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Optimization of pH and direct imaging conditions of complexed methylene blue sensitized poly(vinyl chloride) films

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Abstract. Significant results of our experimental investigations on the dependence of pH on real time transmission characteristics on recording media fabricated by doping PVC with complexed methylene blue are presented. The optimum pH value for faster bleaching was found to be 4·5. In typical applications, the illumination from one side, normal to the surface of this material, initiates a chemical sequence that records the incident light pattern in the polymer. Thus direct imaging can be successfully done on this sample. The recorded letters were very legible with good contrast and no scattering centres. Diffraction efficiency measurements were also carried out on this material.

Keywords. Poly(vinyl chloride); methylene blue; pH; direct imaging; diffraction efficiency.

1. Introduction

Materials with light induced absorption or refractive index changes are of considerable interest for applications in the field of holography, optical storage and integrated optics. In many cases thick samples are required, e.g. components making use of the Bragg conditions.

Innumerable studies were done on dye sensitized polymer films for various holographic applications. We have introduced a new polymer matrix [poly(vinyl chloride)] for holographic recording whose characterization is explained earlier (Ushamani *et al* 2002). We have chosen poly(vinyl chloride) due to its unique properties like excellent optical clarity, colourability, dimensional and environmental stability, ease of fabrication, economical, flexible or rigid, non-toxic, stability against UV light, transparency in the visible spectral region etc. It can also be fabricated to any desired thickness.

The low monomer content in the PVC films is utilized for the light induced absorption change on this material. The wave length of the triggering light may be shifted from UV into the visible spectral region by doping the material with suitable dye such as methylene blue, eosin, neutral red, brilliant green etc. Although methylene blue in poly(vinyl chloride) is a good medium for optical recording, we were able to enhance the sensitivity of this film by converting the dye to a more stable complexed state.

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2. Importance of pH control

It has been found that pH greatly influences the efficiency of a hologram recording material. In methylene blue sensitized DCG holograms, the electron donors especially amines have great influence. It seems that reducing the pH of the gelatin solution of these amines (electron donors) with weak acids, still allows the amines to act as electron donors when pH is above 7. On the other hand, neutralization of the amines with strong acid takes place at low pH i.e. the amines are rendered ineffective as electron donors. At high pH value of 10 or more, damaging of gelatin and at pH values below 9, precipitation of the dye out of the solution in the presence of dichromate is observed (Blyth 1991). Hence a control on pH was essential to make a high sensitive recording material. In the case of DCG holograms, an optimum pH of 6·2 gives maximum efficiency (Ravi Prasad Rao *et al* 1999). To prepare spotless MBDCG plates a high pH of 11 for the photosensitive medium is necessary (Kurokawa *et al* 1998). The effect of pH of the coating solution on the diffraction efficiency of dichromated poly(vinyl alcohol) (PVA) holograms has been studied by Mannivannan *et al* (1993) who reported that the pH variation of the coating solution plays an important role on the diffraction efficiency. It is reported that the diffraction efficiency shows an increasing trend with an increase in pH. Regarding MBPVA and MBPMMA, earlier investigations carried out in our laboratory showed that high pH and high exposure energy gave good results.

As such it appears that a very thorough understanding of pH and exposure effects on bleaching properties of complexed methylene blue sensitized polyvinyl chloride matrix might put us in the right direction before using the material for hologram recording.

In this paper the results of a systematic study of the effect of pH on the bleaching property and diffraction efficiency measurements on complexed methylene blue sensitized polyvinyl chloride (CMBPVC) are presented. Imaging on pure and complexed methylene blue sensitized PVC films are done which reveals the optical quality of the film. An attempt is also made to explain the mechanism of imaging on CMBPVC films.

