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STUDIES ON PHOTOSENSITIVE POLYMERS FOR OPTICAL RECORDING

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DECEMBER 2002.

Certificate

This is to certify that this thesis entitled ***"Studies on Photosensitive polymers for Optical Recording"*** is a report of the original work carried out by Smt.Ushamani.M under our supervision and guidance in the Department of Polymer Science and Rubber Technology, Department of Physics and Department of Applied Chemistry, Cochin University of Science and Technology, Cochin. No part of the work reported in this thesis has been presented for any other degree from any other institution.

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Declaration

I hereby declare that the thesis entitled ***"Studies on Photosensitive Polymers for Optical Recording"*** is the original work carried out by me under the supervision of Dr. Rani Joseph, Professor, Department of Polymer Science and Rubber Technology, Dr. C. Sudha Kartha, Department of Physics, Dr. K. Sreekumar, Department of Applied Chemistry, Cochin University of Science and Rubber Technology, Kochi-682022, and no part of this thesis has been presented for any other degree from any other institution.

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………… *to my husband, Sajeev*

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PREFACE

Holography enables storage densities that can far surpass the super paramagnetic and diffraction limits of traditional magnetic and optical recording. In addition, unlike conventional technologies which record data bit by bit, holography allows a million bits of data to be written and read out in single flashes of light, enabling data transfer rates as high as a billions bits per second. With its powerful combination of high storage densities and rapid data transfer rates, holography stands poised to become a compelling choice for next generation storage needs.

The main aim of the present study was to develop new photosensitive polymers for holographic recording, that is easy to use, is self-developing and to characterize it. This allows holograms to be recorded in a one step process and is useful for applications like non-destructive testing and measurements.

Content of the thesis

The thesis consists of six chapters

- ***Chapter 1*** presents a review of the literature in this field and the scope of the present investigation.
- ***Chapter II*** deals with the materials used and the experimental procedures adopted for the study.
- ***Chapter III*** PVC was used for the first time, as a polymer matrix for holographic recording. We were able to improve the sensitivity and colourfastness of methylene blue by complex formation. Less than 5 sec was necessary for bleaching using a 10 mW He-Ne laser when the

dye was complexed using copper acetate. Characterization and optimization was done to determine the parameters like the concentration of the dye, pH, rate of bleaching, threshold energy and saturation energy, storage, diffraction efficiency etc. Mechanical properties of the doped and undoped films were evaluated.

- ***Chapter 1V*** is divided into four parts. Studies on complexed methylene blue sensitized poly (vinyl alcohol) in water constitute part 1. Improvement in the conventional PVA-water system was done by using complexed methylene blue. Holographic characterization and mechanical property evaluation was done on this material. Part II deals with the study of methylene blue sensitized poly (vinyl alcohol) in methanol for optical recording. Part 111 deals with the synthesis and characterization of methylene blue sensitized polymer blend of poly (vinyl alcohol)/poly (acrylic acid) for optical recording. Part IV deals with a comparative study made on all the methylene blue sensitized polymer systems prepared in the laboratory. Direct imaging was successfully done on all the samples.
- ***Chapter V*** is divided into two parts Part I deals with the studies on eosin doped poly (vinyl alcohol) using Nd:YAG laser. Holographic characterization and mechanical properties evaluation was done to predict the fate of the dye in this matrix. Part II deals with the synthesis and characterization of brilliant green sensitized polystyrene.
- ***Chapter 6*** comprises the summary and conclusions derived from these studies.

At the end of each chapter a list of references has been given. A list of abbreviations used in this thesis is also cited.

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Chapter **1**

INTRODUCTION

The history of optical recording can be traced back to1970's with the invention of the first laser videodisk. Until that time, the recording of sound and images was done through the use of magnetic tape. But during 70's technologists had realized the fact that large amounts of data or informations could be stored and easily retrieved, by using a new technology called optical recording. Today, every thing from CDs to CD-ROMs; from DTS (digital theatre system) to holograms, makes use of optical recording technique to record and store informations. Thus optical technology was established as a mainstream media supplier for audio, video and computer storage. Optical storage sales are exploding; billions of CDs are sold annually. The remarkable success of recordable and rewritable optical discs is based on their removability, compatibility standards and low cost mass production, and also on excellent lifetime [1-3].

The success of CD technology indicated the possibility of data storage based on optical phenomena as an alternative to magnetic storage. A key difference is the ease with which the optical media can be removable. Removability is an attractive feature, but makes standardizing efforts more complex compared with magnetic storage. Significant advances in the enabling technologies made it possible to increase the capacity on the digital versatile disc (DVD) format that was introduced in 1995. The basic structure of DVD-ROM is similar to the conventional CD-ROM, storing the data as a 2-D pattern. The DVD stores 4.7 giga bytes (GBs), which is 7 times the capacity of CD. The implementation of blue-violet diode laser in DVD system will lead to a further increase of storage density by a factor 2.5. The blue DVD family is expected to penetrate the storage market with in the next five years [4-9]. Thus the optical data storage technology offers

- Very high storage density
- Low cost
- Direct access
- Very good performance
- Multiple user concurrent access
- Reduced physical requirements
- Rewritable or permanent media
- Very long archive
- Removable media.

In the future, optical data storage is expected to follow two directions to improve the capacity and performance of discs that are available currently. One-way predicts the further increase of the areal storage density that use only the surface of a medium for writing or reading. On the other hand, optical storage is based on laser material interaction so that an entire spectrum of different optical phenomena can be used to realize an optical memory. Developments of non-linear optical materials that exhibit strong laser induced changes of their optical properties enable various novel approaches to become realizable practically. Using non-linear optical effects, advanced technological solutions for optical storage may take advantage of new spatial and spectral dimensions.

Technologies like holographic storage[10-11], two-photon or fluorescent memories etc are at the various stages of development. Opening a new dimension in addition to the 2-D surface of a storage medium, they have the potential to improve tremendously both capacity and data transfer rates of optical storage systems.

The simplest way to use the third dimension of a storage medium is multilayer storage. Using multiple data layers instead of one, the overall storage capacity will grow linearly with the number of layers. Data layers are separated by thin transparent spacers and addressed separately by a focused laser beam. The number of layer per side of the disc is limited strongly by higher optical power requirements and interlayer cross talk. The aberrations that appeared while focusing to several layers at different depth simultaneously combined with other recording techniques make the multiplayer approach more attractive. In the case of fluorescent memories that use transparent materials as storage media, the number of layers can become very large. Such quasi-3D optical memories use the volume of storage medium by recording the data as binary planes stacked in 3-D. The data is stored by discrete bits in the plane,but also through the volume[12-15].

1.1. Holographic data storage

In holographic storage, the information is recorded through volume. One of the unique characteristics of optical volume storage is the very high bit density that can be achieved. A hologram is actually made of a complex system of fine lines, which form diffraction gratings. These diffract and redirect light to form the 3-D image of the original object. These complex gratings are created during recording of a hologram. When the object and illuminating laser beams are arranged so that the light reflected off the object forms an interference pattern. When the film records the pattern a diffraction grating is formed. Consistent characteristics of holographic images are:

- The images are true 3-D images, showing depth and parallax and continually changing in aspect with the viewing angle.
- Any part of the hologram contains the whole image.
- The images are scalable. They can be made with one wavelength and viewed with another, with the possibility of magnification [15-18].

Holography is a two-step method. The first step is the recording of an interference pattern. In this step the object is illuminated with a coherent light wave. This wave is split into two beams. One beam hits the object directly and one beam (reference beam) hits the film. The object reflects some of the light (object wave). The object is recorded in the hologram superimposed with reference beam (see figure 1.1).

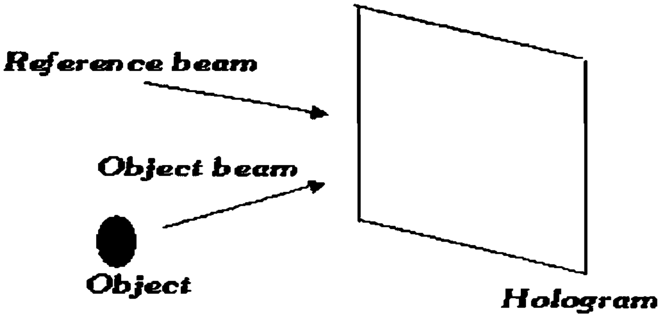

Fig 1.1. Hologram recording

In the second (the reconstruction) step the hologram (suitably processed) is illuminated with the reference wave (figure 1.2). The reference wave has to be the same as in the recording process. This reference wave called reconstructing wave is diffracted by the interference pattern of the hologram so that the object wave (virtual image) is reconstructed. Additionally a second image (real image) is also reconstructed.

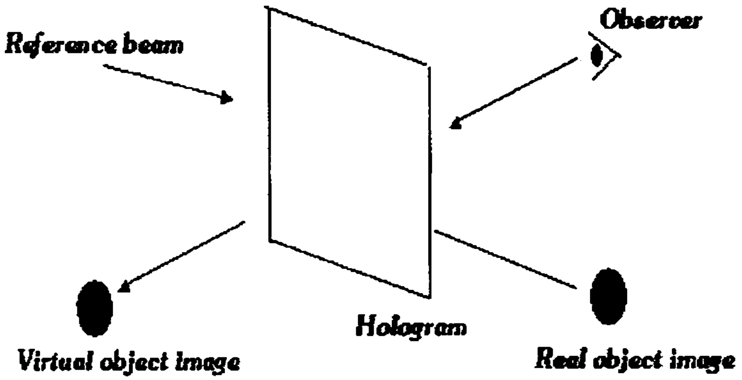

Fig.1. 2. Hologram Reconstruction

Bragg-selectivity allows many holograms to be stored in the same plate by applying appropriate multiplexing methods [26]. Holographic memory [23-25] is a promising technology for data storage because it is a true 3-D system, data can be accessed, an entire page at a time instead of sequentially, and there are very few moving parts so that the limitations of mechanical motion are minimized. Combined with multiplexing, the inherent parallelism of holographic storage can provide a huge increase in both capacity and speed. For more than 30 years, holography has been considered as a storage approach that can change standards and prospects for optical storage media in a revolutionary manner. In the memory hierarchy, holographic memory lies somewhere between RAM and magnetic storage (Table1) in terms of data transfer rates, storage capacity and data accesses times [7,19-22].

Table 1. Comparison on the memory hierarchy of holography, RAM and magnetic storage.

Storage medium	Data Access time	Data transfer rate	Storage capacity
Holographic memory	2.4 μ s	10 GB/s	400 Mbits/cm^2
Main memory (RAM)	10-40 ns	5 MB/s	4 Mbits/cm^2
Magnetic Disk	8.3 ms	5-20 MB/s	100 Mbits/cm^2

Depending on a number of supporting technologies, holographic memories became realizable with advances in photonics technology, particularly with improvement in liquid crystal modulators, charge coupled devices, semiconductor detectors and laser sources. On going research efforts have led to impressive advances.

Another approach to 3-D optical storage offers a compromise by combining bit-oriented storage of CD-DVD and holographic volume recording. Micro lithography expands surface storage into 3-D by storing the data as microscopic volume gratings instead of bits. A thin photopolymer layer is used as a storage medium. The optical system has many components in common with CD-DVD systems. The only additional component is a reflecting unit underneath the disc that is needed for writing. Micro gratings are written holographically with a highly focused laser beam that is reflected back to create a reflection grating. Holographic recording makes it possible to store several gratings in the same position by multiplexing. High densities and data rates can be achieved by combining wavelength multiplexing and multiple layer storage while maintaining the optoelectronic system simple and relatively cheap.

