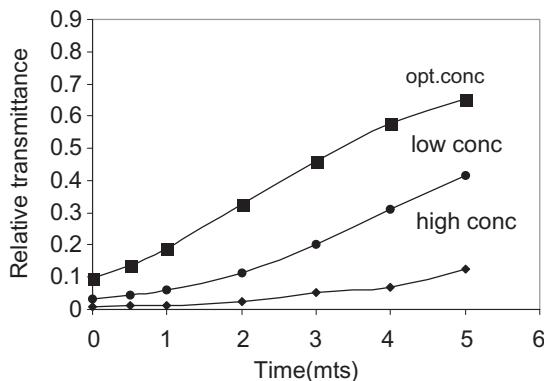


Figure 3. A plot of the relative transmittance (T/T^0) against time for different dye concentrations.

found that as the PVA content in the sample increased, the recovery by the dye of its original form was fast. Since the main motivation behind the study was to delay the recovery process, a 7:3 ratio (PVA/PAA) was found to be the optimum as the recovery was found to be very slow in this case.

4.2. Optimization of sensitizer concentration

Keeping the PVA/PAA ratio at 7:3, the concentration of methylene blue was varied from $9.3 \cdot 10^{-4}$ g/ml to $9.3 \cdot 10^{-6}$ g/ml in the solution. The films thus obtained from this solution were exposed to a laser power of 5 mW/cm^2 for 5 minutes. The change in transmittance was monitored as a function of time. A graph of the relative transmittance (T/T^0) against time was reported in an earlier report [2]. From the graph (figure 3) it is clear that the relative transmittance is maximum for a concentration of $4.67 \cdot 10^{-5}$ g/ml and fast bleaching was observed for this sensitizer concentration.

4.3. Optimization of pH

A very interesting behavior was observed when the pH was changed from 1 to 11 in the PVA/PAA system. The film prepared at low pH lost its clarity and for the films at high pH, a loss in transparency was observed. So the experiments were carried out at a pH between 3 and 6. The films prepared at the optimum dye concentration and a 7:3 (PVA/PAA) ratio but at a different pH were exposed to laser irradiation and the change in absorbance as a function of time is shown in figure 4. It can be seen that as the pH increases the recovery by the dye of its original form is fast. At a pH 3.8 (normal pH of the system) the recovery is slow and at a pH 6, the recovery is very fast.

4.4. Comparative studies on

4.4.1. *Optical absorption measurements.* On irradiating all the three types of samples with an expanded beam of about 5 mW/cm^2 , the films were bleached, i.e. the samples became colorless. The typical absorption spectra of the unexposed, exposed and after 48 h of laser irradiation of the samples MBPVA/alc, MBPVA/PAA blend and CMBPVC, are shown in figures 5, 6 and 7, respectively. The exposure time was 5 min for all the three samples. In the MBPVA/alc system

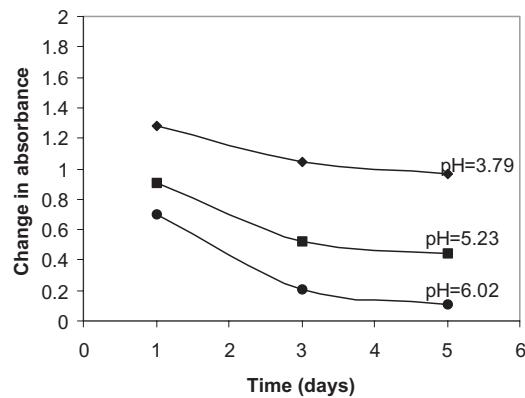


Figure 4. A plot of the change in absorbance as a function of time for the 7:3 blend ratio of PVA/PAA at different pH values.