3. Experimental

The PVC used was of suspension grade with K value 70 (supplied by Reliance Industries, Mumbai) and methylene blue was of MS quality. The preparation of complexed methylene blue sensitized polyvinyl chloride (CMBPVC) films involves the deposition of the sensitized PVC from solution on a suitable substrate and allowing the solvent to evaporate slowly. There are different techniques employed for coating, but in the present work we have adopted gravity settling method. The coating solution consists of a polymer (PVC), a sensitizer (MB), 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 stirred well to get a homogeneous solution. The amount of solution that is poured on the substrate (glass) is a function of the desired thickness of the sensitive layer. After the deposition a cover should be placed above the plate to prevent the dust particles from falling on the film until it is dry ~ 12 h later. This drying period is a function of the amount of materials used in the photosensitive solution. The size of the glass plates used in the experiment was 75 × 25 × 1·4 mm; however, after the drying period it was found that the edges were found to be more thicker than the centre portions. The thickness of the plate in its central region was 0·06 mm and on the periphery 0·1 mm. Therefore, in all the experiments area in the central part was used.

These films were then exposed to a Melles Griot He–Ne laser as explained elsewhere (Pradeep *et al* 2000). UV absorption measurements were performed in the range of 350–750 nm using a UV–vis–NIR spectrometer. The transmitted intensity was measured using a power meter OPHIR model 2000.

The pH of the optimized CMBPVC solution was measured using a digital pH meter (systronics 335). pH was decreased by the addition of glacial acetic acid and increased by adding ammonia solution. The pH in our study has been varied between 3 and 8. Very high and very low pH affects the clarity and transparency of the film.

4. Results and discussion

4.1 *Effect of pH variation*

The effect of pH was studied for an optimum sensitizer concentration of $4 \cdot 1 \times 10^{-4}$ g/ml. Different samples prepared at different pH values were exposed to a power of 4 mW and the change in absorption before and after was observed. Figure 1 shows the absorption spectrum of a 0·06 mm thick layer of CMBPVC for a pH of 4·5 before and after exposure. Since PVC is transparent in the visible region, absorption is due to the dye methylene blue. On absorbing the light of a He–Ne laser beam (632·8 nm) a large part of the dye molecule undergoes excitation to the leuco form. It was found that no shift in the absorption peak at any pH was observed on laser irradiation. Methylene blue in other polymer matrices like PVA, PMMA, gelatin etc on laser exposure, results not only in bleaching but also in a change in state of methylene blue dye (Capolla and Lessard 1991). But in CMBPVC films no shift in absorption band was observed on laser exposure and hence the change of methylene blue to a stable thionine state is ruled out.

To study the time stability of this leuco form of the dye, the absorbance at the irradiated spot was monitored for a sufficiently long time (figure 2). A slight increase in absorbance was observed on the next day itself, which remained almost constant with time. This slight increase

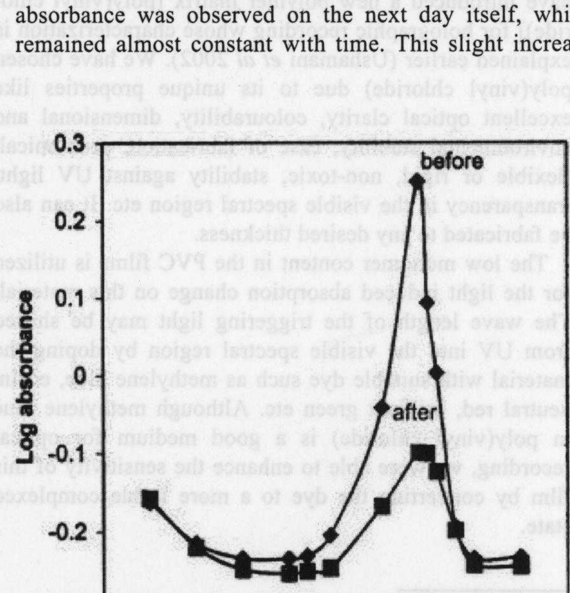


Figure 1. Optical absorption spectra of CMBPVC film for a pH of 4·5 before and after exposure.

in absorbance may be due to the deexcitation of a very few molecules of leuco methylene blue back to its original form.