Volume holographic storage and two–photon or fluorescent storage hold promises for high capacity, high-speed systems. In addition, micro holographic disc or fluorescent multiplayer discs that store the data bit wise as 'fluorescent pits', can also satisfy the requirements for downward compatibility and low cost media. A crucial aspect for the reliability of all these systems is the storage material itself. Many types of materials have been investigated in recent years as optical storage media including inorganic photorefractive crystals, organic photopolymers, and biological systems such as protein bacteriorhodopism or DNA polymer.

Progress in the last few years has been very impressive, particularly in the field of photopolymers that offer a wide variety of possible recording mechanisms including both write-once and rewritable media. In particular new photopolymer materials have been introduced for holographic storage. Optimization and further development of photopolymer media will be the key to success of this and other advanced optical storage technologies.

1.2. Photosensitive materials

These are materials that absorb light of specific wavelength and serve as an activator, also materials that react to light changing their own molecular structure and causing polymerization or cross-linking. Photosensitive materials permanently change their refractive index upon exposure to intense light, enabling a wide range of optical device structure to be rapidly patterned via a single photo-processing step. These materials offer rapid and cost efficient manufacturing of photonic devices that possess unique optical and physical property with direct impact on micro system for nuclear safety and security. The enhanced versatility afforded by the photosensitive materials [27-34] also plays a key role in the development of new hologram recording materials.

There is a need for new photosensitive materials that are as efficient and highly non-linear as conventional photorefractive materials, but more versatile and cheaper.

1.3. Requirement of a photosensitive material

Finding the optimal parameters for the application of holography to data storage is a challenge under taken and the quantitative testing and comparison of a variety of different materials continues to make up significant part of the effort in optical data storage research. There are a number of properties a good holographic storage material should have and is listed below:

- Excellent optical quality
- Phase material
- Thick (>500 microns)
- High recording fidelity
- Large refractive index change
- High sensitivity
- Self-processing
- Non- volatile storage
- Fixable
- Long shelf life, inert
- Cheap

A hologram may be recorded on a medium as a variation of absorption or phase or both. The recording materials must respond to incident light pattern causing a change in its optical properties. In the absorption or amplitude modulating materials, the absorption constantly changes as a result of exposure, while the thickness or refractive index change due to the exposure in phase modulating materials. In the phase modulating materials there is no absorption of light and all the incident light is available for image information, while the incident light is significantly absorbed in an amplitude-modulating medium.

High optical quality and low scatter are required to ensure that the signal bearing wave fronts is not adversely distorted and that the noise level from scattered light is manageable. The resolution capacity of the recording material depends on its modulation transfer function. The non-linear effects of the recording material are minimized for obtaining high quality holographic images.

A thick material is required to use the Bragg effect to its fullest. A large refractive index modulation ensures that there is sufficient dynamic range to multiplex the many holograms and the high recording sensitivity allows high speed at reasonable laser power. The larger the number of holograms that are recorded on a common volume of the material, the weaker each hologram becomes, the signal strength scales as the inverse square of the number of holograms. The greater is the material's ability to respond, the more holograms can be recorded and ultimately greater data density can be achieved.

The self-processing and fixable requirements go hand in hand. If the application calls for only a read only material, then the off-line recording of the hologram permits the use of additional process steps- even wet processing. This, in turn, assures that the holograms are fixed and will not be destroyed upon subsequent reading. The preference, however, is for a read-write material where in data can be recorded, retrieved and erased as required- similar in performance to magnetic or magneto-optic recording. The requirements, therefore, would be for a material that not only self develops upon illumination but one that also can be fixed to render it insensitive to subsequent illumination during the recording of additional holograms or the retrieval of data. The fixing process should also be reversible, so that the information can be erased and a new hologram recorded. Between these two extremes is a recording process where the information can be recorded but not erased; referred to as WORM (write–once-read-many), this process has wide spread applicability in areas such as medical imagery, satellite telemetry, banking and various legal documents. To meet these requirements the recording materials must have a fixing process that is irreversible- the distinguishing feature between WORM and erasable materials.

The materials must faithfully record the data beam amplitude so that high quality image can be reconstructed when the data is read out. Moreover the material should retain the stored hologram for a time consistent with data storage applications, and should do so in the presence of light beam used to read the data. For WORM storage, an irreversible material (such as a photopolymer) can be used, which provides stable recording once exposed. If a reversible material is chosen in order to implement erasable/rewritable data storage, the requirement for non-volatility is in conflict with that of high sensitivity unless a non-linear writing scheme, such as two colour grated recording is used. Long shelf life and inertness imply that the material will remain sensitive over an extended period of time and the hologram, once formed will not degrade. Finally the material must be relatively cheap

If holographic storage has had an archilles heels over years, it has been the recording material. Certainly, many successful materials have been developed, but these requirements, particularly for self-processing and thickness, greatly reduces the number of choices. A material is yet to be discovered which will have high sensitivity of silver halides, high diffraction efficiency and index modulation capability of dichromated gelatin holograms and photopolymers, recyclability of photorefractive crystals and useful at all laser wave lengths.

The ideal material needs to be highly sensitive to light but it should be able to hold a pattern of changes for many years with out degrading, despite variations in temperature, humidity or pressure.

Research in both reversible and write once storage materials continue to be an important and active area for optical storage.

The different materials that are studied for recording purpose and their characteristics are shown in tables 2 and 3. The major advantages and drawbacks of these materials are tabulated in table 4. One of the attractive materials that have several advantages and different applications are photopolymers.

Table 2.Characteristics of photosensitive materials used in optical storage

Materials	Spectral Range (nm)	Recording process	Spatial Freq (cy/mm)
Photographic materials	400-700	Reduction of Ag metal	>7000
Dichromated gelatin (DCG)	250-520 and 633	Photo crosslinkng	>3000
Photoresists	UV-500	Photo crosslinking or photo polymerisation	<3000
Photo thermoplastics	Nearly Panchromatic	Formation of electro static latent image with electric field produced deformation of heated plastic	400-1000 band pass
Photochromics	300-450	Generally photo induced new absorption bands	>2000
Ferro electric crystals	488	Electrooptic effect	>1000
Photopolymer	UV-700	Photopolymerisation/ absorption change	200-1500

Table 3 Characteristics of photosensitive materials used in optical storage

Materials	Types of grating	Processing	Read out	Max. D.E. %
Photographic materials	Plane/Volume amplitude	Wet chemical	Density change	5
DCG	Plane, phase, volume phase	Heat	Refractive index change	20-50
Photo resists	Surface relief	Wet chemical	Surface relief	70-90
Photo thermoplastics	Plane phase	Corona charge and heat	Surface relief	6-15
Photochromics	Volume absorption	None	Density change	1-2
Ferro electric crystals	Volume phase	none	Volume phase	60
Photopolymer	Volume phase	none	Ref.index change/ surface releif	10-85

Table 4. Advantages and disadvantages of photosensitive materials

Materials	***Advantages***	***Disadvantages***
Photographic materials	1.They are sensitive to light at various degree 2.It can be coated on both film and glass. 3.Can cover very large format. 4. High resolving power 5.Easily available 6.It has resolution of about 3000 lines/mm 7.They have excellent shelf life	1.It is absorptive 2. It has inherent noise 3.Limited linear response 4.It is irreversible 5. It needs wet processing 6. It creats print out problems on phase holograms 7. The silver crystals on the developed film cause scattering.
Dichromated gelatin (DCG)	1. It has resolution capacity extending beyond 5000 lines/mm 2. Response is uniform over a broad range of spatial frequency from 100 to 5000 lines/mm 3. The refractive index modulation capacity is high	1. $(Cr_2O_7)^{-2}$ has low sensitivity to light 2. It requires long exposure 3. After processing the emulsion must be isolated from moisture. Scaling in glass is used. This makes DCG holograms thick

	4.It has absorption over a wide range of wavelength. 5. It can give reconstruction without development. 6. The thickness of DCG can be increased or decreased by controlling the exposure and processing conditions. 7. It has less scattering 8. It has high SNR. 9. It is transparent. 10. It has high diffraction efficiency	and fragile. 4. It has poor shelf life. 5. It cannot be commercialized.
Photo resists	1.Can produce thin refeif phase holograms 2. Adequate sensitivity at 458 nm of He-Cd laser	1. Sensitivity at 488 nm is poor
Photo thermoplastics	1.No chemical treatments are needed for development 2. It is highly photosensitive to all visible light 3. Has high diffraction efficiency. 4.Stable at room temperature.	1.The maximum resolution attainable with this material is not greater than 1000 cycles/mm. 2.The equipment required for charging and heating the layer is expensive.

	5. It can be reused a number of times 6. The recorded holograms behave nearly ideally as a plane phase hologram. 7.The material is optically inert when not charged, so there is no degradation from exposure to heat and light. 8. This material is ideal for holographic non destructive testing	3. The format of the thermoplastic film or plate is small. 4. The thermal development of the exposed film is critical 5. This film can record only those interference fringes whose spatial frequencies lie within a limited spatial frequency bandwidth.
Photochromics	1.They are real time recyclable materials 2.The hologram can be read out during or immediately after the recording 3. They require no processing or development and can be erased and reused. 4. There is no inherent resolution limit since they are grain free and operate in atomic and molecular scale. 5. Their storage capacity is	1.Photosensitivity of these material is at least three order of magnitude less than that of silver halide photographic emulsion. 2.Low sensitivity 3. Low efficiency 4.Low storage time. 5. The reconstruction beam usually degrades the stored information. 6. Fatigues limit its reusability

	high.	7.The photosensitivity decreases with increasing number of record–erase cycle until finally they become insensitive to light.
Photorefractive crystals	1.High resolution 2.High efficiency 3.High sensitivity 4.Reversibility 5.No fatigue observed after many recording–erasure cycles. 6. High storage capacity. 7.It is possible to record as hologram with 100% diffraction efficiency in a 1 cm thick crystal. 8. It is also possible to record 1000 holograms with usable levels of diffraction efficiency in the reconstructed image	1.Specific problems are there relating the multiple storage of holograms 2.Low holographic sensitivity 3. Sensitivity is less at longer wavelengths.

1.4. Photopolymers

Polymers are finding their way into a whole host of components for optical communication, either of their own or in combination with conventional substrates [35-41].

Polymers are flexible materials. Not only do they exhibit mechanical flexibility, they also enable flexible production process and their physical properties can be manipulated on a molecular level. These properties make polymers ideal for integration into optical components for various applications. Polymers in general show material properties and optical effects – refractive index, dispersion value, optical loss, thermal and mechanical stability, stress-optic coefficient – that can be tailored and optimized by molecular engineering depending on demand. It is this ability to tailor polymers at a molecular level that allows highly compact components to be made. Moreover with polymers, simple blending and copolymerization of suitably synthesized monomers offer a superior index range that offers optical designers greater freedom in building up polymer photonic structures. The advantages of using polymers over other conventional materials are

- Short cycle
- Low cost
- Minimum number of fabrication steps
- High yield
- Higher performance
- Low scattering loss
- Dynamic provisioning
- Multiple functions
- More compact

So perhaps it is time for the optics industry to accept that polymers have advantages over conventional materials, whether used on their own or in combination with other materials. Thus polymers will be an important material used in the next generation data storage. Their use will be driven in general, by customer's desire for components with increased functionality, smaller size and reduced cost.

