

Fabrication and characterization of methylene-blue-doped polyvinyl alcohol–polyacrylic acid blend for holographic recording

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A methylene-blue-sensitized polymer blend of polyvinyl alcohol and polyacrylic acid is fabricated and tested for holographic recording. It was found to have good characteristics such as high sensitivity, storage stability, ease of fabrication, and environmental stability. Optimization of the ratio of polyvinyl alcohol/polyacrylic acid, the sensitizer concentration, pH, energy, diffraction efficiency measurements, etc., have been done. pH is found to have a great influence on the recovery of the dye in this matrix. The results of experimental investigations into the properties of this new material are reported. © 2004 Optical Society of America

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1. Introduction

Polymer-based recording materials are a promising area of research for holographic storage media. Typically, photopolymers are used for write-once systems. However, all recording materials have limitations that inhibit the performance of holographic memory systems, and such systems are found to be attractive candidates for holographic applications. Some of the polymeric mixtures with their applications that fall in this category are

- Structuralization of gelatin–acrylic acid compounds (amides and salts), which produces high-resolution sensitive media for holographic optics.¹
- Dry acrylamide–polyvinyl alcohol (PVA) films rendered red sensitive with dye, which have been used to record interference gratings, and holograms of diffraction efficiency of 10% for an exposure of 94 mJ/cm² have been attained.²
- A photopolymer film comprising a mixture of acrylamide, methylene blue (MB), triethanolamine,

and PVA, which has potential in photonics applications such as diffractive optical elements and waveguide structures.³

Holographic recording materials are the core of holographic data storage and correlation system. Research in new photopolymeric material is necessary before truly high performance and optical holographic information-processing systems can be realized. Therefore it is tempting both scientifically and technically to try to develop and study systems for holographic information recording that possess both the advantages of easier photopolymerizable systems (such as acrylic acid) and the specific positive properties of PVA.

In the present paper, introductory results are reported in which a mixture of PVA and polyacrylic acid (PAA) are used for holographic storage. MB is used as the sensitizer. The studies include the optimization of PAA in PVA, sensitizer concentration, pH, behavior of absorbance, transmittance, storage, rate of bleaching as a function of exposure over time, and diffraction efficiency measurements. It was found that this polymer mixture exhibited more outstanding properties than the conventional methylene-blue-sensitized polyvinyl alcohol (MBPVA) system.

2. Experiment

Samples were prepared under normal laboratory conditions as follows.

For the preparation of 10% polyacrylic acid, acrylic acid was procured from Merk, Mumbai, India, and

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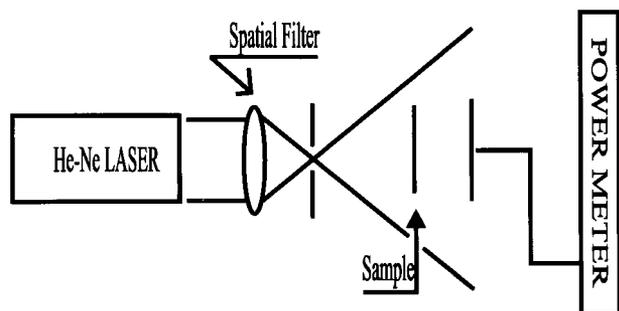


Fig. 1. Experimental setup for laser exposure.

used as such. PAA was synthesized by batch polymerization of acrylic acid by use of ammonium persulphate as the initiator. A three-necked flask fitted with an additional funnel, reflux condenser, thermometer, and a stirrer was charged with 90-g distilled water and heated to 90 °C. 0.2 g of potassium persulphate was carefully added, followed by 10-ml acrylic acid added slowly but with constant stirring. The temperature was maintained at 90 °C, and heating was continued for 2–3 h. The solution obtained was 10% PAA. The molecular weight of PAA was estimated as 3,34,000 with a Ubbelohde viscometer.

For the preparation of 10% PVA, PVA (molecular weight 1,25,000) (10 g) was dissolved in distilled water (100 ml).