As it is observed that CMBPVC films of different pH are exposed to He–Ne laser irradiation, the dye molecules get bleached. Hence real time transmission studies were carried out to find out the rate of bleaching of dye molecules at different pH.

As the exposure time increases the dye gets more and more bleached. The transmittance value for the exposure of the subtrate is taken as $T°$ and the transmittance value obtained for the exposed film is taken as T. In the transmission measurements their ratio ($T/T°$-relative transmittance) is used for standardization. Figure 3 shows the relative transmittance curve for different exposure times for different pH. In all the cases the relative transmittance increases slowly and then reaches a stage of saturation within 120 s for a power of only 4 mW. This explains the high sensitivity of CMBPVC films.

We studied the rate of bleaching at different pH by finding the slopes at different times. Initially rate of bleaching was found to be very rapid which became constant after some time. The rate of bleaching was found to be maximum for a pH of 4·5. A plot of rate of bleaching vs time for different pH is shown in figure 4. To find the optimized pH of CMBPVC films, relative transmittance at 600 s is plotted for different pH. The data in figure 5 demonstrated that very fast bleaching can be attained at a pH of 4·5. Increasing the pH more than 4·5 drastically reduced the rate of bleaching and reduced relative transmittance. Thus it is obvious that the best film for optical recording is that prepared around a pH of 4·5 and having a dye concentration of $4{\cdot}1 \times 10^{-4}$ g/ml.

5. Direct imaging

An attempt was made to do direct imaging on the optimized CMBPVC. The medium consists of an inert poly-

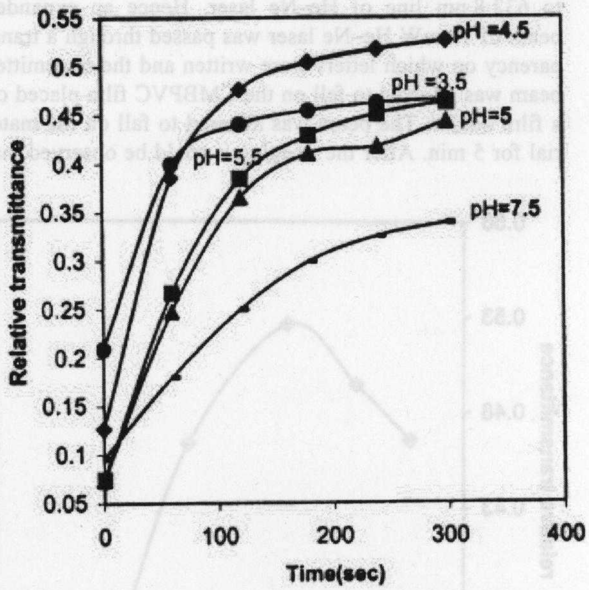


Figure 3. Relative transmittance curve for different exposure times for different pH.

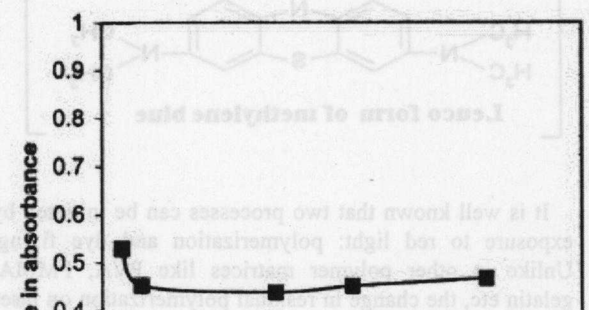


Figure 2. Change in absorbance of CMBPVC films after irradiation with time.