In recent years, a new class of photosensitive polymers has been introduced to satisfy the demand on adequate materials for holographic storage [41-56]. The recording mechanism is based on laser-induced polymerization. Diffusion of monomers supports differentiation of the bright and dark regions. A light induced grating like modulation of the refractive index occurs during exposure by polymerizing monomers and can be fixed after UV cure. In addition, holographic gratings recorded in photopolymers can be thermally processed to obtain higher diffraction efficiency.

Several photopolymer materials have been characterized for holographic data storage including classical photopolymer systems (Dupont holographic recording films), novel materials designed for storage applications (Aprilis CROP photopolymers), azo benzene side chain liquid crystalline polymers, photorefractive polymers, poly (vinyl alcohol) derivatives etc. Photopolymers such as DuPont or Aprilis are suitable for WORM (write once read only applications. In contrast, a circularly polarized laser beam can erase gratings recorded on azo benzene polymers so that rewritable storage becomes possible.

Several photoresists for excimer laser lithography, based on norbomene polymer, poly (vinyl pyrrolidone), cyclized PVA derivatives, has been synthesized and evaluated. Photoresists for printed circuit boards are designed to be cured by both radical and ionic polymerization. Radical polymerization mechanism used for high sensitivity and ionic polymerization mechanism used for photosensitive polymers is as follows:

- It must be able to produce patterns at the desired resolution consistently.
- It must provide an edge profile consistent with the processing requirements.
- It must survive and protect the underlying film during the etching process.
- It must be readily removable after the etching process.

Thus photopolymers have been extensively investigated as holographic recording media for several decades[57-59] for applications including holographic scanners[60-61], LCD displays[62-63], helmet-mounted displays[64], optical interconnects[65-67], wave guide couplers[68], holographic diffusers [69-71], laser eye protection devices[72], automotive lightening [73] and security holograms [74-75]. Holograms (data) are stored in photopolymer materials as spatial modulation of refractive index created in response to an interference pattern generated by the incident laser beam. Because of photoreaction, the refractive index of the irradiated area of a material differ from that of the dark area. The larger the refractive index difference between these two regions, the greater the data storage capacity of the material. The storage capacity of the material is enhanced if the medium is thick (1.5mm), as this enables recording of many holograms in a given volume of the material and results in improved diffraction efficiency of the phase gratings [76-77]. To achieve the desired storage capacity, that would make holographic data storage commercially viable (~100 bits/ μm^2) require developing a large index contrast in thick photopolymer material.

Most of the current research is concentrated in establishing a three-dimensional volume memory. However, high-density 2D memory is also of great interest for archival purposes. Although ideal materials seem to be lacking, functionalized polymers appear to be prosperous candidates. Such materials are easy to process, have high diffraction efficiency, high resolution, fast recording and fast erasure.

The important photophysical process occurring in the prominent members of the polymer family like poly (methy methacrylate), poly (vinyl alcohol), poly (vinyl carbazol), acrylamide, poly (acrylic acid) etc,used as hologram recording medium is considered. The choice of the photopolymer strongly affects the utility of the final recording. For display holograms properties like brightness, contrast, colour range and colour saturation might dominate. For holographic optical elements, the extended range of properties that may require manipulation and the choice of material to obtain each property in the required quantity makes a working knowledge of what can be done extremely useful.

1.4.1. Poly (vinyl alcohol)(PVA)

Poly (vinyl alcohol)(PVA) came into use as hologram recording material from late 70's onwards. PVA has been dichromated and was used as a real time material. The images were fixed by heating the film. PVA is easily available, mix and coat. A variety of dyes have been used as sensitizer in PVA for various applications which include methyl orange, thionine, dichromate, fluorescien, ferric chloride, Erythrosin B, Eosin Y, Rose Bengal, methylene blue, Xanthene, chrysodine, mordant, yellow3R, hydrohalic acid of some metals etc[78-100].

Light sensitivity and photoimaging characteristics of PVA (PVA)-$HAuCl_4$ and H_2PtCl_6 system were investigated and compared with those of silver halide gelatin system [78]. Real time volume hologram recording and reading of transmission holograms were performed on dichromated poly (vinyl alcohol) (DCPVA) and thionine dye-PVA matrix [79,80]. The film obtained in the former case was not erasable where in the latter case a grating reinforcement was observed during the reading process. DCPVA films with and without electron donors and dyes were employed for real time holographic recording and for the fabrication of holographic optical elements. PVA can also serve as a binder for a monomer and act more like other photopolymers. In its dicromated form it is a photo crosslinker and as such has no migration but the latent images in PVA is many times better than the latent images in dichromated gelatin. The integrity of the recording is very high with very little damage done by over writing multiple times. As a crosslinker it is not a saturable media and can be over exposed, however it requires about 100 mJ/cm^2 to form a strong recording.

Fluorescien dye/PVA, eosin dye/PVA, Cr(VI)/PVA and Fe (111)/PVA systems as promising recording media in the application of holography and non-linear optics has been investigated [81,82]. Detailed study on $FeCl_3$ doped PVA containing tert-Bu-hydroperoxide is done by taking various parameters like angular selectivity, frequency response of the media, refractive index change etc [83] .The photochemical reactions of methylene blue in gelatin and PVA matrices due to He-Ne laser exposure were reported[84]. Laser irradiation results in the formation of new absorption peak, which matches, with that of thionine. Retention of this optical absorption change due to irradiation for several months was observed. This study also confirms that on irradiation some irreversible changes are also occurring in methylene blue in addition to the lueco form. Possibility of permanent recording is also suggested. Studies on photo bleaching of three xanthene dyes like ErythrosinB, EosinY, and Rose Bengal was reported by Manivannan [85]. Evaluated quantum yield suggests that ErythrosinB undergo faster bleaching than the other two in the presence of electron donors. The volume holograms recorded on DCPVA sensitized by Rose Bengal was found to be unfit for hologram imaging of three dimensional objects [85,86]

Methyl orange doped PVA posses all the good characteristics of a known polarization sensitive material [87]. Methylene blue and xanthene dye (XD) sensitised PVA with dark reversibility has been employed for application of correlation peak detection. The effect of various amines on the bleaching efficiency was also studied [88]. A systematic ESR spectroscopic investigation was also performed on this system [89]. Measurement of the spatial resolution for different samples of XD/DCPVA was determined and the results were compared [90]. Dark self-enhancement studies done on DC/PVA films showed enhancement gain of 6 in 3 days. The dark reaction was considered earlier to be only a disadvantage. Now it is shown that the dark reaction after the recording does not distort the diffraction efficiency of the grating but increases it. This effect offers the possibility of using DCPVA in real time measurements for longer periods. The use of self enhancement is of great interest in hologram recording by facilitating shorter exposures than general with these materials and thus vibration free exposures [91-95].

Azo dyes like chrysodine and mordant yellow 3R on PVA were found to be erasable with diffraction efficiency (D.E) of about 27% [96]. Another dry polymeric mixture consisting of a mixture of acrylamide, TEA and methylene blue in PVA can record hologram and is found to have high photosensitivity but low storage stability [97,98]. A study of the influence of the beam ratio and intensity on the optical quality of the transmission hologram images of diffuse object stored in PVA photopolymer are reported [99]. The hologram film based on a fine grain silver bromide emulsion suspended on a PVA matrix crosslinked with Cr (111) has been investigated [100]. The introduction of functional groups into PVA matrix transforms it into a pH responsive polymer with swelling property. A trypsin substrate was also introduced into this hologram to create a designed hologram.

One disadvantage is that it does not adhere well to glass, which makes it a perfect candidate for transfer hologram. It is soluble in water and unstable at high humidity but it may be possible to stabilize chemically by converting at least some of its molecules back to poly (vinyl acetate) or by adding cross-linking agents. Borax is used to crosslink PVA. Hologram causes it to return to its original latent image state and stabilizes it somewhat against moisture.

1.4.2. Poly (vinyl carbazol) (PVK)

Poly (vinyl carbazol)(PVK) is not soluble in water but dissolves in chloroform and can be sensitized by a variety of sensitizers like2,4,5,7-tetranitroflueronone [101], 2,4,6-trinitrofluerenone, triphenylmethanedye [105], 9-(3,4,4-tricyano-1, 3butadiene1yl) carbazol containing trinitrofluorenone [106], azo dyes, spiropyran, ketocowmarin [104] disperse red I etc. PVK can also be sensitized by halogen to become a photocrosslinker. It should be used where maximum resistance to water is needed.

Best results were obtained for polymers doped with 2,5 dimethyl4-para(nitrophenylazoanisole),which showed maximum diffraction efficiency of 34% and 105mm thick samples [107]. Spiropyran doped PVK films have been used as erasable reversible holograms. Photoinduced colour change between thermally stable and metastable state of spiropyran molecules can modulate the absorption and refractive index of the doped film [108].

A new non-silver halide photographic system based on PVK was developed and reported by Yang[102]. Some of the holographic characteristics like T_A/H curve, resolution, diffraction efficiency, sensitivity, etc were investigated on this material. Another PVK matrix suitable for holographic recording was explained by Ikegami,Yoshizumi [103] which include illumination of photosensitive solution with a radical sensitizer, a sensitizer dye, which produce free radicals thus improving the sensitivity of the material.

The disadvantage of this matrix is that it has short life and is hard to process uniformly. It is sensitive to blue green light and requires an exposure of only a few mJ/cm^2. It requires the use of noxions chemicals, some of which are known carcinogens. PVK is also a commonly used photoconductor, which could be used to form relief holograms in thermoplastics and for light intensifiers. If used in holography it has to be sensitized by carbon tetra iodide.

1.4.3. Poly (methyl methacrylate)(PMMA)

The properties of PMMA that makes it unique for its use as a recording material are

- Transparent, hard, rigid.
- Absorb very little visible light but there is 4% reflection at each polymer-air –interface for normal incident light.
- It is a polar material and has a rather high dielectric constant and power factor

- Good water resistance
- Better resistance to hydrolysis.
- Outstanding weather resistance
- Good electrical insulator at low frequencies
- High optical quality
- Good mechanical properties

Preparation of large transparent, gelatin coated PMMA sensitized with nitrocellulose, which can record and display hologram has been described in detail[109]. PMMA doped with certain chemicals like p-benzoquinone [28,110], photoinitiators like benzil methyl ketal and titanium biscyclopentadienyl dichloride [111], which under optical irradiation induce scission or crosslinking of the polymer chain. This results in small refractive index change of the material. Holographic characterization like thickness, effects of aging, effect of concentration of the dye [112] are done on azo dye doped PMMA films. These films under actinic light (λ-488nm) showed a local change in refractive index with high diffraction efficiency. The real time kinetics of photoreversibility of azo dye in PMMA matrix is also reported [113,114]. The limiting factor of diffraction efficiency in azo dye doped films were investigated by Blanche [115]. Holographic and spectroscopic characterizations were done on spiropyran doped PMMA films [116].