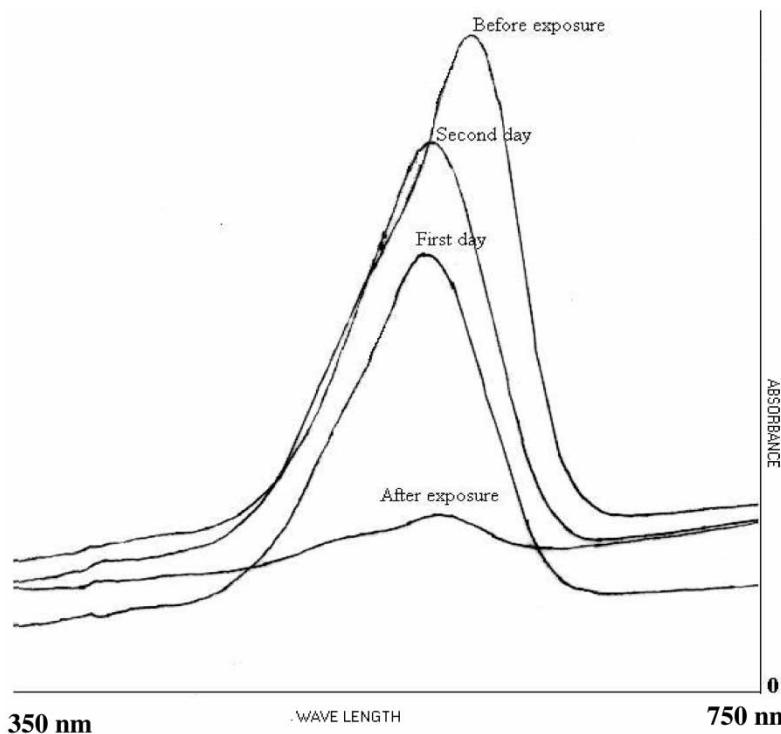


Figure 5. Typical absorption spectra of the exposed and unexposed optimized samples of the MBPVA/alc film.

the recovery by the dye was almost complete in 2 days. A broad shift (650 to 635 nm) in absorption spectra of the irradiated sample was also observed. This can be explained by the conversion of methylene blue molecules to a more stable thionine state [16]. In the case of the MBPVA/PAA blend this conversion was found to be rather slow even though a small shift (664–654 nm) was observed after irradiation. The recovery to the thionine state was almost complete in 3 weeks. It

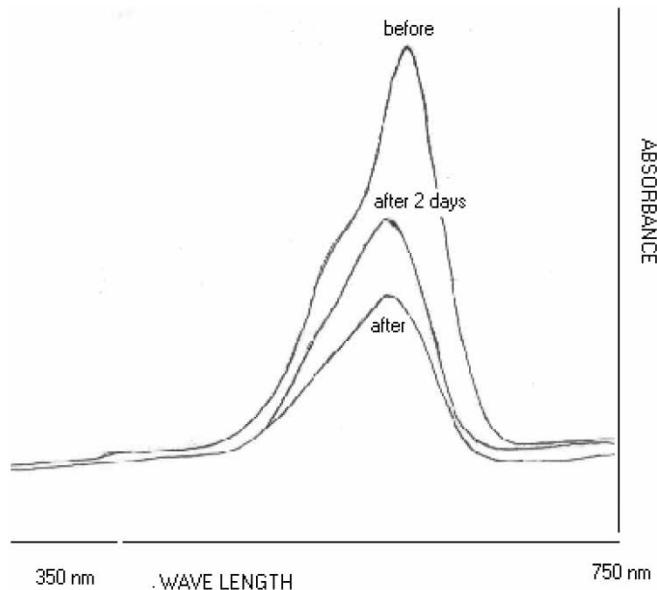


Figure 6. Typical absorption spectra of the exposed and unexposed optimized samples of the MBPVA/PAA film.