For the preparation of the dye solution, MB (0.3 g) was dissolved in distilled water (20 ml).

Different proportions of PVA and PAA were mixed, into which methanol (20 ml) was added to get a clear homogeneous solution. The ratio of PVA/PAA was varied from 10:0 to 0:10. One can obtain a homogeneous photosensitized solution by mixing MB with the above solution.

The film of this MB-sensitized solution is prepared as explained in Ref. 4. For pH measurements, a digital pH meter (Systronics 335) was used. One decreases pH by adding HCl and increases it by adding an ammonia solution. The absorption spectra of the samples in the visible region before and after exposure are taken with a Hitachi 330 UV–visible–near-infrared spectrophotometer. For determining the power necessary for bleaching, the samples were exposed to varying power from 90 μ W to 6.4 mW for 20 s, and the change in transmittance was observed.

3. Exposure to the He–Ne Laser

The exposure beam was derived from a coherent Melles Griot He–Ne laser with emission at 632.8 nm. The laser beam was expanded with a spatial filter arrangement set up in the laboratory, explained elsewhere.⁵ The samples were placed in the expanded beam.

The experimental setup is shown in Fig. 1. The transmitted intensity is measured with a powermeter (Ophir Model 2000). The effects of He–Ne laser irradiation in the absorption spectra of MBPVA–PAA films were studied with a Hitachi 330 UV–visible–near-infrared spectrophotometer. The experimen-

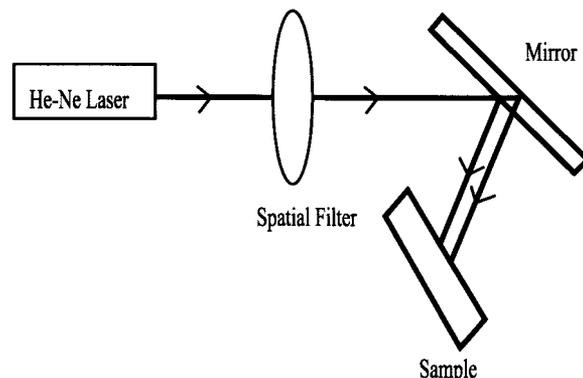


Fig. 2. Experimental setup for diffraction efficiency measurements.

tal setup for diffraction efficiency measurements is shown in Fig. 2. The expanded beam was allowed to fall on a plane mirror. The light reflected from the top surface of the mirror and that from the mercury coating interfere to form an interference pattern, which is photochemically impressed on the film. The angle between the incident beam and the normal was taken as θ . By varying θ (angle), it was found experimentally that we could record the number of lines/millimeter only in the range of 193 to 720 for a particular mirror owing to some experimental difficulties (due to the single-mirror method).

4. Results and Discussion

A. Optimization of the PVA/PAA Ratio

Transparent films were prepared with PVA and PAA at different proportions. It was found that, as the amount of PAA content in the blend increases, the film became sticky and useless for optical recording. This is because it is difficult to remove water from PAA. A decrease in film clarity and nonuniformity was observed when the ratio 6:4 (PVA/PAA) or lower than that was used. So a detailed study was done for the ratios 7:3, 8:2, and 9:1. These films were exposed to a He–Ne laser (wavelength of 632 nm) with laser power of 5 mW for 5 min, and the change in transmittance was monitored. The change in transmittance was found to be almost the same in all three cases. Hence, to optimize the ratio, we monitored the change in absorbance with time to find the recovery of dye back to its original form. Figure 3 shows the change in absorbance with time for three ratios of PVA/PAA. It was found that, as the PVA content in the sample increases, the recovery of the dye back to its original form was fast. Because the main motivation behind the study is to develop a new polymeric material that can be used as a permanent recording medium a 7:3 ratio (PVA/PAA) was found to be optimum, as the recovery of the dye was found to be quite slow in this case.