Erasable holograms can be recorded on either stable or metastable state of the doped film. Different compositions containing PMMA and its copolymers were found suitable as hologram recording materials [117-120]. Thick dye doped PMMA films have been extensively used for real time holography. The characteristics of thick PMMA films as volume type hologram material were investigated theoretically and experimentally [121]. The multiple storage capacity of a polymer system containing PMMA with 8-12% weight of residual monomer and titanocene chloride has been experimentally investigated [122].

Kinetics of photopolymerisation of PMMA with visible light as sensitizer and polymerization initiator was investigated [123]. This material can record stable hologram with high sensitivity and resolution. The relation between photographic properties and kinetics involved was theoretically analyzed using PMMA matrix and anthracene as sensitizer [124].

Photochromism and its application in holography are explained using spiro-pyran doped PMMA [125] and zinc tetrabenzopropyrene doped MMA [127]. Optical storage properties of the unoriented liquid crystal and amorphous side chain azo benzene PMMA films are examined by polarization holographic measurements. The copolymer with 50-75%dye content exhibited largest surface relief. The stored information was stable up to 70°C except in the case of low dye content [126]. Complex computer generated holograms are now fabricated in PMMA by partial exposure and subsequent partial developments [128]. High optical quality, thick (5-mm) samples without shrinkage were made with phenanthrequinone- doped PMMA. Optically induced birefringence is observed in this material.

1.4.4. Acrylamide based polymers

Acrylamide–based poly(vinyl alcohol) films constitute a low cost organic material, and a great deal of attention has been given to the composition of an acrylamide based photopolymeric system initiated by TEA and methylene blue in recent years [129-132]

The limitations of the hologram sensitivity of a photopolymer mostly results from an imbalance between photocrosslinking, copolymerisation and mass transfer process. The developments of new blends containing acrylate and vinyl ether monomer which undergo hybrid–cure polymerization make it possible to evade some of the typical short comings of multiacrylate formulations. Self-processing materials exhibiting hologram sensitivity up to200 cm^2/J and an energetic sensitivity below $20mJ/cm^2$ are reported [133]. The improvement of reciprocity between exposure and hologram intensity opens up attractive prospects for the above materials for applications requiring holographic exposure for a time less than 5 sec.

A composition containing a mixture of acrylamide-5.2, methylene blue-0.02, acetylacetone-0.1,N,N^{l}methylenebis acrylamide-0.6, hydroquinone-0.0004 and 0.1N sodium hydroxide-3 parts, placed on a glass cell having 50 spacers responded to He-Ne laser (632A^0) at $5000mJ/cm^2$[134]. Optimization of an acrylamide photopolymer for use in real time holography is reported in [135]. The optimum sensitivity is obtained by decreasing inhibition time, which is achieved by using another sensitizing system. A sensitivity of 3 mJ/cm^2 at 633nm was observed. The effect of intensities, thickness, variations in concentration of each component, optimum sensitivity etc were studied in detail by Braya Salvador [136]. Schilling and Colvin incorporated several high index organic monomers into high optical quality acrylate oligomer based formulations. Using reactivity ratio, reaction kinetics and component refractive index as guidelines, and a six-fold increase in refractive index has been achieved. Samples prepared from different acrylate formulation have been used to multiplex this number of holograms. Using these resins a protocol for the evaluation of photopolymers, as hologram media has been developed [137].

A new aqueous photopolymer containing the monomers methylene-bis acrylamide and zinc acrylate with initiators like 4,5-diiodo succinyl fluoroscien (2ISF), methylene blue and co initiator sodium p-toluene sulphonate was found to exhibit high energetic sensitivity upon He-Ne laser irradiation. The same mixture with only one dye showed a maximum diffraction efficiency of 15-20% due to the formation of a photogenerated initiator by the ground state formation of an ion pair complex between methylene blue and 2ISF chromopores [138].

The outstanding property of poly (acrylamide) polymer is that it is water soluble to infinite molecular weight. Moreover it is hard, brittle and slightly soluble in organic compounds because of its polarity.

1.4.5. Poly (acrylic acid) (PAA)

Photosensitive materials comprising of acrylic acid and catalyst are used to record holograms in the presence of laser beam[139]. Organic sulfinic compounds are best examples for this. The hologram characterization and quality reconstruction on dichromated poly (acrylic acid)) (DCPAA) have been studied by varying the parameters like concentration of dichromate, electron donor and molecular weight of the polymer matrix. Hologram can be effectively recorded without any post processing of the photomaterial because the complex pattern is fixed during recording by photocrosslinking [141]. A photoredox process (Cr^{VI}-Cr^{III}) was observed when DCPAA films were irradiated for hologram recording under UV-VIS spectroscopy. The photoreaction is assumed to go through an acid-base reaction between dichromate ion in excited state and PAA. The resulting unstable chromium polyacrylate undergo redox process to give Cr (V) and a monoradical $RCOO^{\cdot}$, which decomposes giving carbon dioxide. The presence of DMF makes the overall reaction faster. The direct involvement of Cr(V) in the quality of the resulting hologram is explained [144].

DCPAA [145] can be used as real time medium for transmission holograms. In this study a simple computer generated hologram grating with a sinusoidal amplitude profile is copied on this recording material by contact copying technique. The theoretical and experimental diffraction efficiency for computer generated hologram copy is evaluated and is reported in [140].

DCPAA films with dimethyl formamide (DMF) can be used to photofabricate surface relief grating [142]. The modulation depth of these gratings and the spatial frequency response to the DCPAA-DMF films were chosen to characterize the self-developing of these photopolymer system. Laser structuralization of gelatin with acrylic acid compounds for producing high-resolution sensitive media for holographic optics are also discussed by Volkov in [143].

1.4.6. Dupont's photopolymers

The characteristics of a holographic photopolymer made by E. Du Pont de Nemours and Company have been described in [146-152]. These are all real time recording materials with the migration of monomer. They work as is or may be enhanced with post exposure baking with the addition of a monomer to swell them to a thicker state. Swelling shifts play back colour and angle in reflection holograms. The sensitivity of some films is down to a few mJ/cm^2 but as with DMP-128 they cannot be over exposed. Some films are panchromatic and good full colour holograms can be made with them. The films are over 8 microns. They play back with smaller bandwidths but look clear in about any light. The normal backing is mylar and is birefringent causing some problem with production and making it difficult to make holographic optical elements (HOE's) with high integrity. The liquid film has been made available so that it can go in glass and then good quality HOE's are possible. Large number of display holograms have been produced in this material, which is sold in sheets and rolls with machines to expose and process it.

The limited modulation prevents this material from being used in some tasks, but it is a big plus for others. When high angular selectivity or a narrow notch filter is needed it is the material of choice, especially if it is possible to get coatings of 50 microns or more. Optical memories have been made with it. The dye never bleaches all the way out of some of their films so it is useless at short wavelengths, as in DCG and PVK.

One of Dupont's materials forms an excellent embossed surface upon exposure and is great for copying binary or possible shaded masks. The shading may copy with poor linearity depending on light intensities, spatial frequencies and migration rates and distance. This is a very widely used material.

1.4.7. Polaroid Photopolymers

The commonly used Polaroid photopolymer in transmission display holograms is DMP-128. It is a flexible film and is useful for making high-density reflectors. Because of the unique open structure it can be filled with liquid crystals to make disappearing holographic optical elements and DFB laser and narrow band filters. It is easier to stabilize than dicromated gelatin and has about the same high modulation in films of 7 to 15 microns. This material is used mostly with red light but can be made panchromatic more easily than DCG and is much more sensitive, requiring only about 25 mJ/cm^2 to expose fully.

This material is saturable, once the polymerization material is used up the effects of exposure are nil. This is a great advantage in production because over exposure has almost no effect, except it may compress the contrast range a little. This is true of all migratory photopolymer systems, including all of Dupont's photopolymer products.

One disadvantage of this material is that it is coated on a substrate that has a higher index than the unexposed film so that all recordings have a mirror in them and the film is not generally available in liquid form. Environmental controls are important at the exposure station, because the film has to be activated by a fairly precise percentage of water or it will produce noisy holograms. The display holograms are the best and brightest among the mass produced products and last a very long time.

Polaroid has announced the introduction of another photopolymer that needs no wet processing and therefore is much more suitable for precision holographic optical elements making.

1.5. Doping

A variety of organic–polymeric based materials have been investigated for optical recording, including dyes (pigments), dye polymer solution and polymer metal layered or particulate structures. In all instances, the light absorption function is provided by the dye or metal and the polymer serves the role of binder and film former. Dye polymer solid solutions / films appear to offer the most attractive approach for producing high sensitivity. To form a true molecular dispersion, the dye and the polymer must be soluble (compatible) at the appropriate loading. For the film thickness and uniformity required for optical recording, spin-coating methods could be used. The coating and drying dynamics that control the film thickness and morphology have been experimentally [153] and theoretically [154] determined. Dye concentration will depend on the absorption and extinction coefficients at the recording wavelength, and for typical dyes, loadings of 10-50-wt % are necessary. Optimising film thickness and recording structures to achieve an optical interference condition aid in maximizing absorption in the film at reduced dye levels.

Dye polymer solutions have been studied in a number of laboratories [155-156] and detailed recording sensitivity analyses have been published. On the basis of published information, a set of design criteria for dye and polymer materials can be defined for optical recording. The primary function of dye molecule is to absorb the incident laser energy. Several groups have shown that the sensitivity of the dye polymer media is largely determined by the optical efficiency of the thin film. Optical efficiency is a measure of the optical energy coupled into the film and is a function of the dye concentration, dye absorption coefficient and the layer thickness.

Dyes should have absorption coefficient as high as possible at the writing wavelength, because this characteristic will maximize the optical density at minimum dye loadings. Maximizing optical density is an advantage because dye polymer solubility control can be a difficult problem. There is also a limit to increase recording film thickness to increase absorptivity. Dye concentration in the polymer is determined by the chemical structure and solubility characteristics of the dye and the binder polymer molecules. For most dye polymer combinations, dye loadings beyond 40 to 50 wt% results in heterogeneous films with undesirable micro crystals. The electronically excited dye molecules can undergo a number of decay process including radiative deactivation by fluorescence or phosphorescence and nonradiative deactivation by internal conversion and intersystem crossing [157].

One of the major difficulties encountered in dye films is the propensity of the amorphous material to undergo crystallization with subsequent deterioration of recording performance.

An ideal material for optical recording especially holography needs to be highly sensitive to light but it must also be able to hold a pattern change for many years without degrading, despite variations in temperature, humidity or pressure.

This thesis reports the attempts made to develop and characterize polymer materials doped with dyes, which satisfy the conditions needed for an ideal material for holographic recording that is easy to use and is self-developing. This allows holograms to be recorded in a one step process.

1.6. The specific objectives of the work can be summarized as follows

1. To develop and characterize different dye doped polymer systems having sensitivity in different optical regions.
2. To develop new polymer matrix for methylene blue, which can be used as a permanent recording material.
3. To prepare and characterize a new polymer blend of PVA/PAA system for methylene blue for its use as an optical recording material.
4. To compare the effect of methylene blue in different polymer matrices.

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Chapter 2

EXPERIMENTAL TECHNIQUES

The materials used and the experimental procedures adopted in the present investigation are given in this chapter.