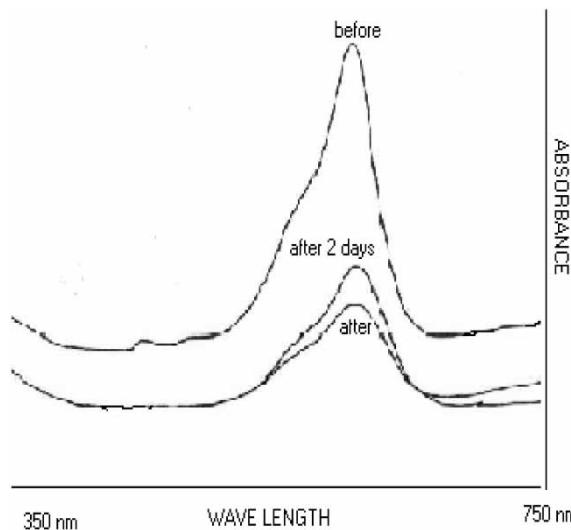


Figure 7. Typical absorption spectra of the exposed and unexposed optimized samples of the CMBPVC films.

was found that as the polyvinyl alcohol content in the blend increased the rate of reconversion of the dye increased. So the polyacrylic acid content in the blend plays a very important role in the recovery by the dye in this matrix. From figure 7 it is clear that no shift in the absorption spectrum was found on irradiation in CMBPVC films, i.e. the leuco form of methylene blue is very stable in the PVC matrix and no recovery of dye was observed in this matrix for months

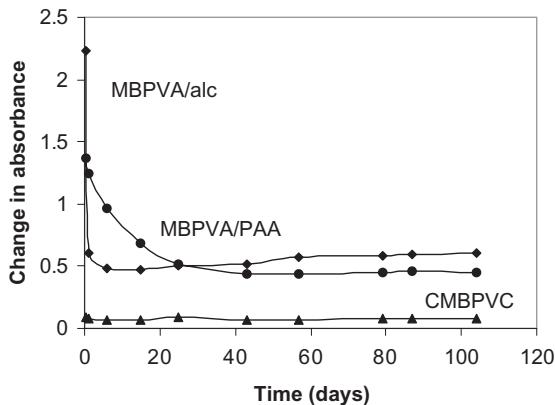


Figure 8. A plot of the change in absorbance against time of the irradiated spot of the MBPVA/alc, MBPVA/PAA and CMBPVC films.

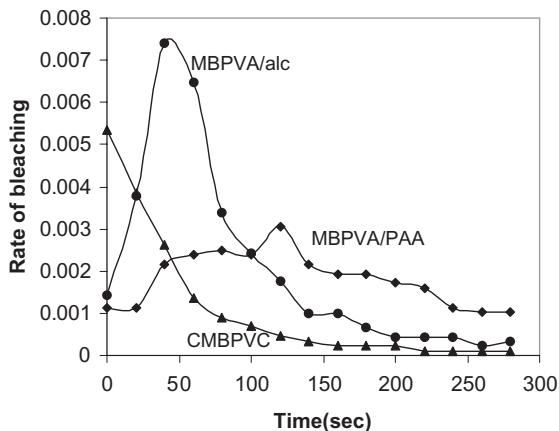


Figure 9. A plot of the rate of bleaching against time of the irradiated spot of the MBPVA/alc, MBPVA/PAA and CMBPVC films.

A detailed study was performed by monitoring the recovery by the dye for a number of days. From figure 8, where change in absorbance is plotted against time, we can infer that the leuco form is more stable in the CMBPVC and PVA/PAA blends.

To study the rate of bleaching of methylene blue in all the three samples, the optimized samples were exposed to the same laser power for about 5 min. The variation in transmittance in terms of T/T^0 with time was calculated and plotted, from which the rate of bleaching was determined by finding the slopes at different times. The rate of bleaching with time for all the three samples is plotted in figure 9. It is very interesting to note that while the rate of bleaching constantly decreases for CMBPVC, the rate increases fast for MBPVA/alc, reaches an optimum and then decreases. The blend also shows a similar behavior to that of MBPVA/alc, but the rate increases only slowly. It is therefore inferred that the conversion of leuco methylene blue observed in MBPVA/PAA and CMBPVC takes some time whereas in MBPVA/alc most of the conversion is over quickly.