B. Optimization of the Sensitizer Concentration

Keeping the PVA/PAA ratio at 7:3, we varied the concentration of MB from 9.3×10^{-4} to 9.3×10^{-6}

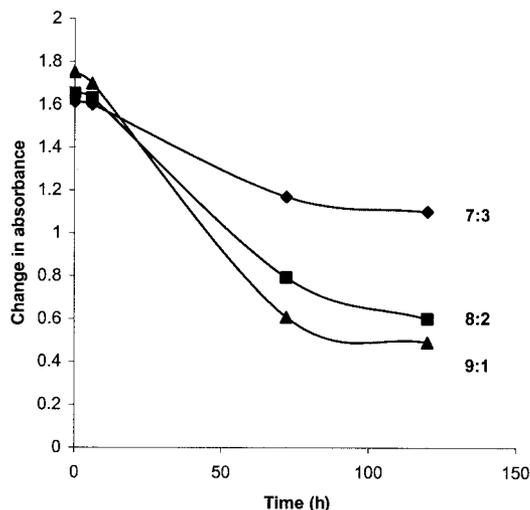


Fig. 3. Variation of the change in absorbance with time for three ratios of PVA/PAA.

g/ml in the solution. The films thus obtained from this solution were exposed to a laser power of 5 mW for 5 min. The change in transmittance was monitored as a function of time. A graph was plotted between relative transmittance (T/T^0) and time as described in our earlier paper.⁵ A1, A2, A3, and A4 in the graph represent the different concentrations of dye employed. From the graph (Fig. 4), it is clear that the relative transmittance is maximum for a concentration of 1.46×10^{-4} mol/l (A4), and fast bleaching was observed at this sensitizer concentration. This is because at high sensitizer concentration a greater number of molecules will be present in the illuminated area, thereby requiring more intensity for its excitation in a fixed time.

C. Optimization of pH

Interesting behavior was observed when pH was changed from 1 to 11 in the PVA–PAA system. The film prepared at low pH lost its clarity, and, for films

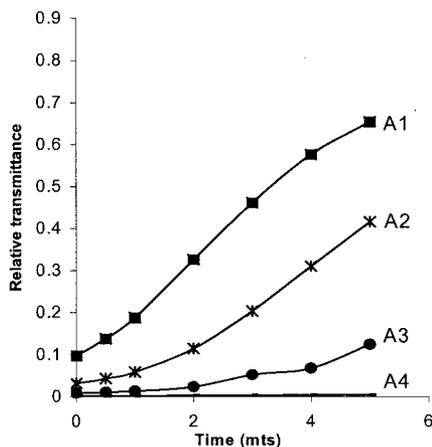


Fig. 4. Variation of relative transmittance with time for different dye concentrations.

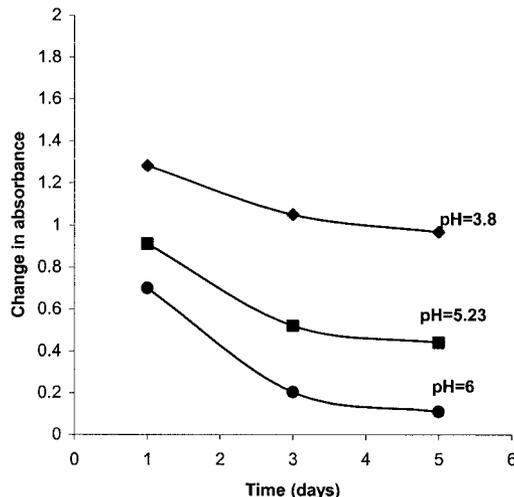
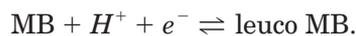


Fig. 5. Variation of the change in absorbance with time for different pHs.

at high pH, 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 different pHs were exposed to laser irradiation, and the change in absorbance as a function of time is shown in Fig. 5. It can be seen that as the pH increases the recovery of the dye back to its original form was found to be fast. At a pH 3.8 (normal pH of the system), the recovery was quite slow, and, at pH 6, the recovery was quite fast.

