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Reusable recording medium based on MBPVA and vinyl acetate

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A new photopolymerizable recording media is introduced based on poly (vinyl alcohol) and vinyl acetate sensitized with methylene blue. It is observed that this MBPVA/VAc system can be reused a number of times without significant decrease in diffraction efficiency. The PVA-VAc ratio was optimized at 2:1. Diffraction efficiency of 6.3% was obtained without any fixing at a dye concentration of 9.3×10^{-4} mol/l at an exposure of 750 mJ/cm^2. The material is attractive on account of its reusability.

1. Introduction

There is an ever-increasing demand for inexpensive rewritable storage media with high capacity and high data transfer rate. In recent years, many types of photopolymerizable systems have been developed as holographic recording media. These materials have characteristics such as good spectral sensitivity, high resolution, high diffraction efficiency, high signal to noise ratio, temporal stability and processing in real time, which make them suitable for recording holograms. Because of these properties, photopolymer materials are useful in applications such as optical memories, holographic displays, holographic optical elements, optical computing and holographic interferometry [1, 2].

A photopolymerizable recording medium generally consists of a polymer binder with a high refractive index (an inert polymer matrix), photopolymerizable monomer with a low refractive index, a photosensitizer and a charge transfer agent (usually an amine). The hologram formation in a photopolymer media can be explained by the polymerization of the monomer and its diffusion. The basic recording mechanism involves several stages: in the first stage, the incident energy is absorbed by the photoinitiators (dye and amine) that form monomer radicals. In the second stage, monomer depletion in the exposed regions causes a concentration gradient, which then induces monomer diffusion from the unexposed regions and in the final stage,

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termination occurs by radical recombination [3]. During recording, polymerization initiated by the illumination of an interference pattern gives rise to diffusion induced compositional variations, which eventually modulate the medium refractive index, corresponding to volume phase gratings. Formation of volume gratings in polymer provides an attractive recording mechanism for holographic storage, allowing for relatively large permanent refractive index modulation ($\Delta n \sim 10^{-2}$) in an inexpensive media with high recording sensitivity [4, 5].

The most widely used photopolymer recording medium consists of acrylamide and poly(vinyl alcohol). Modifications are done by incorporating crosslinking agents such as methylenebisacrylamide [6] and charge transfer agents such as toluenesulfinic acid, acetyl acetone and diphenyliodonium chloride, different plasticizers and onium salts, etc. Studies have been reported on the use of various dyes such as methylene blue and eosin in a PVA/acrylamide system. In addition to acrylamide, acrylic acid [7], lithium acrylates [8], and mixtures of methacrylates [9] are also used with PVA. Though a variety of photopolymer recording media have been developed with long shelf life and high diffraction efficiency, they are 'write-once-read-many-times' (WORM) materials.

In this work, the properties of Poly (vinyl alcohol) were modified by incorporating a new monomer, the aim being to increase the diffraction efficiency and sensitivity of PVA. The photopolymer formulation used in this study comprises of vinyl acetate in partially polymerized form, to undergo photopolymerization, embedded in a matrix of polyvinyl alcohol sensitized with methylene blue and initiated with triethanolamine. Here the diffraction efficiency of grating recorded in the photopolymer media with allowance for diffusion of vinyl acetate monomer is analysed. From the studies it was observed that this material is a reusable recording media unlike other photopolymer [6–9] WORM materials. The aim of the current work is to explore the possibility of further taking advantage of the reusable property of this material. To the authors knowledge this is the first report of a reusable photopolymer recording media.