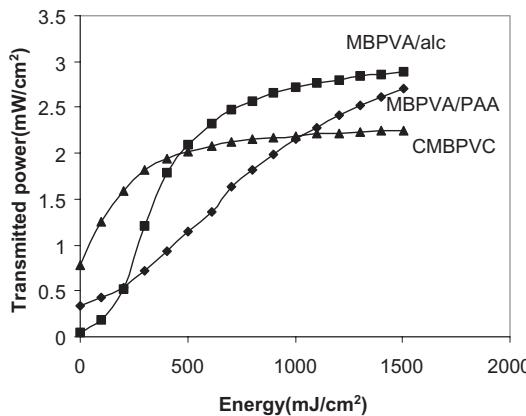


Figure 10. Variation of the transmitted power with exposure energy for the MBPVA/alc, MBPVA/PAA and CMBPVC films.

No bleaching was observed in all the samples when exposed to a power density as low as $76\text{ }\mu\text{W}/\text{cm}^2$. It was found that minimum energies of about 200, 300 and $200\text{ mJ}/\text{cm}^2$ were necessary for a photochemical change to take place in these MBPVA/alc, CMBPVC and MBPVA/PAA blend samples, respectively. From this we infer that a minimum amount of energy called the threshold energy is necessary for the excitation of the dye molecules to the leuco form in these polymer matrices and this threshold is high for CMBPVC.

To determine the saturation energy, samples were exposed to a laser power density of $5\text{ mW}/\text{cm}^2$ for 10 min. A stage of saturation was observed at exposure energies of 900, 400 and $1200\text{ mJ}/\text{cm}^2$ for the MBPVA/alc, CMBPVC and MBPVA/PAA blends, respectively. Beyond the threshold region very fast bleaching was observed for MBPVA/alc and CMBPVC, but the MBPVA/PAA blend showed only a slow change with the exposure energy (figure 10). In the case of the blend, it was found that very high exposure energy was necessary for saturation. This is due to the presence of polyacrylic acid in the blend, which delays the excitation of dye molecules.

4.4.2. Interferometric Studies. Interferometric experiments were performed in order to characterize these photosensitive media. Interference gratings were recorded and the value of the diffraction efficiency as a function of the incident angle is shown in figure 11. The maximum diffraction efficiency was observed for a fixed exposure at the interfering angles of 40° and 10° for MBPVA/alc and the CMBPVC and MBPVA/PAA blends, respectively. So a detailed study was carried out at these angles for different exposures (figure 12a and 12b). Maximum diffraction efficiencies of about 20%, 4.8% and 10.88% were achieved for the MBPVA/alc, CMBPVC and MBPVA/PAA blends, respectively at a fixed spectral frequency of 588 lines/mm. Even though the film property of the polymer blend is not superior to that of PVA films, a maximum diffraction efficiency of 10.88% was achieved for this polymer blend. The reason for this may be due to the following facts: when the exposure energy is increased, initially the bleaching process takes place in the exposed regions thus converting the dye to the leuco form and hence the light gets diffracted more. The increase in diffraction efficiency with increase in

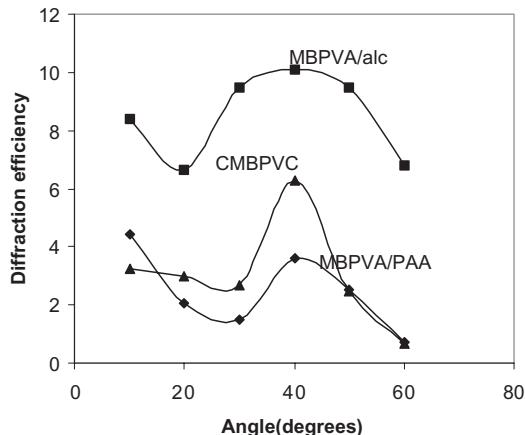


Figure 11. A plot of the diffraction efficiency as a function of incident angle for the MBPVA/alc, MBPVA/PAA and CMBPVC films.