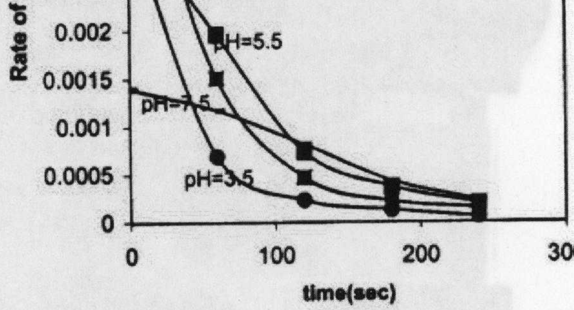


Figure 4. A plot of rate of bleaching vs time for different pH.

mer host on which the complexed methylene blue molecules are uniformly suspended. The recording wavelength of this material is determined by the photosensitizer (CMB), which in this case has an absorption peak close to 632·8 nm line of He–Ne laser. Hence an expanded beam of 10 mW He–Ne laser was passed through a transparency on which letters were written and the transmitted beam was allowed to fall on the CMBPVC film placed on a film holder. The beam was allowed to fall on the material for 5 min. After the imaging it could be observed that the letters were very legible with good contrast and no scattering centres (figures 6, 7). It could be observed that the fabricated films were of good optical quality, we could also ascertain that the films could record letters of small size. This could give a qualitative idea about the resolution capacity of the material.

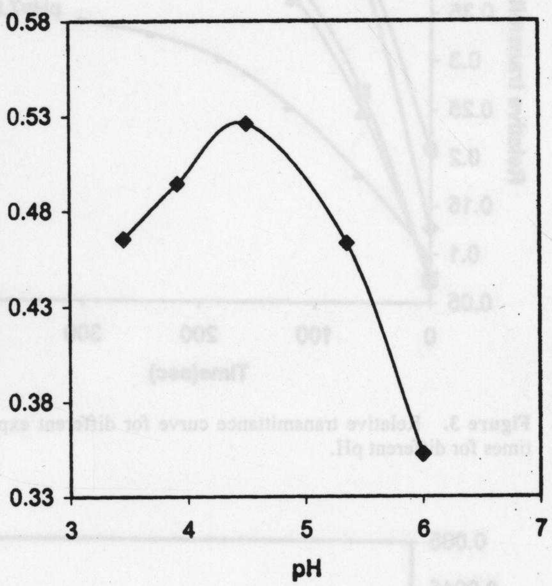


Figure 5. A plot of relative transmittance at different pH for a fixed time.

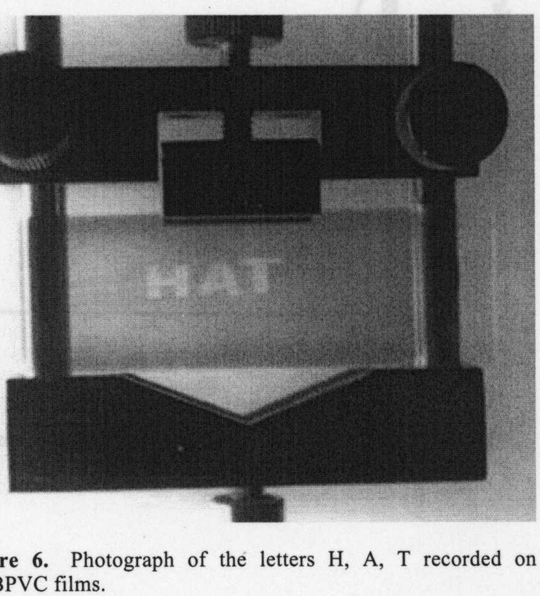
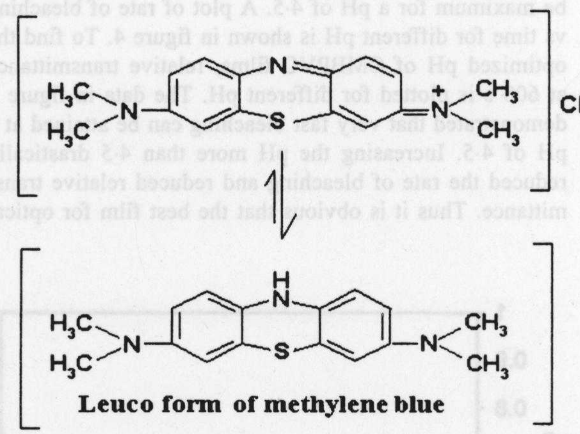


Figure 6. Photograph of the letters H, A, T recorded on CMBPVC films.