2. Experimental procedure

2.1 *Film preparation*

Poly (vinyl alcohol) with molecular weight 1,25,000 (MERCK), vinyl acetate (Lancaster), methylene blue (M.S. quality), triethanol amine (S D Fine) and methanol (Universal) were used for the preparation of the films. Partially polymerized vinyl acetate (VAc) was prepared by refluxing vinyl acetate (20 ml), methanol (20 ml) and benzoyl peroxide (0.1 g) at 70°C in a two-necked flask fitted with an additional funnel, reflux condenser, thermometer and a stirrer. Just after the initiation, the temperature was lowered to 50°C and continuous stirring was given for 30 minutes. The partially polymerized vinyl acetate/methanol solution thus obtained was mixed with 10% PVA solution. The mixture was then sensitized with methylene blue solution and triethanol amine. A thin layer was produced on a glass slide using a gravity settling method. The layer was left to dry for about 48 hours. These films were then exposed to a He–Ne laser. The experimental set up used for measuring diffraction efficiency is the same as that detailed in earlier work [7]. Diffraction efficiency was calculated as the ratio of the intensity of first-order diffracted beam to that of the incident beam. The refractive index before and after exposure was measured using an Atago DR-M2 refractometer and absorption spectra were recorded using a Hitachi 330UV-visible-NIR spectrophotometer.

3. Results and discussion

3.1 *Optimization of PVA/VAc ratio*

The PVA/VAc ratio was varied, keeping the total volume of the solution fixed at 10 ml. On adding VAc/methanol mixture to 10%PVA solution, an oily layer was formed on the surface. A homogeneous solution was obtained by adding methanol to the above solution with constant stirring. Solutions were prepared by varying the (PVA): (VAc/methanol) v/v ratio from 10:0 to 0:10. MBPVA/VAc system was prepared by sensitizing the above solution with methylene blue and by keeping the dye concentration as 4.2×10^{-4} mol/l and triethanol amine concentration as 0.005 g/ml. Transparent films with good optical clarity and lack of scattering centres were obtained. Exposing the sample to a power density of 5 mW/cm^2 for 5 minutes, real time transmission studies were carried out and the relative transmittance versus exposure (figure 1) was plotted [10]. From the graph it is clear that the relative transmittance remains the same above 500 mJ/cm^2. So gratings were recorded

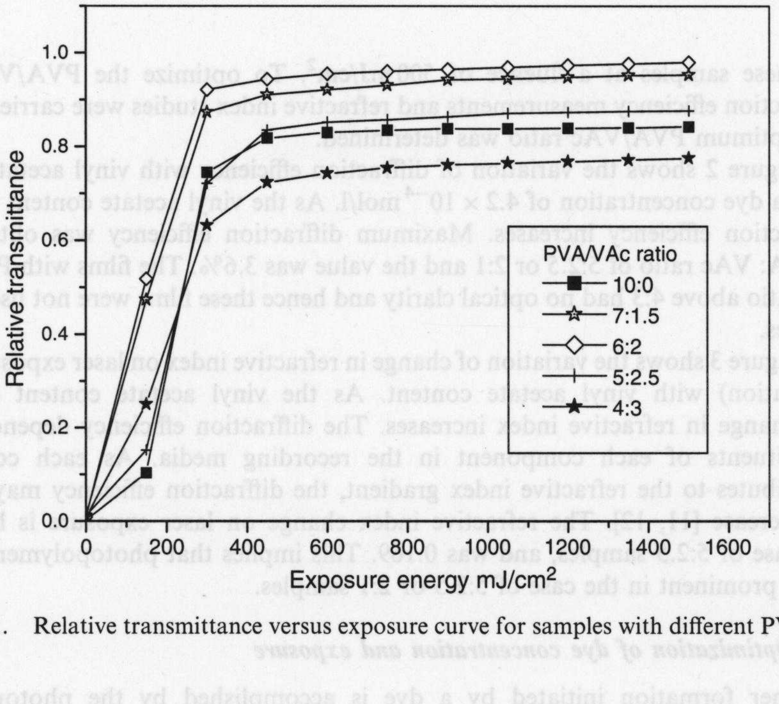

Figure 1. Relative transmittance versus exposure curve for samples with different PVA/VAc ratios.