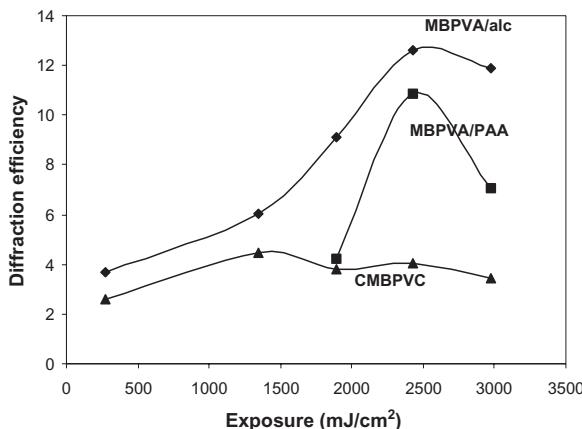


Figure 12a. A plot of the diffraction efficiency against exposure energy for a fixed incident angle of 10^0 for the MBPVA/alc, MBPVA/PAA and CMBPVC films.

the exposure energy may also be due to the resultant polymerization taking place at the exposed area. But when the energy increases there is a chance that dye molecules get converted into the thionine state itself, which has a dark blue color and hence the contrast between the exposed and unexposed regions decreases. This may be the reason for the reduction of the diffraction efficiency observed at high exposure energies. These diffraction efficiencies were achieved on all the samples without any fixing or development.

The recording of interference gratings of holograms assumes some spatial modulation of the photosensitive medium. For photographic plates a spatial change in the absorbance was present after irradiation and development. In photopolymers, the modulations could be present in the form of variations in the index of refraction or variation in the thickness of the layer. Attempts are under

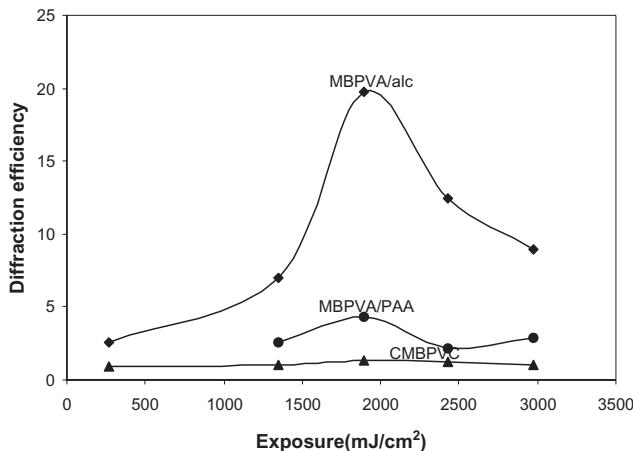


Figure 12b. A plot of the diffraction efficiency against exposure energy for a fixed incident angle of 40^0 for the MBPVA/alc, MBPVA/PAA and CMBPVC films.

way to predict these variations and to improve the diffraction efficiency of these polymer systems.