The mechanism of recording in this material is shown in figure 8.

Before recording, the complexed dye molecules were evenly distributed throughout the medium. On illumination from one side, normal to the surface of these materials, initiates a chemical sequence that records the incident light pattern in the polymer. The high optical density of the film and the unidirectional illumination leads to a concentration gradient of the reacting species and their consequent excitation to the leuco form. The structure of methylene blue and its leuco form is shown below.



It is well known that two processes can be initiated by exposure to red light: polymerization and dye fixing. Unlike in other polymer matrices like PVA, PMMA, gelatin etc, the change in residual polymerization on laser exposure is very less in PVC since the monomer is a gas and its concentration is very low in the polymer. In the exposed area, the complexed dye molecules absorb energy and gets excited to its leuco form, which is found to be very stable. Thus the concentration gradient developed due to illumination remains almost fixed and the recorded images are permanent. Materials that are described here have also recently been developed for holographic memories (Steckmann *et al* 1998). An outstanding property of this material is that it is least affected by humidity, since PVC has no affinity towards moisture. Moreover, it does not need any dark room storage as other methylene blue sensitized conventional polymer system.

Preliminary studies on the diffraction efficiency of CMBPVC films were carried out. The first order-diffracted pattern of CMBPVC film is shown in figure 9.

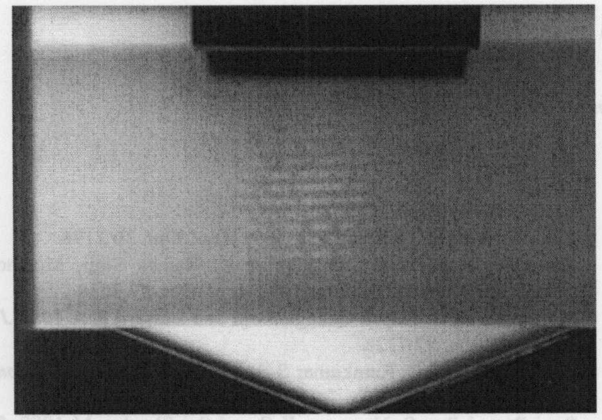


Figure 7. Photograph of very small letters taken with the macro lens recorded on CMBPVC films.

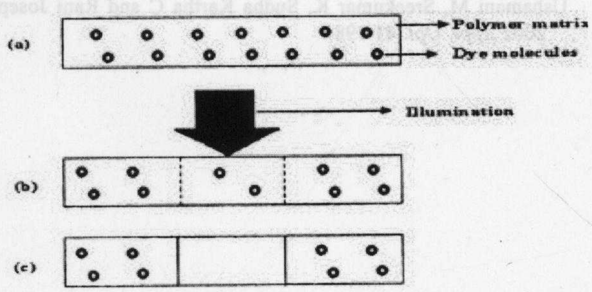


Figure 8. (a) Medium with a uniform distribution of the dye molecules, (b) illumination starts the conversion of the dye molecules to its leuco form, and (c) after irradiation the bleached area remains unchanged.

