Complex methylene-blue-sensitized polyvinyl chloride: a polymer matrix for hologram recording

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A new polymer matrix sensitized with methylene blue for use as an optical recording material is described here. The characterization is done to determine the optimal recording conditions. These films need no chemical development and are found to be stable for several months. The matrix has excellent shelf life and needs an exposure only as short as 20 s. Direct imaging was done on this material. © 2002 Optical Society of America

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1. Introduction

Success in hologram recording depends both on selection of the laser and on production of the necessary recording medium. Currently available materials for hologram recording with the most available He–Ne lasers are unstable and require long exposure time, and fixation processes are affected by the atmosphere and possess insufficient sensitivity.

Of the many materials tried for holographic information recording, polymers have proved to be versatile because they are easy to prepare and have a variety of possible applications. They are also inexpensive and easily available. Numerous studies were done on methylene-blue-doped polymers such as polyvinyl alcohol (PVA), poly(methyl methacrylate) (PMMA), gelatin, and polyacryl amide for various holographic applications.[1–10]

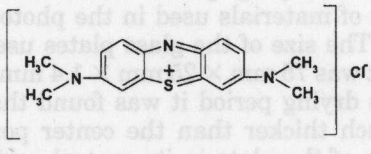
In this paper we report the use of polyvinyl chloride (PVC) film for holographic recording. PVC is a promising material that can be produced relatively easily in the form of thin films. Further advantages of this polymer are its excellent optical quality, its transparency in the visible spectral region, and its stability in UV light. This polymer can be easily doped with dye. Here we report the use for the first time to our knowledge, of dye-doped PVC for hologram recording.

The recording material described in this paper is generally of a planar type in which a polymer material, in this case PVC, of higher index is coated on a substrate of lower index. We have chosen complex methylene-blue-sensitized PVC as the recording material for the present study. Details of sample preparation, exposure and transmission studies, dye behavior, and storage effect are presented. Efforts have been made to make the procedure as well as the techniques simple to facilitate production and repetition.

2. Dye Behavior

The photosensitizing action of dyes results from the ability of the dye to act either as a strong oxidizing or as a strong reducing agent in the presence of a reduced or oxidizable substance, subsequently regenerating and returning to the normal state. Moreover, in many reactions, dyes are predestined sensitizers, because the chemically more reactive triplet state is produced in the dyes with high efficiency by intersystem crossing from the first excited singlet state.[11] In addition, aggregated or complex dye molecules are able to react in the excited state with contacting systems, thereby inducing important physical and chemical processes that could not start without the influence of light on the dyes.

The structure of methylene blue is



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Methylene blue (MB) is a basic dye of the thiazine group. We were able to improve the stability of MB and make it more colorfast by complex formation (by using copper acetate). MB when irradiated with red light is excited to MB* where it is converted to a stable leuco form. According to the mechanism the photoexicted dye [in the (n, π^*) triplet state] is reduced by the oxidizable reactant through a transfer of electron or hydrogen. The semireduced dye radical is either reoxidized to the ground state by oxygen or is not regenerated but is transformed to the leuco dye, i.e., photobleached. In most studies with MB in different polymer matrices,[12,13] it is observed that the exposed part of the plate can recover its original color after some time[1] and chemical or thermal treatment is necessary for fixing the data. In the case of MB-sensitized gelatin (MBG), chemical methods are employed to convert MBG into a permanent recording material. 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.[11] In the present study on complex methylene-blue-sensitized polyvinyl chloride (CMBPVC) the conversion of the leuco form back to its original form was observed to be a much slower process because the information stored could be retained for several months without much deterioration.

3. Experimental Procedure

The PVC was of suspension grade with K value 70 (supplied by Reliance Industries Mumbai) and the methylene blue was of microscopic stain quality. The preparation of complex CMBPVC films involves the deposition of the sensitized PVC from a solution on a suitable substrate and allowing the solvent to evaporate slowly. There are different techniques employed for coating, but in the present study we have adopted a gravity-settling method. The coating solution consists of a polymer (a PVC), a sensitizer (MB), a complex agent (copper acetate), a solvent for the polymer (cyclohexanone), and a solvent for the dye (glacial acetic acid).