Direct imaging was done on all four samples at pH values of 3.79, 5.02, 5.23, and 6.02 to study the recovery of the dye. For this, the letter O was imaged, and the fading was observed. For pHs 6.02 and 5.2, the recovery of the dye was almost complete in 36 and 72 h, respectively, and the letter O vanished from the film. For pH 5, the recovery was slow, and it was almost complete in eight days. The film of pH 3.8 was found to be stable for several days, and the recorded information was found to be long lasting. This is because, as the pH increases, the solution becomes less acidic, and the leuco form becomes unstable, the reconversion becomes very fast:



Hence the pH of PVA–PAA was optimized to be 3.8 for this study.

D. Optical Absorption Measurements

The typical absorption spectra of the exposed and unexposed optimized samples of MB in PVA–PAA are shown in Fig. 6. The exposure time was fixed as 5 min. The spectra showed a peak around 663 nm, which is characteristic of MB. On laser exposure, the material got bleached, and the absorption spectrum was broadened. A shift in the absorption spectrum was observed after irradiation. It is clear from the figure that the recovery of dye in this matrix is slow even after two days, unlike MB in conventional

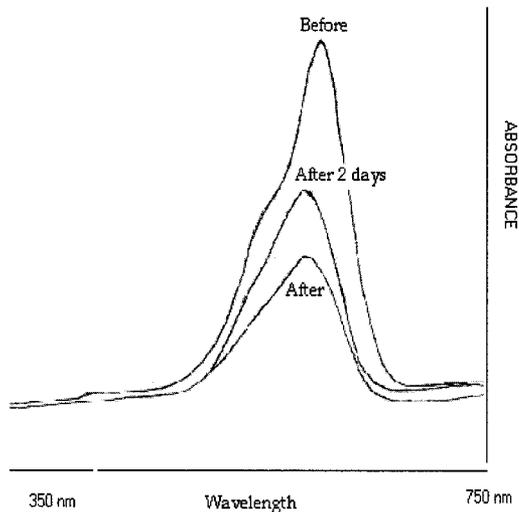


Fig. 6. Optical absorption spectra of MBPVA-PAA films before and after exposure and after 48 h after exposure.

PVA systems. In MBPVA systems the recovery was almost complete in 48 h. Thus by blending PVA with PAA we can delay the recovery of dye in this polymer matrix. Hence it is evident that there is a change in the absorption property of the material, and hence it can be used as an optical recording material.

E. Rate of Bleaching

For determining the rate of bleaching of the optimized sample, it was exposed to a laser power of 5 mW. The transmitted intensity was measured at regular intervals (at every 20 s) for 10 min with a powermeter. The variation of transmittance in terms of T/T^0 with time is calculated and plotted. We found the rate of bleaching by finding the slopes at different times. The rate of bleaching with time for the optimized sample is shown in Fig. 7. The

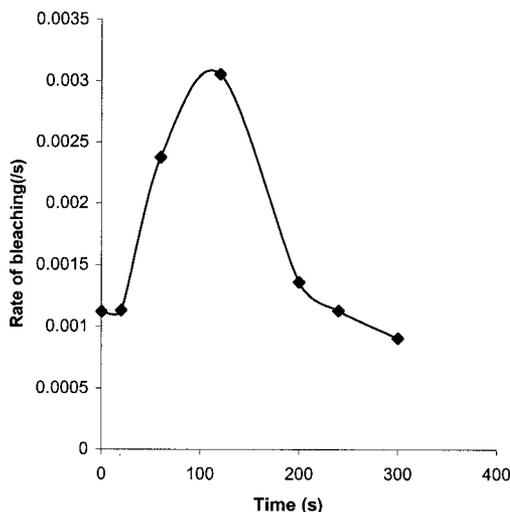


Fig. 7. Variation of rate of bleaching with time for the optimized MBPVA-PAA films.