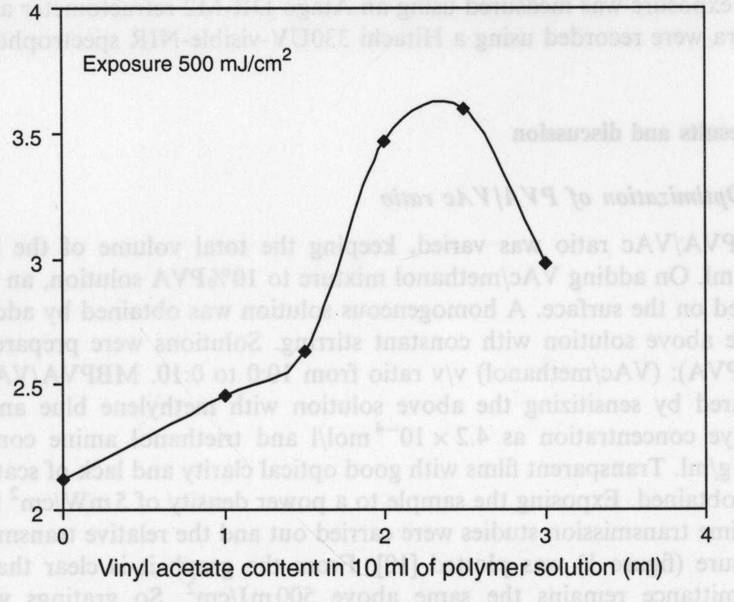

Figure 2. Variation of diffraction efficiency with vinyl acetate content.

on these samples at a fluence of 500 mJ/cm^2. To optimize the PVA/VAc ratio, diffraction efficiency measurements and refractive index studies were carried out and the optimum PVA/VAc ratio was determined.

Figure 2 shows the variation of diffraction efficiency with vinyl acetate content with a dye concentration of 4.2×10^{-4} mol/l. As the vinyl acetate content increases, diffraction efficiency increases. Maximum diffraction efficiency was obtained for a PVA: VAc ratio of 5:2.5 or 2:1 and the value was 3.6%. The films with PVA: VAc v/v ratio above 4:3 had no optical clarity and hence these films were not used for the studies.

Figure 3 shows the variation of change in refractive index on laser exposure (up to saturation) with vinyl acetate content. As the vinyl acetate content increases, the change in refractive index increases. The diffraction efficiency depends on the constituents of each component in the recording media. As each component contributes to the refractive index gradient, the diffraction efficiency may increase or decrease [11, 12]. The refractive index change on laser exposure is highest in the case of 5:2.5 samples, and was 0.169. This implies that photopolymerization is more prominent in the case of 5:2.5 or 2:1 samples.

3.2 *Optimization of dye concentration and exposure*

Polymer formation initiated by a dye is accomplished by the photopolymeric reaction produced by the absorption of light by the photoinitiator in the regions of constructive interference with conversion to its triplet state. A redox reaction then takes place between the excited dye molecule and the amine, generating

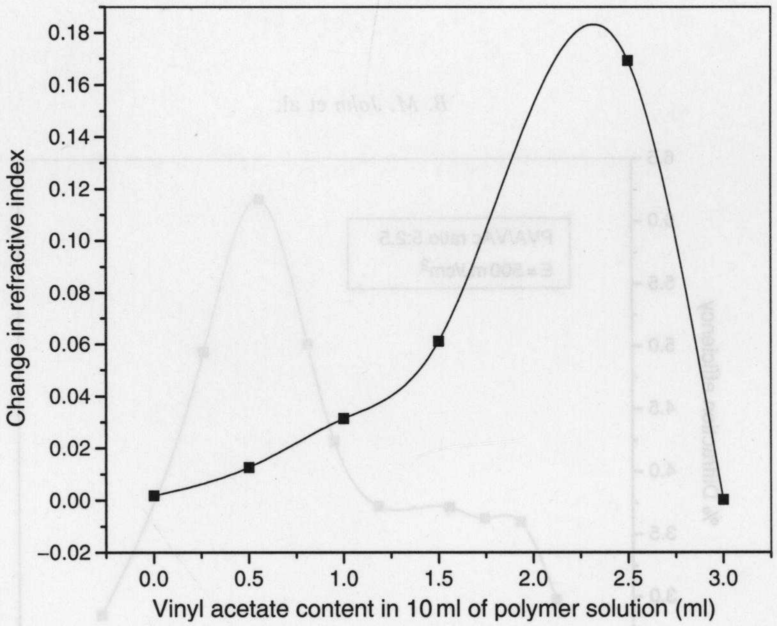

Figure 3. Variation of change in refractive index on laser exposure with vinyl acetate content.