2.1 Materials Used

2.1.1 Polymers

1 Poly (vinyl chloride) (PVC)

Poly vinyl chloride (molecular weight 2,60,000) used was of suspension grade with K value 70 supplied by Reliance Industries Ltd, Mumbai, India.

2 Poly (vinyl alcohol) (PVA)

a) Hot PVA

Poly (vinyl alcohol) with molecular weight 40,000 used was supplied by Lobachemie Pvt, Ltd; Mumbai, India

b) Cold PVA

Poly (vinyl alcohol) with molecular weight 1,25,000 used in the present study was supplied by Lobachemie Pvt, Ltd; Bombay, India

2.1.2 Dyes used for sensitization

1 Methylene blue

Methylene blue dye of microscopy grade used was supplied by Ranbaxy Laboratary, S.A.S.Nagar, Punjab.

2. Eosin Technical

Eosin used for sensitization in the present study was supplied by Ranbaxy Laboratary, S.A.S.Nagar, Punjab.

3. Brilliant Green

Brilliant green used for sensitization was supplied by E.Merk (India) Ltd; Mumbai.

Solvents and other common chemicals were of reagent grade which were further purified by standard methods.

2.2 Experimental methods

2.2.1 Cleaning of micro slides

The glass substrate must be completely free from dust, grease and other contaminations for good adhesion of the film. A procedure, which gives a very clean substrate, is described below:

The microscopic slides are soaked in warm (55-70^{0}C) soap solution for about 2-3 hours. The slides were ultrasonically cleaned by keeping them in the same warm soap solution. The slides were then washed using distilled water and soaked in freshly prepared chromic acid overnight. They were then taken out and again washed with distilled water followed by pure 2-propanol and dried in a jet of hot air. These dried plates can be used for film preparation at once or they are kept in 2-propanol for future use.

2.2.2 Film preparation

The preparation of dye doped polymer films involved the deposition of the respective dye sensitised polymer solution on a suitable substrate and allowing the solvent to evaporate slowly. There are different techniques for coating the substrate with the polymer solution. Some of them are dip coating[1], doctor blading [1], gel casting [2], gravity settling [3], film transfer [2], spinning [1], spraying [1] etc.

The gravity settling method was adopted in the present work. The method resulted in fairly uniform film though the edge effect due to surface tension could not be avoided. The method was easy to set up and the procedure was simple. The procedure is as described below:

The slightly viscous dye sensitzed polymer solution was used for coating. The coating was done by pouring a fixed volume of this solution over the cleaned micro slides, which were kept on a levelled surface. A known volume can be measured using a pipette or by adjusting the number of drops. The solution equally spreads over the slides. These slides were then covered to protect them from dust, and kept at room temperature (~28^0 C) for about 24 h for drying. The dried films were kept in a desiccator.

2.2.3. Exposure

The minimum requirements needed for the exposure of samples were laser, a beam expander (spatial filter), a vibration isolation table and a film holder. The laser beam was expanded using a spatial filter. Laser power was measured using a power meter (OPHIR PD 2000 model) whose sensitivity ranges from 2µW-200mW

2.2.4. Laser

a) A 10 milli watt He-Ne (Melles Griot) was used as a source for exposing the samples. It is a continuous wave laser with emission at 632.8 nm, which produces a Gaussian intensity distribution.

b) A 0.6 milli watt Melles Griot He-Ne laser was used for measuring the diffraction efficiency of the films.

c) A diode pumbed Nd:YAG laser (CASIX-LED-1500) laser with its second harmonic was used to irradiate polymer films having sensitivity in the green region. The wavelength of emission was 532 nm. By adjusting the diode current, the power of the laser could be varied from 0-30 mW.

2.2.5. Vibration Isolation table

Holographic work requires a table, that picks up vibrations and the relative path length changes across the table surface should not exceed a quarter of a wavelength, during exposure. For the optimum results a good mechanical stability during the exposure was needed. An isolation table that has a good mechanical stability against vibrations was used. The isolation table used for this study is as shown in figure (2.1). This table has top dimensions 1.5 x 1 x .005 m^3. The table has 6 legs made of 0.5 m diameter mild steel and metal bushes, 0.002m thick, are attached to the bottom of the legs. Rubberised coir sheets, which provide dynamic rigidity, and plywood, which is a good vibration absorber, were used to ensure static rigidity.

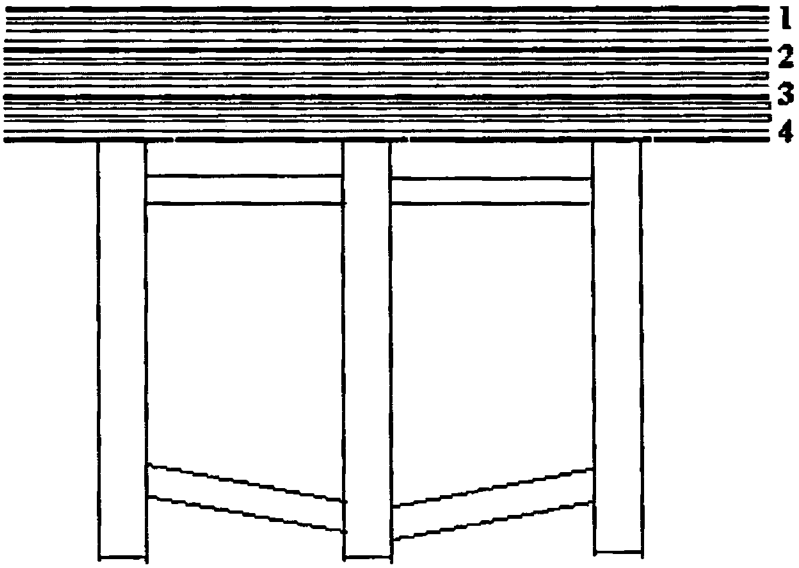

Fig 2.1 Isolation table used in the present study

The thickness and number of plywood and rubberised coir sheets were adjusted to obtain an optimum performance. The height of the entire set up is 0.9 m, which conveniently served the purpose of a standard experimental table. The three primary criteria for comparing table performance are the structural frequencies, damping and compliance values. Damping rate measured using Tektronix storage Oscilloscope was found to be 68.54Db/S. It is explicit that a table whose compliance is small is a good optical table. Very low compliance value was obtained for this table by optimising damping, stiffness and mass. This table exhibit good mechanical stability [4].

2.2.6. Film holder

The plate holder should be simple, stable and be able to hold the film firmly in the position every time. We used a stable film holder for which the position can be finely adjusted using screws. Movements in the horizontal plane are arrested by these screws and help in an exact repositioning of the developed plate.

2.2.7. Spatial Filter

Usually the diameter of a laser beam is about 1mm. So for illuminating the entire sample, we had to expand the laser beam uniformly. If we use a lens or mirror, aberration will occur. In order to avoid this, we used optical frequency filtering. The laser beam was brought to focus by a lens and a pinhole was placed at the focal point (figure 2.2). Simple microscopic objective can serve both to focus and expand the beam. The pinhole passes only lower spatial frequencies.

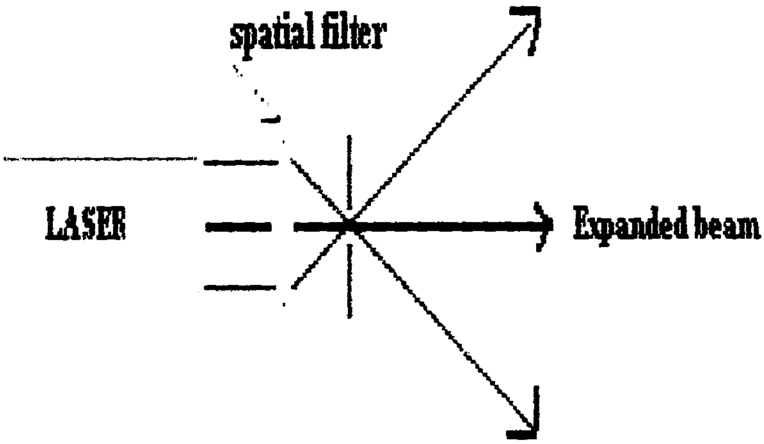

Fig.2.2. ***Laser beam expanded using a spatial filter arrangement.***

The spatial filter arrangement we used consists of short focal length converging lens, which is movable along the three axis and a pin hole movable along X and Y axis. Commercially available microscope objective of power 10x as converging lens was used. Pinholes whose aperture ranges from about 70 to 80 microns were made in the lab. The pinholes were prepared by drilling fine holes on thin aluminium foil by using optical fibre. The photograph of expanded beam with and without spatial filtering is shown in figure2.3 & 2.4.

2.2.8. Measurements of transmittance

In order to study the effect of exposure on transmittance, the intensity of transmitted beam through the sample must be continuously measured. For this a power meter OPHIR PD 2000 model was used. The experimental set up is shown in figure 2.5. As the film gets bleached, the transmittance increases.

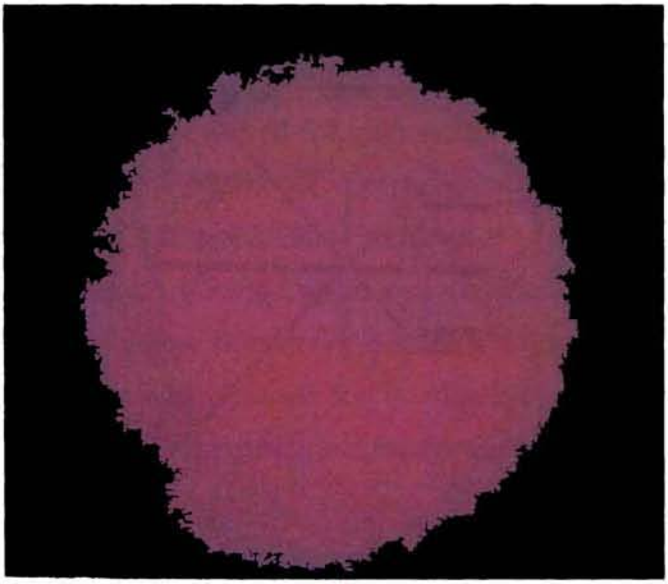

Fig.2.3. Expanded laser beam without spatial filtering

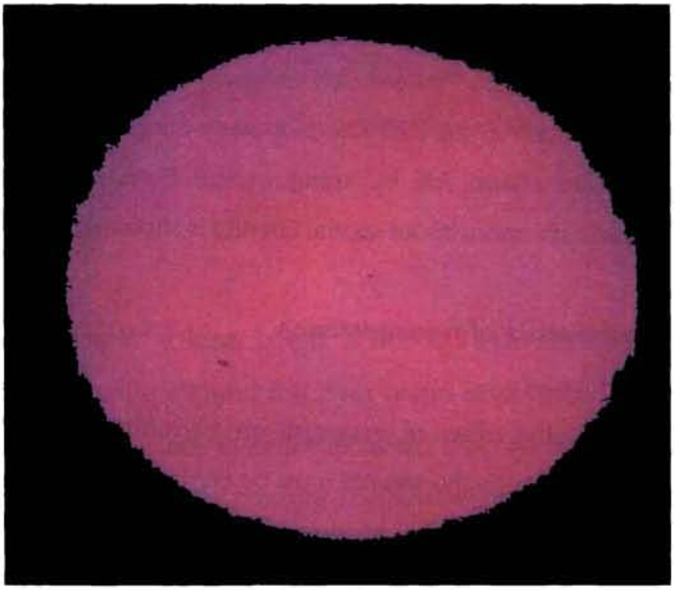

Fig.2.4. Expanded laser beam with spatial filtering

The transmitted power was noted at regular interval (T) using the power meter. The reading with a pure undoped sample was taken as (To). Then (T/T^0) gives a standard measure of transmittance.