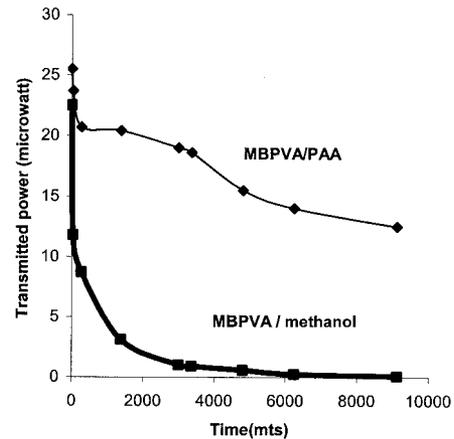


Fig. 8. Effect of storage on MBPVA and the PVA-PAA blend.

rate of bleaching initially increased slowly and then rapidly, reached a maximum, and then decreased. The rate was found to be maximum at 120 s. By that time, most of the MB molecules had absorbed sufficient energy and were converted into the leuco form. The slow rate of bleaching of MB in this polymer mixture can be due to the higher deactivation energy of PAA in the blend. In the case of a conventional MBPVA system, the rate of bleaching was found to be fast initially, and no threshold was observed at this laser power.⁵

F. Effect of Storage

Even though the possibility of optical recording in MBPVA is suggested by many researchers, they have found that the information stored was not stable for a long time. The conversion of the leuco dye back to its original form was the reason attributed to this observation.

In the present study on MB in PVA-PAA films, the change in absorption maxima occurring during irradiation remained almost unchanged for a long period of time. To study the effect of storage, we subjected the optimized sample to a maximum power so as to reach the saturation point. We monitored the transmittance variation of the irradiated sample as a function of time by sending a laser beam of low power (less than threshold power), and it is plotted in Fig. 8. A slight decrease in transmittance at the irradiated spot was observed initially for MB in PVA-PAA film where a sharp decrease was observed in the case of MBPVA films. Thus it can be proved beyond a doubt that the MBPVA-PAA system is a more efficient material for storing information than MBPVA.

G. Threshold and Saturation Energy

As in the case of the concentration of the material component, power is also an important factor to be optimized because bleaching of the dye depends on the power of the He-Ne laser used. No bleaching was observed when the sample was exposed to low laser power. It was found that a minimum power of 181 μ W was essential for the photochemical change

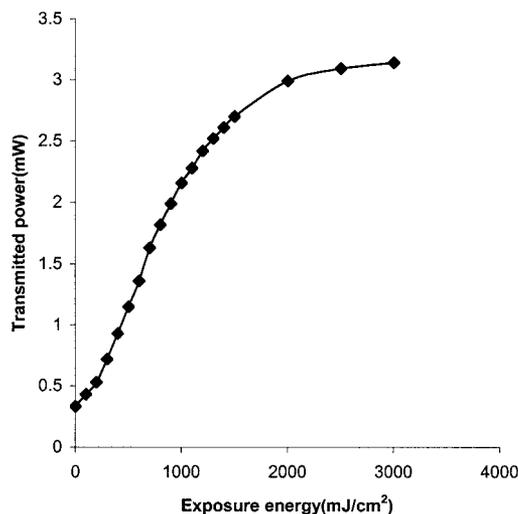


Fig. 9. Variation of exposure energy with transmitted power.

to take place. For determining the saturation energy of the sample, the optimized sample was subjected to a maximum power of 5 mW, and the change in transmittance was monitored. The transmittance first increased slowly and then rapidly. Finally, a stage of saturation was attained, as is clear from Fig. 9. The threshold and saturation energy of the sample are 300 and 2×10^3 mJ/cm², respectively.