the semi-reduced dye radical [13, 14], which is not involved in the initiation of polymerization reaction. A second electron transfer between the amine and the radical and a protonation process gives rise to a leucoform of the dye. The amine cation radical loses a proton to become the α-amino radical, which subsequently adds to the carbon–carbon double bonds of the monomer, thus initiating the polymerization reaction. When the photopolymer material is exposed to a laser beam, in addition to the refractive index change, a change in absorbance also takes place. So in this case the grating formation is due to the combined effect of both absorbance and refractive index modulation. As the dye molecule initiates the photopolymerization reaction, the dye concentration plays a major role in the diffraction efficiency of the medium.

To find the optimum dye concentration of a MBPVA/VAc system with PVA/VAc ratio 2:1, the MB concentration in the sample was varied from 3.5×10^{-4} mol/l to 12.4×10^{-4} mol/l. To optimize the MB concentration, gratings were recorded on these samples for an exposure of 500 mJ/cm^2 and diffraction efficiency measurements were carried out. As the dye concentration increased the diffraction efficiency increased, reached a maximum and then decreased (figure 4). The optimum dye concentration was found to be 9.3×10^{-4} mol/l and the diffraction efficiency obtained was 6.2%.

To optimize the exposure energy required for highest diffraction efficiency, gratings were recorded on the sample at different fluences. Figure 5 shows the variation of diffraction efficiency with exposure energy. As the exposure energy

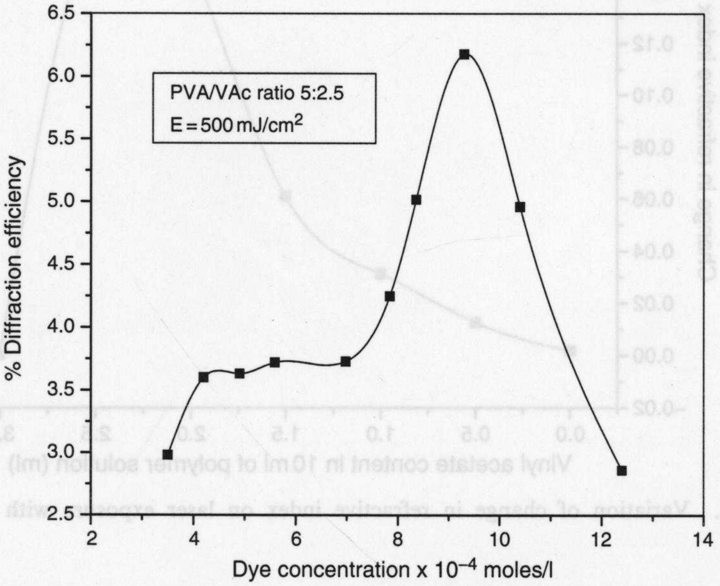

Figure 4. Diffraction efficiency variation with dye concentration.

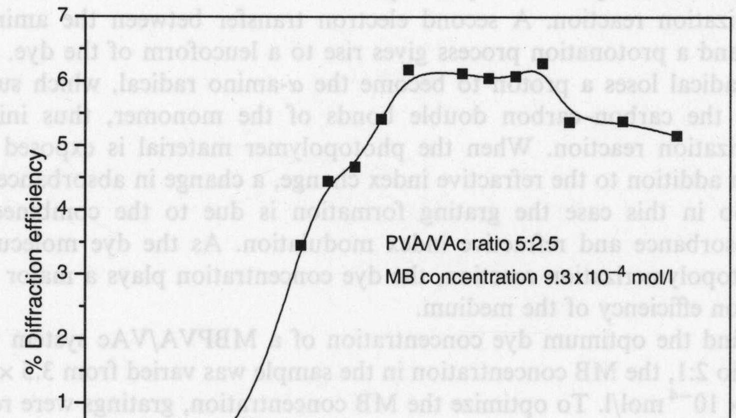

Figure 5. Variation of diffraction efficiency with exposure.