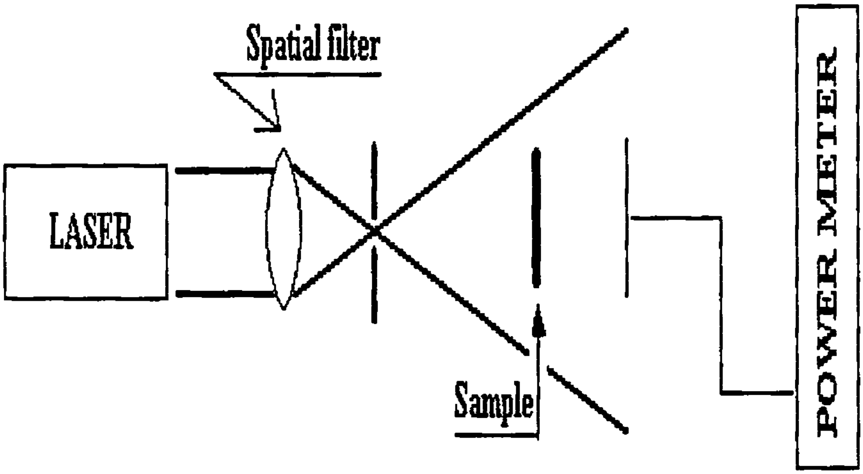

Fig.2.5. Experimental set up for exposure and transmittance study

2.2.9. Optical absorption measurements

A Hitachi Model No:330 UV-Vis-NIR spectrophotometer was used to take the optical absorption spectra of the dye sensitised sample before and after exposure. The absorption spectra were taken with reference of the undoped sample on a clean glass plate. The position of the sample was adjusted so that the light passes through the same region before and after exposure during scanning.

2.2.10. Thickness measurements

The thickness of the samples coated was controlled by adjusting the number of drops of the solution used for coating over single glass slides. The thickness of the sample with different number of drops was measured using a screw guage.

2.2.11. pH measurements

pH of the dye doped polymer solution was determined using Systronics Digital pH meter. It was standardised using buffer tablets of pH 4,7 and 9. For this the buffer tablet was completely dissolved in 100 ml distilled water to get the desired pH value. Using this solution the instrument was calibrated.

2.2.12. Direct Imaging

To demonstrate the feasibility of data storage in the dye doped polymer films, a pattern of very small letters, alphabets, words, pictures etc were recorded on the optimised films by direct imaging. For this transparency containing desired letters, words, pictures were prepared from the negatives and were placed in the expanded laser beam. The laser beam passing through these films were allowed to fall on the dye doped polymer films, so that we will get an exact copy of these letters, words, pictures etc on these films. The average power of the laser irradiation used was 4 mW. We could record very small letters on all these dye-doped films, which explains the resolution capacity of the dye doped polymer matrices.

2.2.13. Recording of grating

For recording gratings on the sample a simple method was used. 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 this angle we can adjust the fringe width. By adjusting the distance between the film and the mirror the fringe width can be controlled. The set up for recording the interference pattern is shown in figure 2.6.

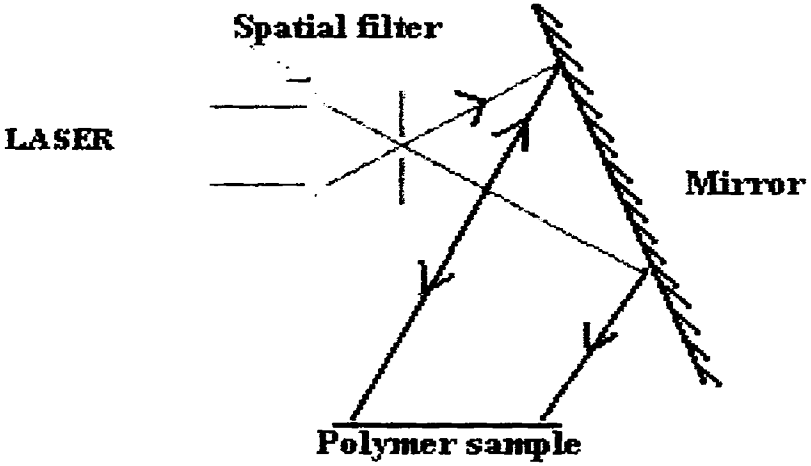

Fig. 2.6. Experimental set up used for recording interference pattern.

2.2.14. Measurement of diffraction efficiency

For diffraction efficiency measurements a He-Ne laser of very low power (~0.6mW) was used. Again this power was decreased by using attenuators.

The recorded film was then placed in front of that arrangement. A screen was placed about 1 m away from the film. A diffraction pattern of the grating was obtained as shown in figure 2.7. The pattern consists of central bright spot and a pair of spots on either side. Experiment was repeated by changing angle of incidence, exposure energy etc

Experimental set up for calculating diffraction efficiency is as shown in figure 2.8. The power of the first order beam as well as that of the directly transmitted beam were measured by a OPHIR PD 200 model power meter. If P_D is the power of the first order diffracted beam and P_T the power of transmitted beam then diffraction efficiency is calculated using the following equation

Diffraction efficiency = P_D / P_T

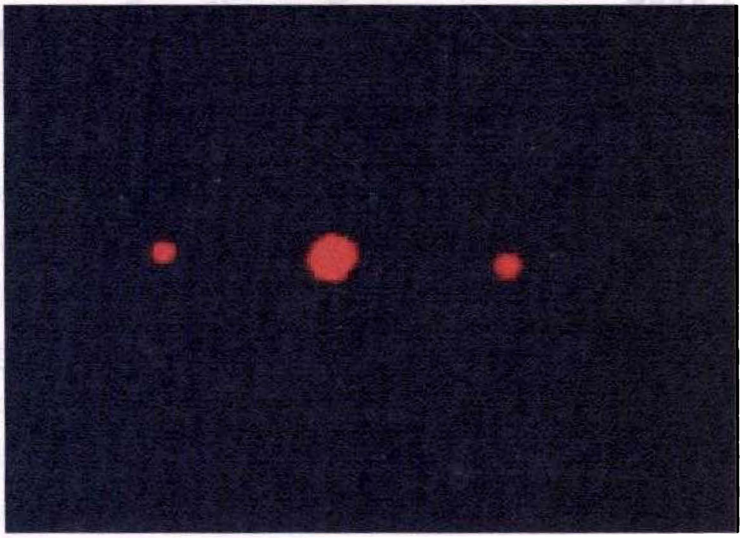

Fig.2.7. A first order diffraction pattern of the grating obtained on methylene blue sensitized polymer films

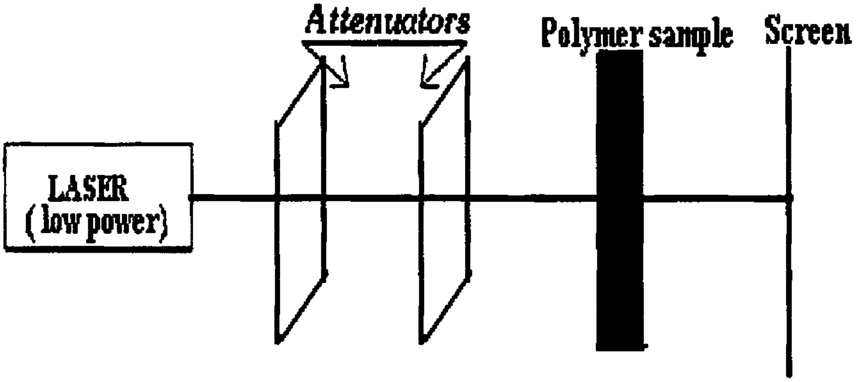

Fig. 2.8. Experimental set up for measuring the diffraction efficiency

2.3.Physical test methods

For parameters described below, at least three specimens per sample were tested for each property and the mean values reported.

2.3.1. Tensile strength and elongation at break

These parameters were determined according to ASTM D 412 (1980) test method, using dumb bell shaped test pieces. The samples were casted into sheets. The thicknesses of the narrow portion of specimens were measured using a screw gauge. The specimens were tested on a Zwick universal testing machine (UTM) model 1445 at 28±2°C and at a crosshead speed of 500 mm per minute. The tensile strength and elongation at break were recorded on a strip chart recorder. The machine had a sensitivity of 0.5 % of full-scale load.

Ultimate tensile strength = Force (N)/cross sectional Area (mm^2)

The elongation at break (EB %) of the sample was measured in terms of its initial length 'L_0' and final length 'L_1' as,

$$EB = (L_1 - L_0) \times 100/L_0$$

2.3.2. Molecular weight determination

Molecular weight of the polymers (polystyrene and poly(acrylic acid)) synthesized in the laboratory was determined by Ubbelohde suspended level viscometer (USLV). This viscometer is a simple glass capillary device. In USLV the design is like that the measurement is unaffected by the volume of the solution taken. The main advantage of USLV is that only a single solution of a known concentration is required to be made to start with. A known volume of the solution was taken in the viscometer and the flow time was measured. Subsequent concentration can be achieved by adding known volumes of pure solvent and mixing inside the viscometer itself. This yields sufficient data for computing flow times at different concentrations. In the experiment, solution of concentration of the polymer sample whose molecular weight is to be determined was prepared. The solvent flow time (t^o) and the solution flow time (t) for different concentrations were measured using USLV. For each concentration, the corresponding reduced viscosity and the inherent viscosity was calculated. The double extrapolation plots of reduced viscosity against concentration and inherent viscosity against concentration (both extrapolated to zero concentration) were prepared. The common ordinate intercept of these graphs gives the intrinsic viscosity. From intrinsic viscosity the molecular weight can be calculated with the help of famous Mark-Houwink equation

$$[\eta] = KM^a$$

Where $[\eta]$ is the intrinsic viscosity; M- the molecular weight and K and a are constants for a particular polymer/solvent/temperature system.

To get reproducible results the following are the points to be noted:

- The viscometer should be mounted perfectly vertical all the time.
- All the measurements should be done at constant temperature.
- The flow time of a particular solution or solvent must be sufficiently long so that the difference in flow time between two successive concentration is at least of the order of 3 to 5 second.
- All solutions should be free from suspended impurities.

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Chapter 3

STUDIES ON METHYLENE BLUE SENSITIZED POLY (VINYL CHLORIDE) AS A NEW OPTICAL RECORDING MEDIUM

3.1. INTRODUCTION

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

Of the many materials studied for holographic information recording, polymers are found to be much versatile due to their ease of preparation and a variety of possible applications. They are also cheap and easily available.

Methylene blue is a commonly used sensitizing dye, which has absorption near the red part of the spectrum. Moreover its wavelength coincides with the most inexpensive He-Ne laser. Studies done on methylene blue sensitized polymer matrices like poly (vinyl alcohol), poly (methyl methacrylate), gelatin, poly (acrylamide) [1-9] etc shows that the information stored on these films were not stable for a long time and chemical treatment was necessary for fixing the data. Our aim was to introduce a new polymer matrix doped with methylene blue for permanent recording without any chemical treatment or fixing process.