PVC is dissolved in cyclohaxanone, and a few drops of complex methylene blue in glacial acetic acid are added. The mixture is stirred well to 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 keep dust particles off the film until it is dry ~12 h later. This drying period is a function of the amounts of materials used in the photosensitive solution. The size of the glass plates used in the experiment was 75 mm × 25 mm × 1.4 mm. However, after the drying period it was found that the edges were much thicker than the center 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 the area in the central part was used. Earlier studies on the absorption spectra of MBPVA, MBG, and MBPMMA in our laboratory

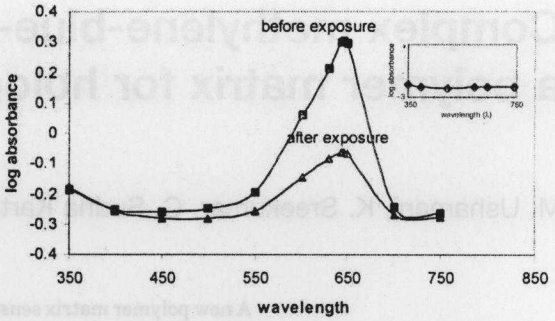

Fig. 1. Optical absorption spectra of undoped PVC (inset). CMBPVC before and after exposure are shown.

showed a sharp peak at 660 nm and that of MB showed a peak shift after irradiation.[1]

Very fast bleaching was observed when a 10-mW laser source was exposed to CMBPVC films. Hence further studies in the laboratory were done with a spatial filter arrangement set. To study the effect of bleaching, we exposed samples of nearly the same thickness (0.06 mm), pH (7), and a concentration of 4.133×10^{-4} g/ml to a power density of 6.4 mW. The transmittance of the plate as a function of exposure (power density × time) was measured. The transmitted intensity was measured at regular intervals by a power meter (OPHIR Model PD-2000). In all cases the beam size was kept constant.

The change in absorption at the irradiated spot was observed for months, and it was found that a slight increase in the absorption was observed the next day itself and remained almost the same for months.

4. Exposure

The exposure beam was derived from a 10-mW coherent Melles Griot He–Ne laser giving emission at 632.8 nm. The effect of He–Ne laser irradiation on the absorption spectra of CMBPVC films was studied with a Hitachi 330 UV-visible-NIR spectrophotometer in the same way as described in Ref. 1.

5. Results and Discussion

A. Optical Absorption Studies

The absorption spectrum of the undoped PVC (shown in the inset) CMBPVC film before and after exposure to laser irradiation is shown in Fig. 1. The spectra of CMBPVC showed a sharp peak at 649 nm. A peak shift was not observed on the absorption spectra after irradiation. A peak position at 649 nm was attributed to the presence of a complexing agent (copper acetate) that has strong absorption at the red part of the spectrum. After exposure the magnitude of this peak decreased, because methylene blue molecules are converted into a leuco form (colorless) during laser exposure. Figure 2 shows the variation of log absorbance for the same exposures after irradiation at different time intervals (5, 10, 15 min) for a power of 4 mW.

When different samples with the same pH and thickness but varying dye concentration were sub-

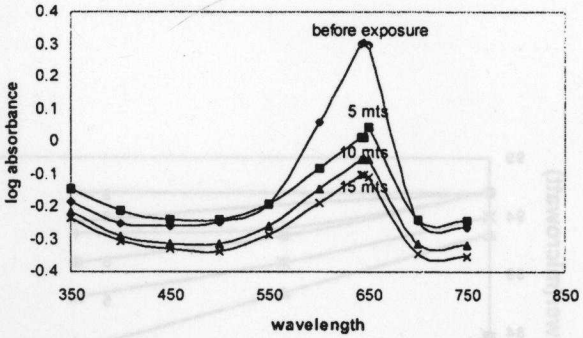

Fig. 2. Variation of optical absorption spectra for the same exposures after irradiation at different time intervals for a power of 4 mW. mts, minutes.

jected to laser irradiation, it was found that the absorption increases with the increasing dye concentration and faster bleaching was observed at an optimum concentration of 4.133×10^{-4} g/ml. It is not possible to increase the concentration of the dye indefinitely, because the compatibility and the solubility of this dye in the polymer film are limited. At a high concentration the dye will precipitate over the surface of the film. Unlike MB in various polymer matrices such as PVA and PMMA, very fast bleaching was observed in the case of the CMBPVC films. Fewer than 5 s were necessary for bleaching when 10 mW was applied directly without expanding the beam. Hence further experiments were done with an expanded laser beam by using a spatial filter arrangement set up in the laboratory.