increased, the efficiency increased. This is because as the incident energy increases, more dye molecules are excited and hence the number of radicals, which initiate the polymerization reaction, also increase. As a result the polymerization rate and monomer diffusion rate increases and the efficiency increases. From 500 mJ/cm^2

Figure 6. Photograph of the diffracted pattern obtained. (The colour version of this figure is included in the online version of the journal.)

onwards the diffraction efficiency remained almost the same and the highest value of diffraction efficiency obtained was 6.28% for an exposure of 750 mJ/cm^2. The diffraction efficiency decreased above 750 mJ/cm^2. A photograph of the diffracted pattern obtained is shown in figure 6.

3.3 *Diffraction efficiency on storage*

A sharp decrease in diffraction efficiency was observed in this sample after 30 minutes and then the efficiency decreased very slowly. After 4 hours the diffracted pattern became blurred, and no diffraction pattern was observed after 24 hours. The decrease in diffraction efficiency with time is plotted in figure 7.

This decrease in efficiency is due to the migration of monomer in the unexposed region to the exposed region and the de-excitation of dye molecules from leucoform to the original form. The recovery of dye molecules was monitored by measuring the transmittance of a completely bleached sample, keeping the input power below the threshold power. The transmittance at different times is plotted in figure 8, where it is observed that there is a drastic decrease in transmittance value over the first 30 minutes. The sharp decrease in diffraction efficiency observed within 30 minutes is therefore suspected to be due to the de-excitation of dye molecules.

From reported work, it is clear that methylene blue has different behaviour in different polymer matrices. In the case of MBPVC [10] the change of state occurring for methylene blue was found to be permanent, and no recovery of dye back to the original state was observed on storage. However, in most studies with

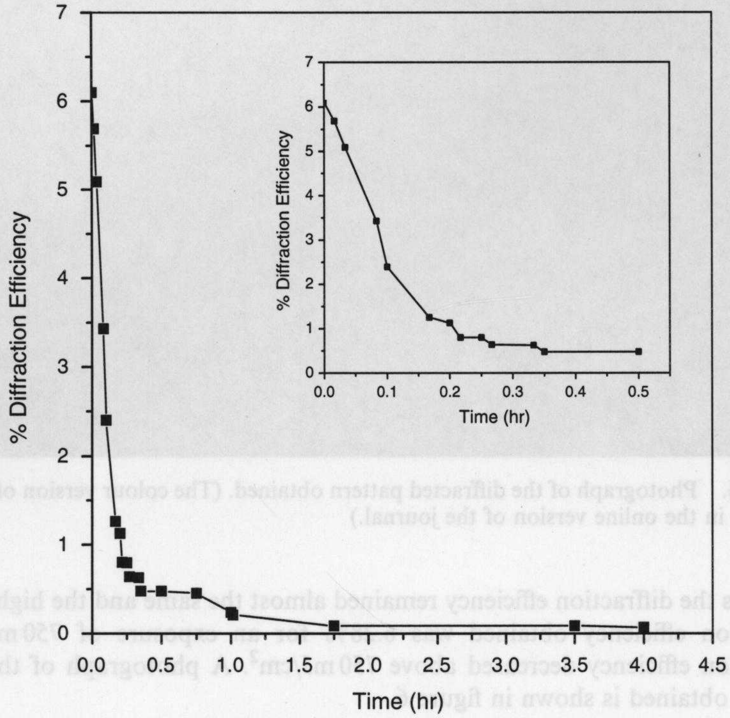

Figure 7. Decrease in diffraction efficiency with time.