4.5. Dye Behavior

The dye used to sensitize these polymer matrices was methylene blue, because it has high absorption at the red part of the spectrum. Several interesting phenomena were noticed after the recording of interference patterns in these samples. In the exposed area, the dye gets partially or totally bleached; however when the plate was kept in the dark after a few hours the dye recovered its former state and presented a different color in the MBPVA/alc system. This can be explained by the conversion of leuco form of the dye to a stable thionine [16], which is clear from the shift in absorption spectra. In the case of the MBPVA/PAA blend, this recovery was found to be very slow and the change to the leuco form was found to be fixed in the case of CMBPVC. Direct imaging was carried out successfully on these samples and the recorded images were permanent in the case of CMBPVC. A photograph of direct imaging performed on CMBPVC film is shown in figure 13. Moreover, when the irradiated area was investigated with a low power He-Ne laser, the diffraction orders were seen. A strong enhancement effect, or reinforcement, has been demonstrated in these methylene blue sensitized polymer films. The observed self-enhancement for methylene blue sensitized films is a remarkable change in the diffracted beam. After the recording was stopped the diffraction efficiency started to increase at a higher rate. The diffraction efficiency was detected over 6 days and it continued to increase all the time. The diffraction efficiency of 15% of the MBPVA/alc grating increased to 38 % over 6 days after the recording process, the self enhancement gain thus being approximately 2. In the case of the blend, the diffraction efficiency of 6% increased to only 7.5%, over 6 days, showing that the enhancement process was rather slow. For the CMBPVC films no self-enhancement was observed. The grating was stored all the time in the same room conditions in which the recording took place. This dark reaction was considered earlier to be a disadvantage. Now we know that the dark reaction after recording does not distort the diffraction efficiency of the grating but

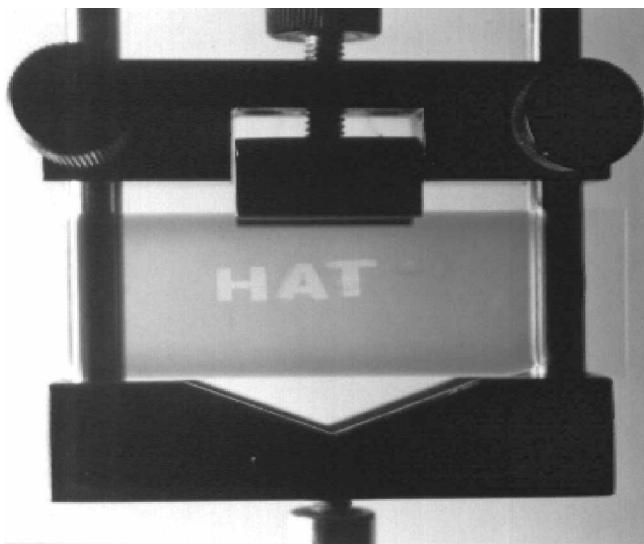


Figure 13. A photograph of the letters H, A, T recorded on a CMBPVC film.

increases it. This effect offers the possibility of using these materials in real time measurements for longer periods. The use of self-enhancement is of great interest also in hologram recording by facilitating shorter exposures than is the case in general with these materials and hence vibration free exposures.

The conversion of methylene blue to its leuco form could be fixed by changing the polymer matrix. We have already explained [15] that complexed methylene blue in polyvinyl chloride can be used as a permanent recording material. In this case the conversion of leuco methylene blue back to its original form was found to be a very slow process (even after 6 months the recovery was not observed) and hence this material proves to be useful for optical recording without any chemical treatment. But the diffraction efficiency was very low. The MBPVA/PAA blend gives approximately 11% diffraction efficiency and shows only very slow recovery. This has an intermediate characteristic between those of MBPVA/alc and CMBPVC.

6. Conclusion

The feasibility of using dry methylene blue sensitized PVA/PAA blend-based film as hologram recording material has been presented. Among its characteristics is its usefulness as recording material of approximately 11% diffraction efficiency with an exposure of 2000 mJ/cm^2 , which can retain fringes for approximately 10 days. But the studies on the rate of bleaching and exposure energy reveal that this material needs more exposure than the MBPVA/alc and CMBPVC films. The recovery by dye of its original form was observed to be very fast in the case of the MBPVA/alc system. A maximum diffraction efficiency of about 35% was achieved on the MBPVA/alc system due to self-enhancement. As a permanent recording material, methylene blue sensitized PVA/PAA blend or CMBPVC can be used without any fixing process whereas MBPVA/alc can be used to record hologram, however a suitable fixing technique is necessary.

Acknowledgment

Financial support by DRDO is gratefully acknowledged.

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