H. Interferometric Studies

The experimental setup for measuring diffraction efficiency is shown in Fig. 2. By varying the number of lines/millimeter and adjusting the angle, we recorded the gratings on MBPVA-PAA. In all the cases, diffraction efficiencies were determined. The diffraction efficiency with different angles for this film is plotted in Fig. 10. The diffraction efficiency decreases at first, reaches a minimum, then increases gradually, reaches a maximum value, and then de-

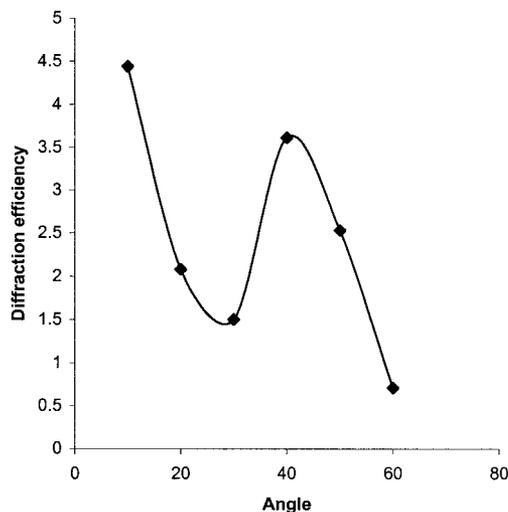


Fig. 10. Variation of diffraction efficiency with different angles for MBPVA-PAA films.

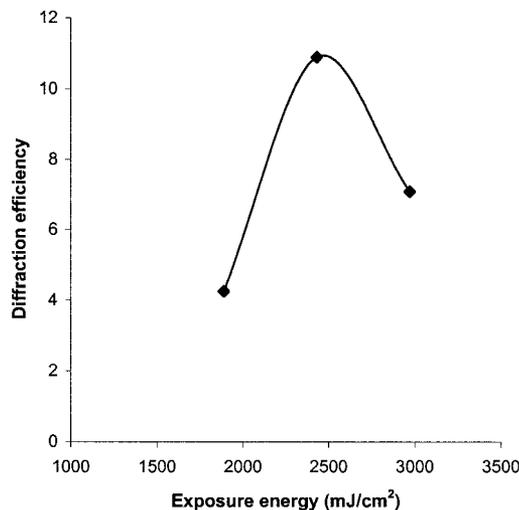


Fig. 11. Variation of diffraction efficiency with exposure energy at an angle of 10°.

creases. From the variation of diffraction efficiency with the angle, it is understood that the resolution of the material is limited as the diffraction efficiency decreases when the number of lines is increased beyond a certain value. The grating produced may be merging and cannot yield more diffraction efficiency. We recorded the gratings by keeping the angle fixed and varying the exposure energy and measured the power of the combined recording beam falling on the film by using a powermeter.

The beam is allowed to fall on the film for a fixed time. We repeated the experiment by changing the exposure time. In each case, exposure energy was calculated with the equation exposure energy = power \times exposure time.

In all the cases, diffraction efficiency was measured as before. It was observed that at lower exposure energies diffraction efficiency was low; it then gradually increased with exposure energy, reached a maximum value, and then decreased. This was true for the angles 10° and 40° that we studied. The variation of diffraction efficiency with exposure energy for these two angles was plotted as shown in Figs. 11 and 12. The reason for this may be due to the following reason. When the exposure energy was increased, initially the bleaching process takes place in the exposed regions, thus converting the dye into its leuco form, and hence the light gets diffracted more. But when the energy increases there is a chance for the dye molecules to get converted into the thionine state, which has a dark blue color; hence the contrast between the exposed and unexposed regions decreases, thus causing a reduction of diffraction efficiency at high exposure energies. The photograph of the diffracted pattern obtained on this material is shown in Fig. 13. First- and second-order patterns were obtained on this material. Holograms were also recorded on these samples.

I. Dye Behavior

The structure of MB and its leuco form is shown in Fig. 14. MB is a basic dye of the thiazine group.