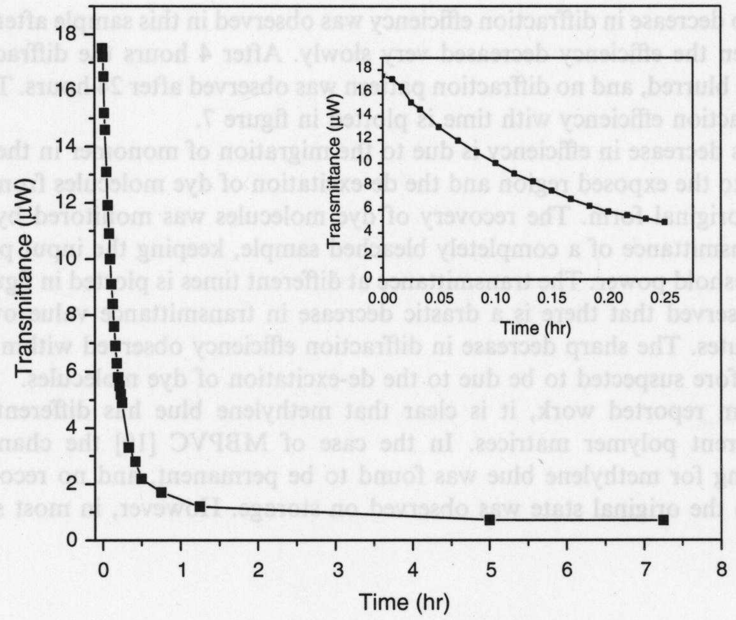

Figure 8. Recovery of the dye: transmittance versus time.

methylene blue in different polymer matrices, it is observed that the exposed area recovers its original colour after some time, and chemical or thermal treatment is necessary to 'fix' the data. In the case of MBPVA/acrylamide [12] and MBPVA/PAA [7] a change in state of methylene blue was observed on laser irradiation, shown by a shift in absorption spectrum after exposure. In MBG also a shift in the absorption spectra occurs and the dye molecules are converted to the thionine state [15]. The wavelength shift in the absorption spectrum of MBPVA is also due to the formation of a thionine state on de-excitation. Figure 9 shows the absorption spectra of the MBPVA/methanol system before and after exposure to a laser beam.

In the case of MBPVA/VAc, from the UV-VIS absorption spectrum of the sample before, after irradiation, and after 24 hours (figure 10), it is clear that this leucoform returns to its original state within 24 hours. No shift in absorption band was observed, which indicates that the leuco methylene blue is de-excited to the original state and not to the thionine state as in the case of conventional systems such as MBPVA/acrylamide, MBPVA/PAA blend and MBG. Since the material showed the same absorption spectra after de-excitation it is felt that this material could be reused.

To check the reusability of the MBPVA/VAc system, gratings were again recorded on the same area of the same film after 24 hours (i.e. after the absorption spectra showed complete recovery) and the diffraction efficiency was measured.

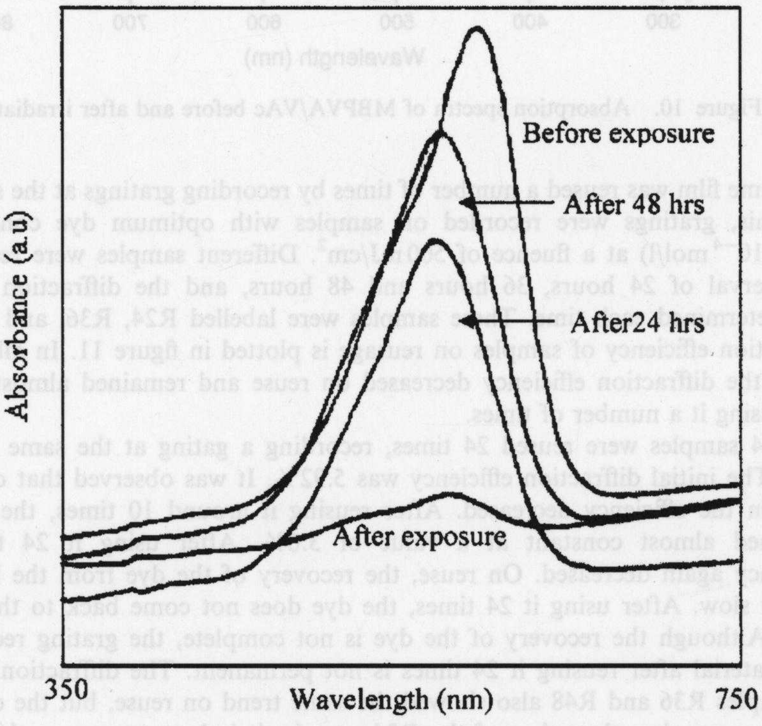

Figure 9. Absorption spectra of MBPVA/methanol before and after irradiation.