We have chosen poly (vinyl chloride) (PVC) as the polymer matrix due to its unique properties like excellent optical properties, colourability, dimensional and environmental stability, ease of fabrication, economical, flexible or rigid, non-toxic, stability against U.V light, transparency in the visible spectral region, insensitive to humidity etc. It can also be fabricated to any desired thickness. Moreover PVC is a promising material, which is prepared by the polymerization of vinyl chloride monomer. Vinyl chloride monomer is a colourless gas at ambient temperatures under atmospheric pressure and has a slightly sweet odour. It is flammable and form explosive mixture with air [11]. It is soluble in most of the common organic liquids like hydrocarbons, oil, alcohol, and other chlorinated hydrocarbons and is only sparingly soluble in water. The polymerization of vinyl chloride can result in the formation of molecules with a number of isomeric forms

$$n(\,CH_2{=}CHCl\,) \xrightarrow{\qquad} -(\!-CH_2\text{-}CHCl-\!)\text{-}_n$$

The structure $CH_2{=}CHCl$ can add to the polymer chain in two ways: Head to tail or head to head. Polymerization characterization studies show that it grows mainly by head to tail addition.

The optical properties of PVC are superior and comparable to other polymers like PVA, PMMA etc. The refractive index of PVC at room temperature is 1.54. The exact value is sensitive to thermal history, and it has been suggested that the changes are related to the degree of crystallinity [11]. When cast from solvents, PVC is highly transparent and colourless. Inevitably, processed material has a slightly inferior appearance due to the presence of additives.

Colour is widely used as an empirical assessment of degree of degradation in the material.

Thermal stability of PVC is less compared to other polymers, above 100^{0}C or exposing to UV light or gamma rays, causes the polymer to degrade. The polymer emit HCl gas that catalyses the elimination of HCl form the next monomer unit, resulting in dehydrochlorination to give polyene sequence with a mean length of 6-14 conjugated double bond and a maximum length of 30 units[12,13]. But there are additives like dioctyl tin dilaurate which make PVC stable with out affecting the transparency.

PVC has good resistance to a wide range of chemicals like inorganic solutions, detergents, aliphatic hydrocarbons including oil and waxes. Water absorption by PVC is very low and many properties are insensitive to humidity. Strong oxidizing agents attack PVC. PVC is soluble in solvents like tetra hydro furan, cyclohexanone etc. The solubility parameter of PVC has been measured as being approximately 9.5-9.7 [14].

The low monomer content in the PVC films is utilized for the light induced absorption changes on this material. The wave length of the triggering light may be shifted from U.V into the visible spectral region by doping the material with a suitable dye such as methylene blue, eosin, neutral red, brilliant green etc. Dyes are commonly employed to extend the spectral response of the polymers [15] into the visible range either by dispersion throughout the polymer or by the formation of a surface layer. Suitable dyes include rose Bengal, methyl violet, methylene blue etc. The sensitization process probably involves electron transfer between excited state of the dye and an active charge transfer species.

Methylene blue doped on various polymer matrices like poly (vinyl alcohol) (PVA), poly (methyl methacrylate) (PMMA), gelatin etc are found to be very unstable and need dark room storage. Moreover most of them are sensitive to humidity and needs some fixing process. In this context we are introducing a new polymer matrix for methylene blue, which was found to be very stable. Here we report for the first time[10], the use of dye doped PVC for hologram recording. 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. In the absence of complexing agent, high exposure energy was necessary for the photochemical change to take place on laser irradiation. Copper acetate was used as the complexing agent since it has absorption in the same region as that of the dye and the wavelength of the laser used.

3.2.FILM PREPARATION

A wide variety of PVC resins are commercially available. A choice must be made to meet the combinations of processing methods and end uses. The most important property influencing the processing and mechanical properties is the molecular weight, characterized by the K-value; PVC resins are available with K-value ranging from 50 to 90. The PVC used in the present study was of suspension grade with K value 70(supplied by Reliance Industries Mumbai) and methylene blue was of microscopic quality. The preparation of complexed methylene blue sensitized poly (vinyl 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).

All the samples were prepared under normal laboratory conditions as follows:

1. Poly (vinyl chloride) was dissolved in cyclohexanone at room temperature to yield a solution having 13.5 weight % of PVC.
2. Crystals of methylene blue and copper acetate were dissolved in the ratio 2:1 in glacial acetic acid to obtain the desired dye concentration.
3. A homogeneous solution of the dye and PVC was obtained by mixing a fixed volume complexed methylene blue with the PVC solution.

A thin film was prepared by pouring this solution over a 75 x 25 x 1.4 mm glass plate kept on a leveled surface and the film thickness was maintained to be 0.06 mm. After the deposition a cover should be placed above the plate to prevent any dust particles from falling on the film until it is dry approximately 12 hours later. This drying period is a function of the amount of solution poured on the glass plate. However, after the drying period it was found that the edges were thicker compared to the center portions. The thickness of the plate in its central region was 0.06 mm and on the periphery 0.1mm. Therefore the central part was used for all experiments.

3.3 LASER EXPOSURE

To study the effect of laser exposure on these films a Coherent Melles Griot He-Ne laser with emission at 632.8 nm was used. The laser beam was expanded and filtered using a spatial filter arrangement set up in the laboratory. The samples were placed in the expanded beam. The experimental set up used for the real time transmission study is explained in 2.2.8. The transmittance value of the undoped sample was taken as T^0 and that obtained for the film was taken as T and their ratio T/T^0 was found out for standardization. The effect of He-Ne laser irradiation on the absorption spectra of the methylene blue sensitized films was studied using a Hitachi 30 UV-VIS-NIR spectrophotometer. Samples of CMBPVC with different concentrations were made with similar thickness of the film. The concentration was varied from 1.3×10^{-4} to 19.38×10^{-4} and the thickness of the film was 0.06mm. The samples were bleached using a He-Ne laser. Very fast bleaching was observed when a 10 mW laser source was applied on CMBPVC films. Hence further studies were done using a spatial filter arrangement set up in the lab. To study the effect of bleaching, samples of nearly same thickness, pH and concentration was exposed to a laser power of 6.4mW. Transmittance of the plate as a function of exposure (power density x time) was measured. The transmitted intensity was measured at regular intervals using a power meter (OPHIR Model PD-200). In all the cases the beam size was kept constant. 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 to 8. Very high and very low pH affects the clarity and transparency of the film. 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 on the next day itself, which remained almost same for months.

The experimental set up used for diffraction efficiency measurements are shown in figure 2.6. 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 two phases 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 the normal from the mirror was taken as θ.

3.4. RESULTS AND DISCUSSION

3.4.1.Optical characterization

a) Optical absorption studies

When the sample was exposed to laser light, it got bleached i.e. the sample became colorless. The absorption spectra of the CMBPVC film before and after exposure to laser irradiation are shown in the figure 3.1. The spectra of CMBPVC showed a sharp peak at 649nm. Peak shift was not observed on the absorption spectra after irradiation. The peak position at 649 nm is attributed

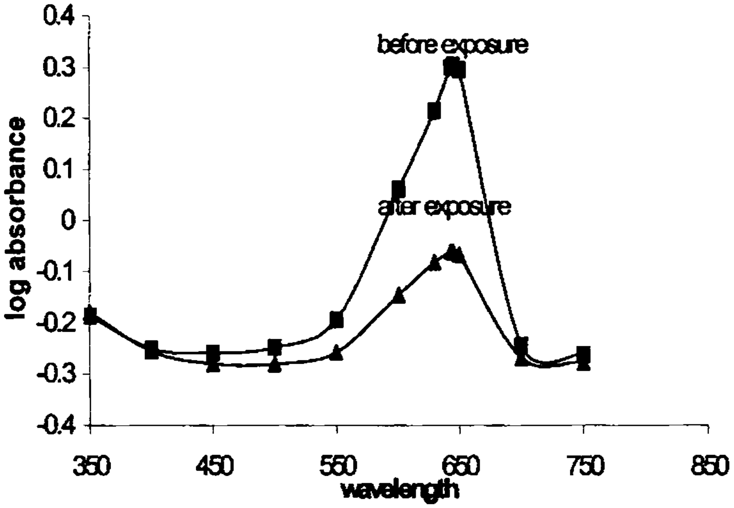


Fig. 3.1 The optical absorption spectra of complexed methylene blue doped PVC films before and after exposure.

due to the presence of complexing agent (copper acetate), which has a strong absorption at the red part of the spectrum. After exposure the magnitude of this peak is decreased. This is because; the absorption peak of the chromophore was bleached during irradiation. Figure 3.2 shows the variation of absorption for different exposure time (5min, 10 min, 15 min) for a fixed power of 4 mW. When the time of exposure increases more and more molecules are converted to the leuco form that is clear from the decrease in the peak intensity in figure 3.2

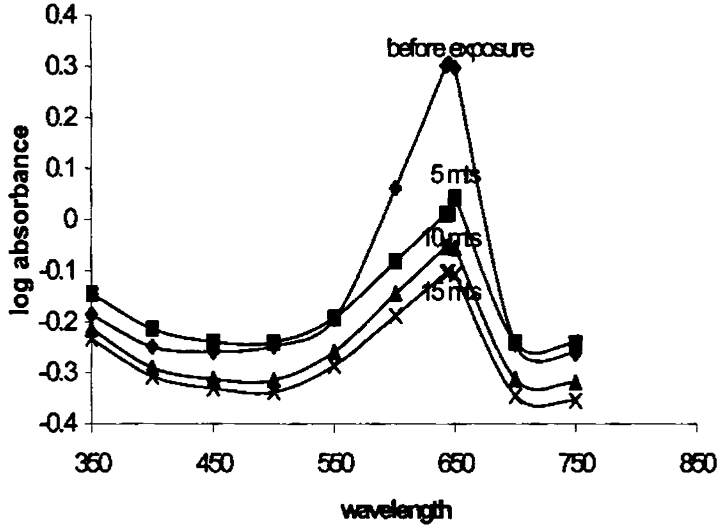


Fig. 3.2 Variation of optical absorption spectra of CMBPVC for different exposure times.

a) *Optimization of the sensitizer concentration*

Initially, an increase in the concentration of complexed methylene blue produces high sensitivities. There is a linear increase in the rate of bleaching with dye concentration up to some concentration (figure 3.3), after which we speculate that the clustering of dye molecules occurs. This clustering can cause the formation of dimers, trimers and more complex structures [16]. The bleaching rates of these aggregated molecules differ from the bleaching rate of a single molecule. From our measurements, it was found that it occurs above the doping level of 12.8 x 10^{-4} mol/l, ie the sensitivity of the material decreases with further increase in concentration of methylene blue. 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 high concentration of the dye, it will precipitate over the surface of the film.