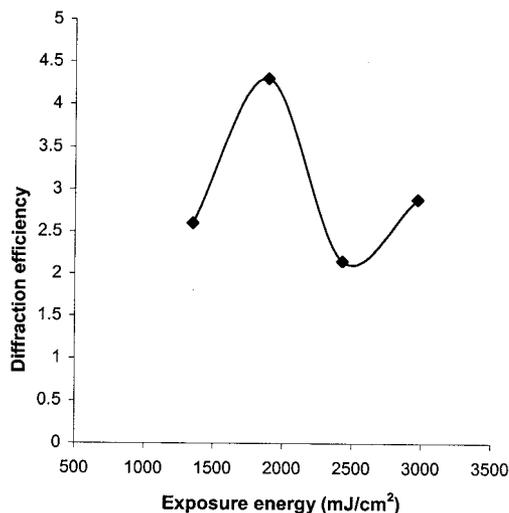


Fig. 12. Variation of diffraction efficiency with exposure energy at an angle of 40°.

When MB is irradiated with red light, it is excited to MB*^{*}; it is then converted into a stable leuco form:



According to the mechanism, the photoexcited dye [in the (*n*, π*) triplet state] is reduced by the oxidizable reactant by a transfer of an electron or hydrogen. The semireduced dye radical either is reoxidized to the ground state by oxygen or is not regenerated, but it is transformed into the leuco dye, i.e., photobleached.

This sensitized oxidation can also lead to a sensitized photodestruction of the dye. In these cases, MB serves as an oxidizable substrate as in the bleaching of aerated chlorophyll by high intensities of light.

The triplet excitation transfer may be efficient in many photobleaching processes of MB, but only a few exact studies have been made so far. In most of the studies with MB in different polymer matrices, it has been observed that the exposed part of the plate can

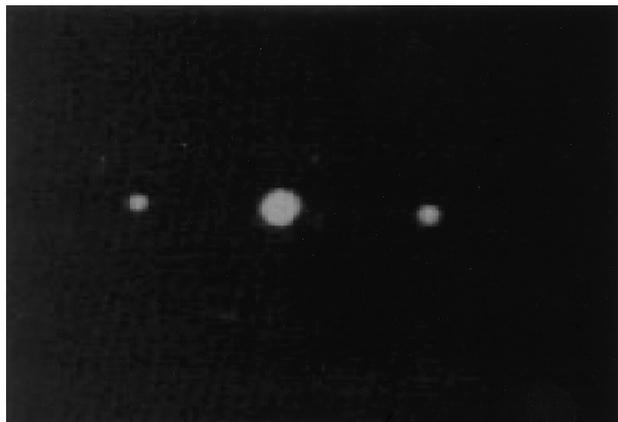


Fig. 13. Photograph of the diffracted pattern obtained on illuminating the planar MBPVA-PAA films.

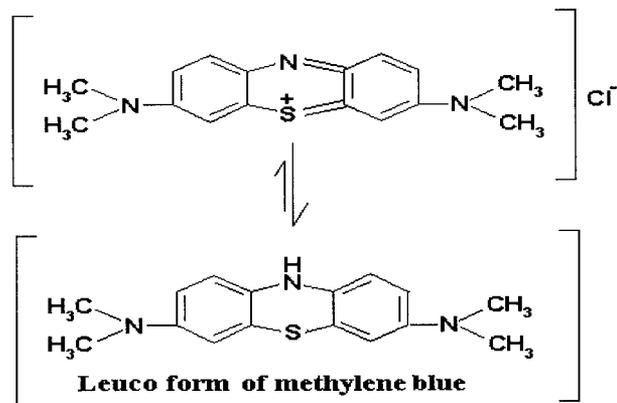


Fig. 14. Structure of MB and its leuco form.

recover its original color after some time, and chemical or thermal treatment is necessary for fixing the data. This is due to the reoxidation of the leuco form of the dye. The dye can return to the unexcited state when it is in contact with molecular oxygen. In the present study on the MBPVA-PAA blend, the conversion of the leuco form back into the original form was observed to be a much slower process, as the information stored could be retained for several weeks without much deterioration. The recovery of the dye in the polymer matrix can be delayed more, by one's increasing the amount of PAA. But PAA cannot be increased in the polymer blend because that makes the film less sensitive to lasers and sticky. The role of PAA in this matrix is important and yet to be predicted.