No bleaching was observed when the sample was exposed to an incident power as low as 76 μW. It was found that a minimum laser power of ~4 mW was essential for a photochemical change to take place. From this it is clear that a minimum amount of energy, called threshold energy, is necessary for the excitation of the dye molecules to the leuco form. The threshold energy of the sample is found to be ~100 μJ as seen in Fig. 3. To determine the saturation point, different samples of the same pH, thickness, and concentration were exposed to different

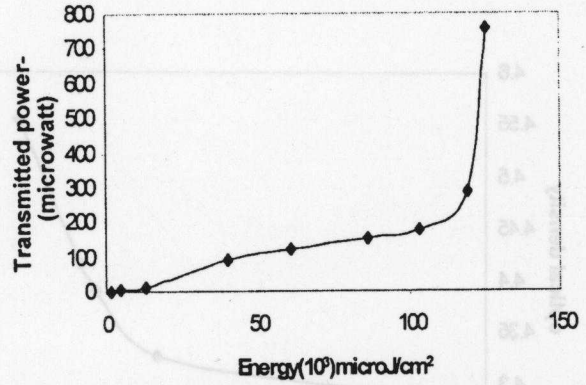

Fig. 3. Threshold energy of this sample [plot of energy (10^3) mJ/cm^2 versus transmitted power (mW)].

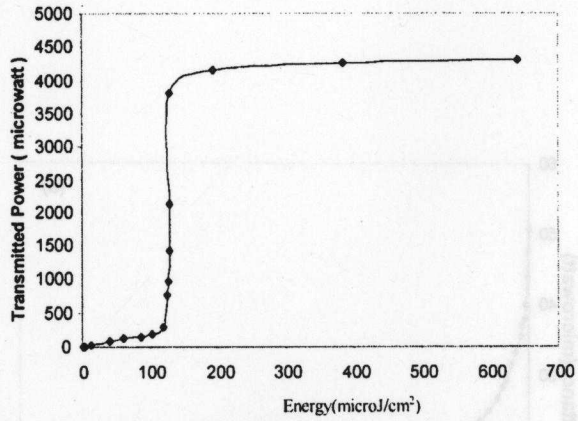

Fig. 4. Saturation energy of the sample [plot of energy (10^3) mJ/cm^2 versus transmitted power (mW)].

laser powers, 20 s for each case. A stage of saturation was observed at an exposure of ~129 μJ. Beyond the threshold region very fast bleaching was observed with a change in exposure, but after the saturation point no change in transmitted power was observed with the increase in exposure values (Fig. 4).

The slight increase in absorption at the irradiated spot on the bleached samples was observed for different dye concentrations ranging from 4.18×10^{-5} g/ml to 3.11×10^{-4} g/ml and is shown in Fig. 5. Hence a detailed study of the recovery of the dye on the CMBPVC films was done. For this the sample was subjected 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). Transmittance at the irradiated spot decreased with time, and the variation in transmittance with time was plotted [Fig. 6(a)]. Exponential behavior is shown, and an exponential fitting

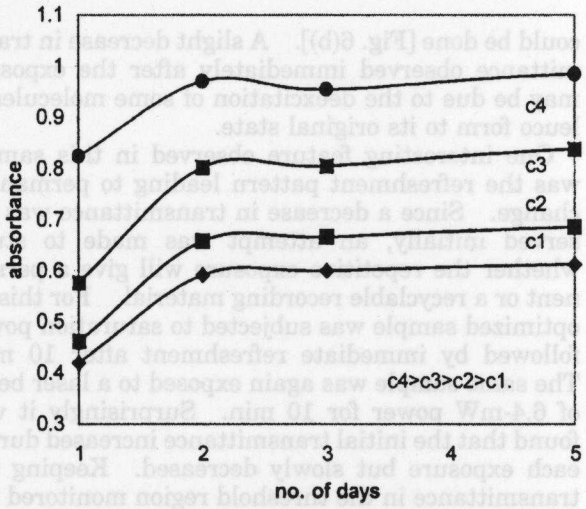

Fig. 5. Change in absorption at the irradiated spot with time for different dye concentrations (c).