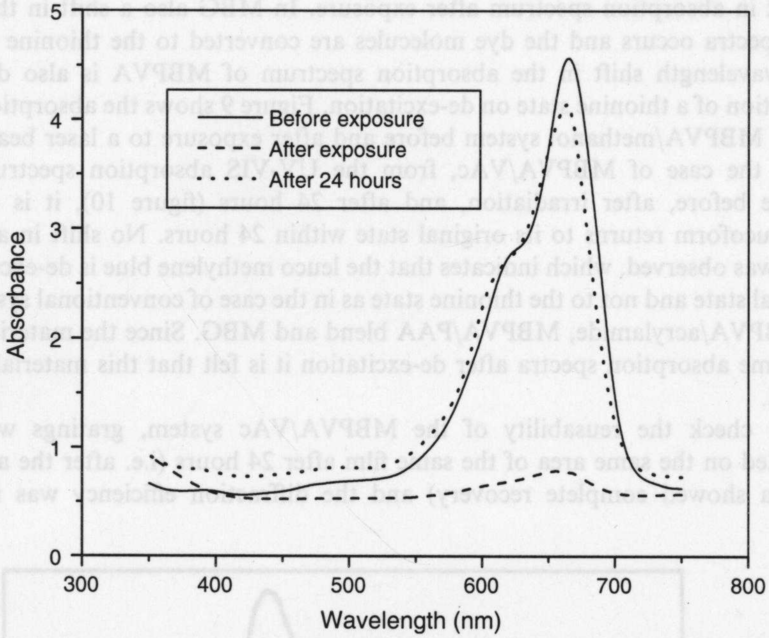

Figure 10. Absorption spectra of MBPVA/VAc before and after irradiation.

The same film was reused a number of times by recording gratings at the same spot. For this, gratings were recorded on samples with optimum dye concentration (9.3×10^{-4} mol/l) at a fluence of 500 mJ/cm^2. Different samples were reused after an interval of 24 hours, 36 hours and 48 hours, and the diffraction efficiency was determined each time. These samples were labelled R24, R36, and R48. The diffraction efficiency of samples on reusage is plotted in figure 11. In all the three cases, the diffraction efficiency decreased on reuse and remained almost constant after using it a number of times.

R24 samples were reused 24 times, recording a gating at the same spot each time. The initial diffraction efficiency was 5.92%. It was observed that on reusing the film the efficiency decreased. After reusing it around 10 times, the efficiency remained almost constant at a value of 3.6%. After using it 24 times, the efficiency again decreased. On reuse, the recovery of the dye from the leucoform is very slow. After using it 24 times, the dye does not come back to the original state. Although the recovery of the dye is not complete, the grating recorded on this material after reusing it 24 times is not permanent. The diffraction efficiency of samples R36 and R48 also showed the same trend on reuse, but the diffraction efficiency was less than that of the R24 sample; it is better to reuse the material after 24 hours.

The reusability of MBPVA/VAc can be explained as follows. When the material is exposed to an interference pattern, monomer in the region of constructive interference becomes polymerized. According to the diffusion model [16], there will be free monomer remaining in the material after the gratings are formed, even for long