J. Direct Imaging

Before exposure the MB molecules are uniformly distributed throughout the medium. However, during the imaging process the modulated pattern produces a corresponding change in the film. We believe that this change results from the conversion of the dye molecules into the leuco form. Because the reconversion is a slow process in this mixture, the concentration gradient developed owing to the excitation of the dye molecules as a result of illumination remains fixed in its location. Thus the recorded images are more or less permanent. The photographs of direct imaging done on MBPVA-PAA films are shown in Fig. 15.

K. Self-Enhancement

A strong enhancement effect, reinforcement, has been demonstrated in this MB-sensitized polymer blend. The observed self-enhancement for MB-sensitized film 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 for 15 days, and it continued to increase during the entire time. The self-enhancement observed in MBPVA-PAA is shown in Fig. 16. However, it should be remembered that these studies were done without



Fig. 15. Photograph of a few letters recorded on these samples.

any fixing or chemical development processes on these dye-sensitized films. In the case of the blend, the diffraction efficiency of $\sim 11\%$ increased to $\sim 14\%$, over 15 days, showing that the enhancement process was rather slow. The rate of self-enhancement was highest during the first day after the recording, appearing to be near saturation after ~ 15 days. The humidity was not changed during the storage of the MBPVA–PAA grating, and the grating was stored the entire time in the same room conditions under which it was recorded. After 20 days the diffraction grating recorded on these samples almost vanished. This shows that a proper fixing method is necessary to fix the leuco dye in the polymer matrix. This self-enhancement may be due to the following reasons: dark reaction, diffusion, polymerization, and internal stress on the film.

In our opinion the dark reaction–polymerizations are mainly responsible for the self-enhancement of the holographic grating in MBPVA–PAA films. The mechanism is yet to be evaluated. This dark reaction was considered earlier to be a disadvantage.

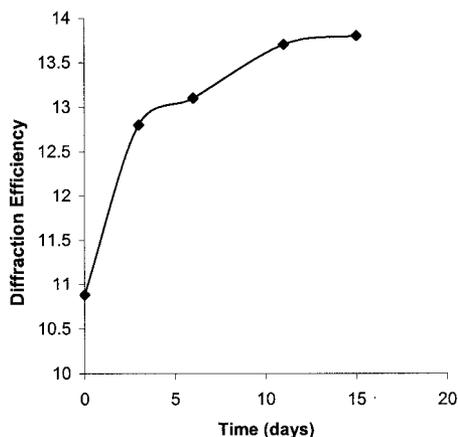


Fig. 16. Change in diffraction efficiency after exposure for MBPVA–PAA films.

Now we know that the dark reaction after recording does not distort the diffraction efficiency of the grating but 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 because it facilitates shorter exposures than general for these materials and thus vibration-free exposures.

Further results concerning the improvement of sensitivity, diffraction efficiency, and recording parameters of this polymer mixture and details about the mechanism involving the interaction of light with the polymer will be presented later.

5. Conclusion

Optimization and characterization of the methylene-blue-sensitized PVA–PAA blend gave best results at a sensitizer concentration of 1.46×10^{-4} mol/l and pH 3.8. By changing the pH, we can control the recovery of dye in this matrix, and the recovery was found to be slow compared with MBPVA films. The information stored was stable for two weeks and does not need any fixing processes. The material preparation is easy and has high sensitivity, low threshold energy, and longer shelf life and storage life. It is a self-developing polymeric mixture and is environmentally stable. It has excellent storage life compared with MBPVA prepared by the same method. This holographic material can record real-time holograms, and a diffraction efficiency of 11% was achieved. Self-enhancement in the diffraction efficiency exhibited by MBPVA–PAA films facilitates shorter exposures than general for these materials and thus vibration-free exposures. Thus many engineering applications may become possible with this low-cost polymeric material.

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