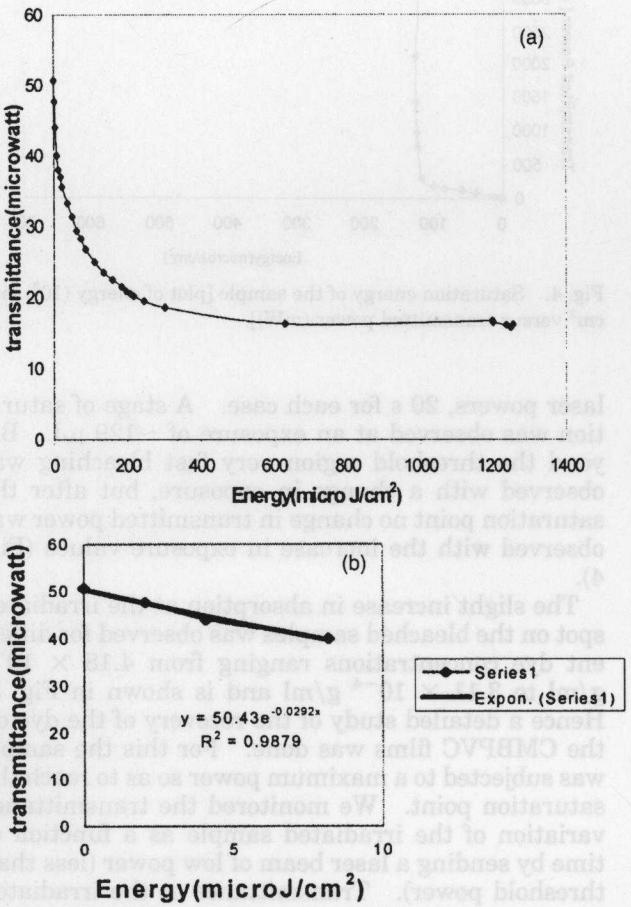

Fig. 6. (a) Recovery of the dye on CMBPVC film after irradiation [plot of energy mJ/cm^2 versus transmitted power (mW)]. (b) Exponential behavior of the recovery of the sample [plot of energy mJ/cm^2 versus transmitted power (mW)].

could be done [Fig. 6(b)]. A slight decrease in transmittance observed immediately after the exposure may be due to the deexcitation of some molecules of leuco form to its original state.

One interesting feature observed in this sample was the refreshment pattern leading to permanent change. Since a decrease in transmittance was observed initially, an attempt was made to study whether the repetitive exposure will give a permanent or a recyclable recording material. For this an optimized sample was subjected to saturation power followed by immediate refreshment after 10 min. The same sample was again exposed to a laser beam of 6.4-mW power for 10 min. Surprisingly it was found that the initial transmittance increased during each exposure but slowly decreased. Keeping the transmittance in the threshold region monitored the recovery. This refreshing process was repeated a number of times. It was observed that the transmittance remains the same after a few exposures. Figure 7 shows the gradual change in transmittance after each exposure, leading to a permanent change. Numbers 1–9 in Fig. 7 indicate the number of times the process is repeated.

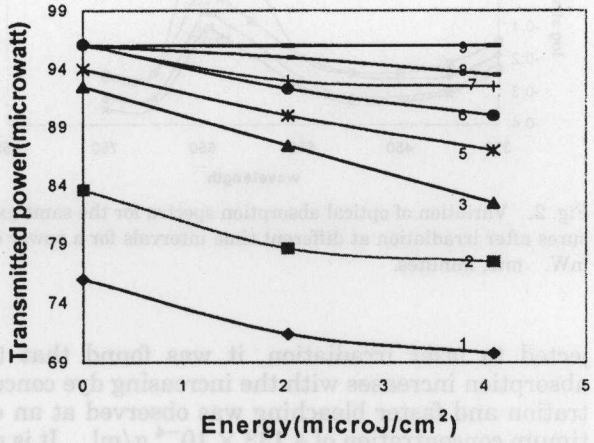

Fig. 7. Recyclability of the material [plot of energy mJ/cm^2 versus transmitted power (mW)].

B. Transmittance Curves

The response of photosensitive materials to exposure to light is normally represented by H&D curves in which the optical density of the material after it has been developed and fixed is plotted against the logarithm of the exposure. A typical H&D curve for CMBPVC film is shown in Fig. 8. Although the H&D curve is used almost universally for photography, it is a convenient way to specify the response of material for holography for which a curve showing the amplitude transmittance of the material as a function of the exposure is preferred and plotted in Fig. 9.