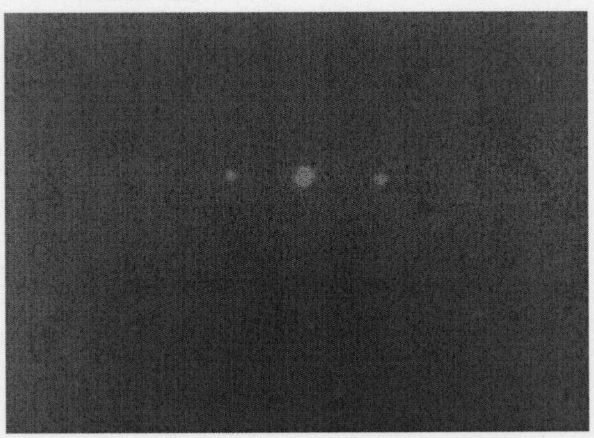


Figure 9. Photograph of the first order-diffracted pattern recorded on CMBPVC films.

Diffraction efficiency measurements on these films at different angles showed a maximum at 10° and 40°. Diffraction efficiency decreased initially and then showed a small increase at 40° (figure 10). So a detailed study was

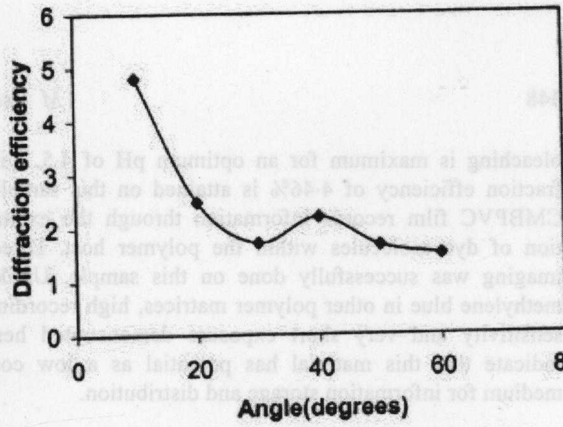


Figure 10. A plot of diffraction efficiency vs angle.

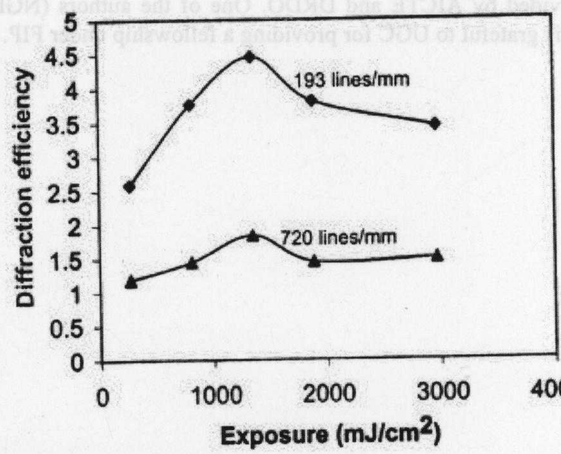


Figure 11. A plot of diffraction efficiency vs exposure energy.

carried out at these two angles for this material. The results are shown in figure 11. Maximum diffraction efficiency of about 4·46% was achieved on this material for an angle of 10° (193 lines/mm) and attempts are going on to improve the diffraction efficiency of the sample. Even though the diffraction efficiency of CMBPVC is low, it can be used as a permanent recording material unlike methylene blue in other polymer matrices like PVA, PMMA, gelatin etc.

6. Conclusions

The study shows that time and exposure energy have a role to play on the stability, storage and diffraction efficiency of CMBPVC holograms, the role of pH appears to be crucial and profound. Dark room storage is not needed for CMBPVC films compared to other methylene blue sensitized conventional polymer system. The effect of pH on real time transmission property shows that the rate of bleaching is maximum for an optimum pH of 4·5. Diffraction efficiency of 4·46% is attained on this sample. CMBPVC film records information through the excitation of dye molecules within the polymer host. Direct imaging was successfully done on this sample. Unlike methylene blue in other polymer matrices, high recording sensitivity and very short exposure demonstrated here indicate that this material has potential as a low cost medium for information storage and distribution.

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