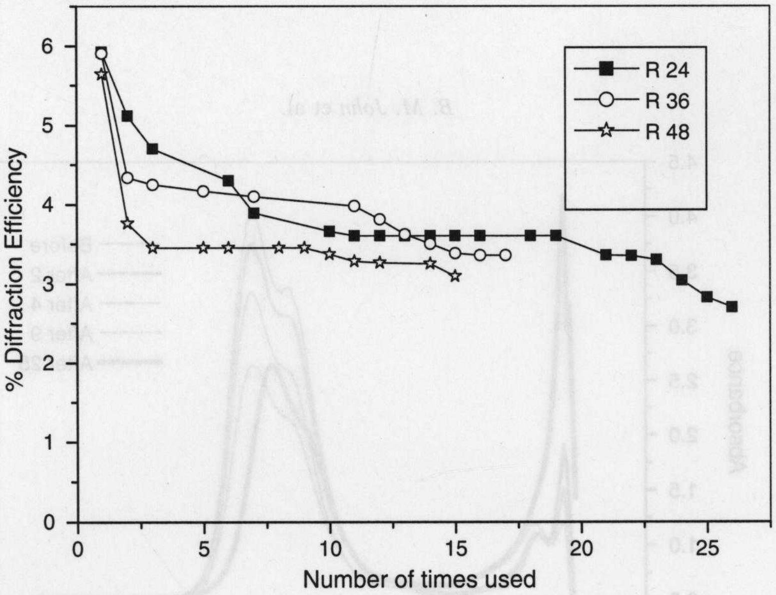

Figure 11. Diffraction efficiency on reusing the sample.

exposure times. So the unreacted monomer diffuses from the unexposed to the exposed region. In MBPVA/VAc the dye molecules de-excite to the original state, and this contributes the same change in absorbance on reuse. So both the unreacted monomer diffusion and the de-excited dye molecules contribute to the reusability of the MBPVA/VAc system. However, on reusing it several times, the used region is smearing out of monomers, and as a result no diffusion takes place and the film behaves like a pure MBPVA system. Thus, the diffraction efficiency decreases on using it 8–10 times. After that the only contribution is from the change in absorbance. The diffraction efficiency also decreases further on reusing it and also reconversion back to the original state is not observed. On reusing the sample, a shift in the absorption spectra was observed. On reusing it around 20 times, there was a strong shift in the absorption spectrum showing conversion to the thionine state (figure 12). We found in our studies that the material could be reused more than 20 times with considerable readability.

Usually in holography, photorefractive materials that are used as rewritable media are very expensive and their synthesis is very difficult. The use of photopolymers for this purpose is very advantageous due to their low cost and ease of fabrication. The development of MBPVA/VAc as a rewritable media will be a major achievement. Attempts are being made to make the material also erasable.

4. Conclusions

A new holographic recording medium has been developed and characterized. The vinyl acetate based holographic recording medium has a diffraction efficiency

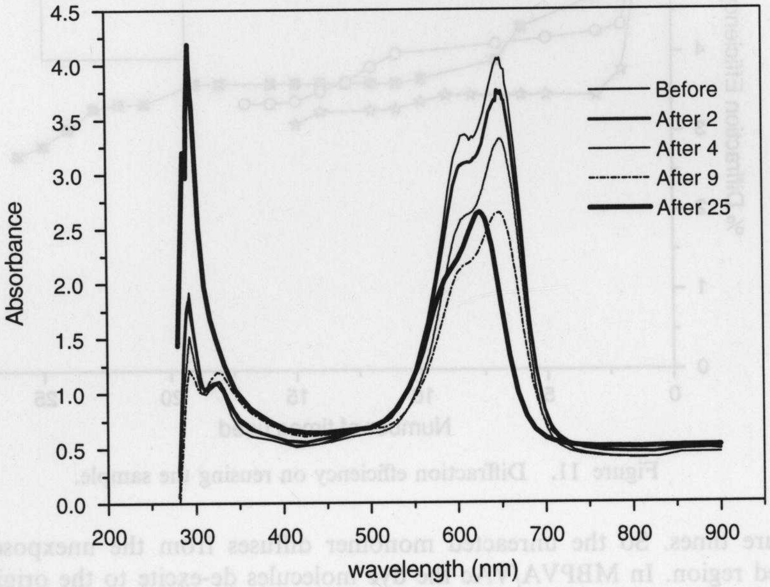

Figure 12. Absorption spectra on reusing the sample.

of 6.3% at 750 mJ/cm^2. The recorded gratings were found to remain in the material for 24 hours with a continuous fall in diffraction efficiency. The major attraction of this material is its reusability. Experimental studies showed the MBPVA/VAc system to be capable of reuse 24 times. Being an inexpensive, nontoxic material with high environmental stability and good optical clarity, this material can contribute much to holographic data storage.

Acknowledgment

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