Figure 10 shows transmittance behavior as a function of the recording time for the optimized sample. The action of light on the photosensitive material is twofold: It bleaches dye and promotes polymerization. The result is a medium with spatial changes in refractive index and absorption. If only absorption were present after irradiation of the polymer, the desirable gamma of the exposed film to achieve holo-

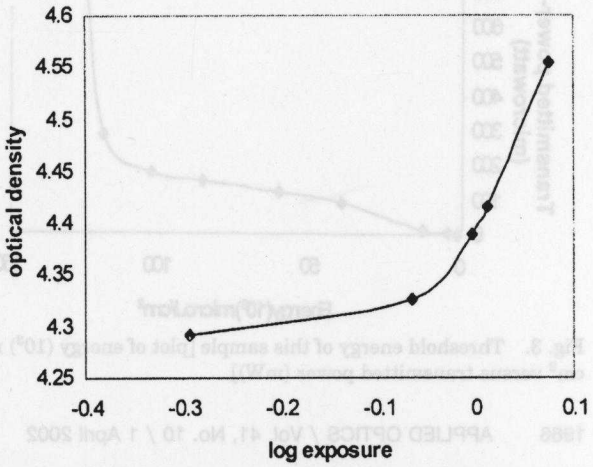

Fig. 8. H&D curve for CMBPVC film. Plot of optical density versus logarithmic exposure.

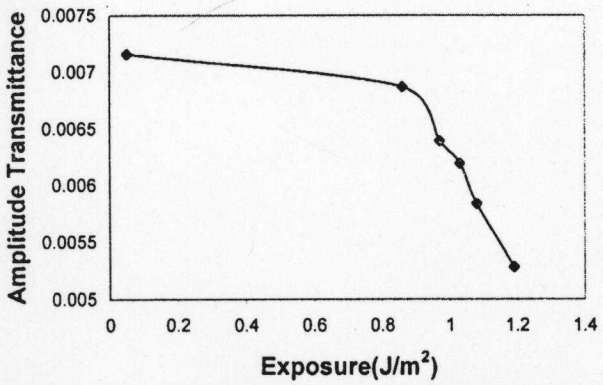

Fig. 9. Variation in the amplitude transmittance of the material as a function of exposure (J/m^2).

graphic linear recording would need to have a value of 2.[3,14] The PVC was of suspension grade with a monomer concentration of less than 0.001 ppm. So the possibility of further polymerization due to the presence of a residual monomer and hence a change in the refractive index on the irradiated part is ruled out. From the experimental data in Fig. 10 we can see that the curve that presents the highest value of the gamma is the one that was induced by the beam with highest power. So, by calculating the optical density as a function of the logarithmic exposure, we obtain Fig. 8. The value of gamma in the linear region is ~2.1, which is very close to the optimum value.

Direct imaging was successfully done on this sample. For this an expanded laser beam passing through a transparency containing some letters is allowed to fall on the CMBPVC for minutes. There were no scattering centers, and the letters were very legible, which shows the quality of the sample.

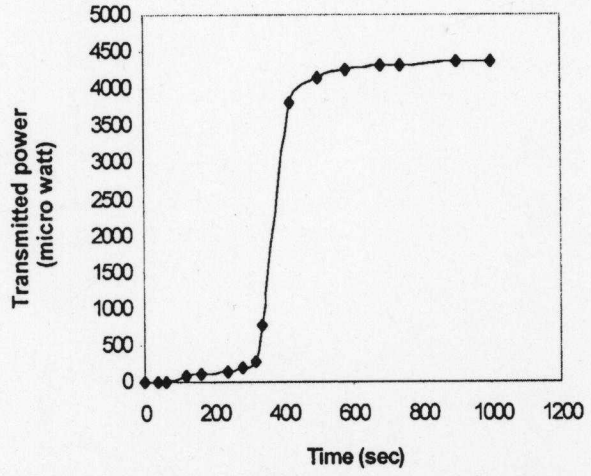

Fig. 10. Variation of transmittance as a function of recording time for an optimized sample [plot of time (s) versus transmitted power (mW)].

6. Conclusions

From all these results we can conclude that the new dye-doped polymer described here presents interesting properties for use as hologram recording material. The polymer is easy to prepare and handle. It has high transmittance after irradiation, excellent shelf and storage life and needs only brief exposures. This recording material also satisfies some stringent criteria, including high photosensitivity, optical clarity, millimeter thickness, and environmental stability. Further work is in progress along these lines. The present study on complex methylene-blue-sensitized polyvinyl chloride films reveals their potential use in many engineering applications.

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