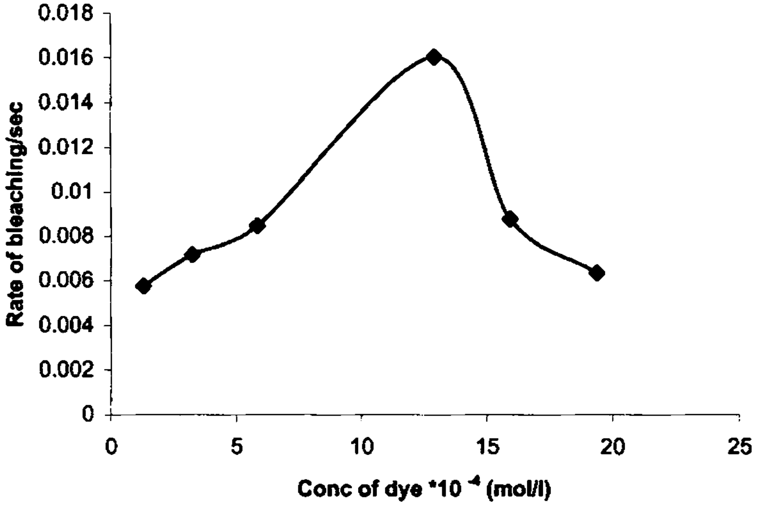


Fig. 3.3. The bleaching rate of bleaching as function of concentration of the dye.

c) Rate of bleaching

To study the rate of bleaching of methylene blue in CMBPVC films, the optimized sample was exposed under the laser power of 5 mW for about 5 minutes. The variation in transmittance in terms of T/T^0 with time was calculated and plotted, from which the rate of bleaching was found out by finding the slopes at different time. The rate of bleaching with time for CMBPVC films is plotted in figure3.4.

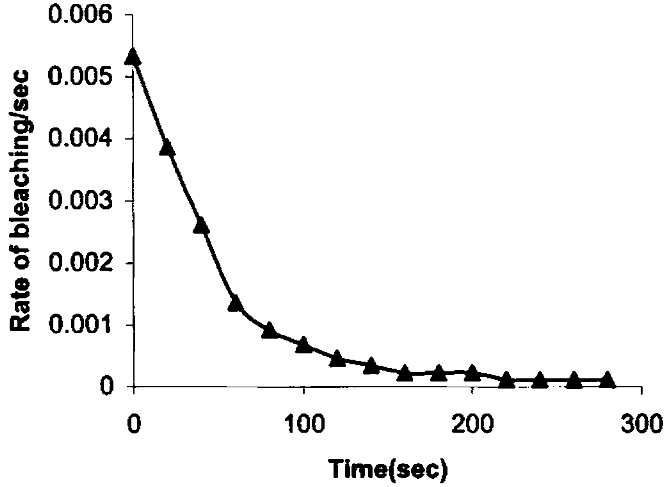


Fig. 3.4 Variation of rate of bleaching with time for the optimized CMBPVC films

From the graph it is clear that the rate of bleaching decreases with time, reaches a minimum value and then remains constant. This is because initially large number of dye molecules are present in the polymer matrix. On laser exposure these molecules are converted to the leuco form and hence the number of dye molecules in the exposed area decreases with progress of time of exposure, and reaches a constant value after some time. Unlike MB in various polymer matrices, very fast bleaching was observed in the case of CMBPVC films. Less than 5 seconds was necessary for bleaching when 10mW was applied directly without expanding the beam.

b) *Optimization of exposure energy*

Like concentration of the dye and pH, intensity is also an important parameter to be optimized, because bleaching of the dye depends on the intensity of light used. No bleaching was observed when the sample was exposed to an incident power as low as 76μ watt. It was found that as the laser exposure energy is increased initially bleaching occurs slightly. But when the exposure energy is increased to about 120 mJ there occurs a fast and linear bleaching as evident from the graph. 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 was found to be approximately 100mJ/cm^2 as from the figure 3.5.

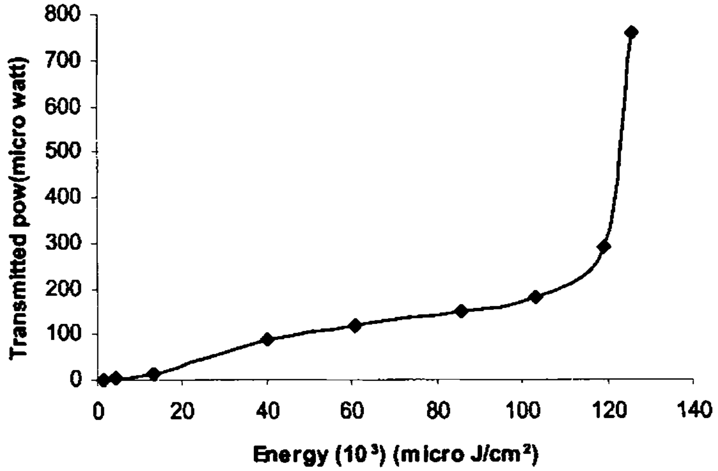


Fig. 3.5. Variation of transmitted power with exposure energy

To determine the saturation point, different samples at same pH, thickness and concentration were exposed to different laser powers, each case for 20 sec. A stage of saturation was observed at an exposure of approximately 129mJ/cm^2. After the threshold region very fast bleaching was observed with the change in exposure, but after saturation point, no change in the transmitted power was observed with the increase in the exposure values (figure 3.6)

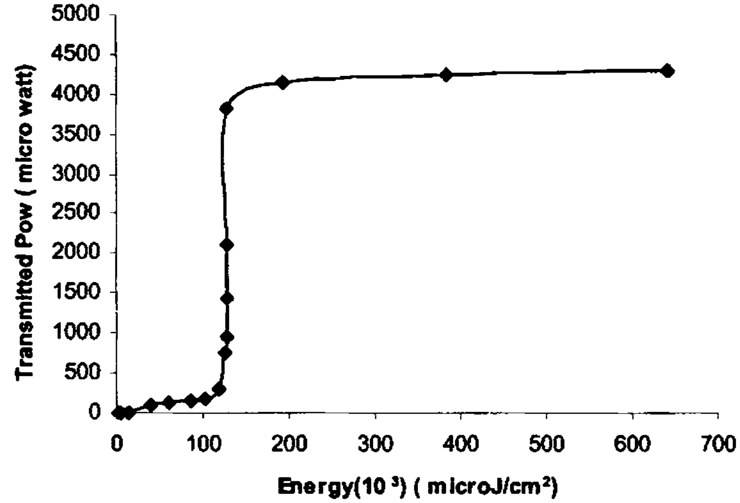


Fig.3.6. Variation of transmitted power with exposure energy till saturation is attained

c) *Effect of storage*

Even though many researchers have suggested the possibility of optical recording in methylene blue sensitized films, they have found that the information stored is not stable for a long time. The conversion of the dye into its leuco form and again back to its original form was the mechanism attributed to this observation.

The present study carried out has shown that the absorption change that has occurred on CMBPVC films due to irradiation with He-Ne laser remains almost unchanged for a considerably long period of time. Figure 3.7 shows the variation of absorption for different concentrations with days of storage. C1, C2, C3, C4 in the graph indicate the different concentrations of the dye employed (the values ranges from 1 x 10^{-4} to 3.1 x 10^{-4} gm/ml). A slight increase in absorption was observed on the next day itself. Hence a detailed study on the recovery of the dye on CMBPVC films was done.

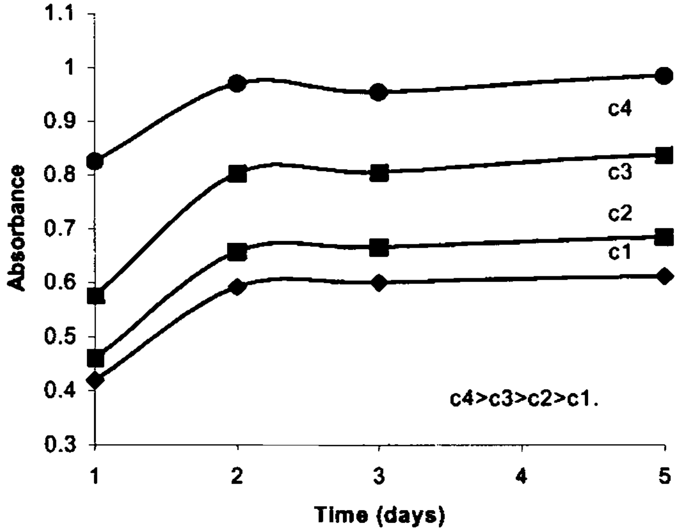


Fig.3.7.Variation of absorption for different concentration with days of storage

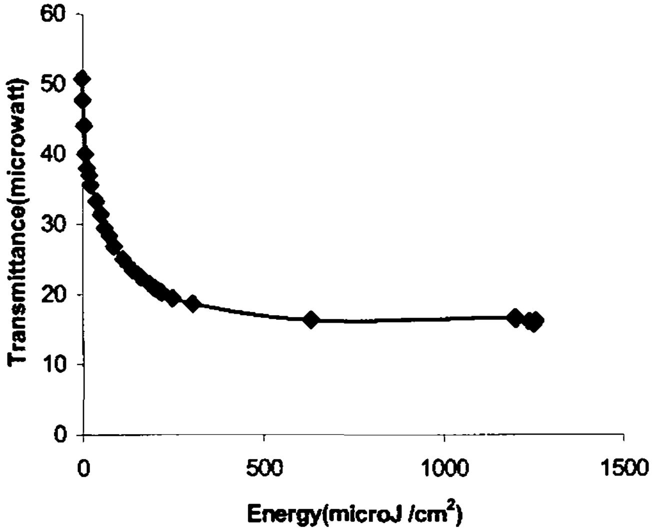


Fig. 3.8A. Recovery of the dye on CMBPVC film after irradiation

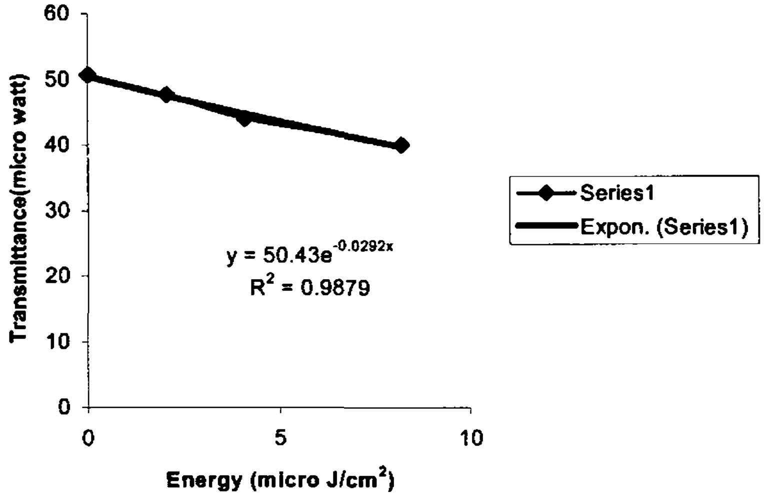


Fig. 3.8B Exponential behaviour of the recovery of the sample.

For this the sample was subjected to a maximum power so as to reach the saturation point. The transmittance variation of the irradiated sample was monitored as a function of time by sending a laser beam of low power (less than the threshold power). Transmittance at the irradiated spot decreased with time and the variation of transmittance with time was plotted (fig 3.8A). The graph showed an exponential behavior and an exponential fitting could be done (Fig 3.8B). The 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 of the interesting features observed in this sample was the refreshment pattern leading to a 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 a saturation power followed by immediate refreshment after 10 min. The same sample was again exposed to laser beam power of 6.4mW for 10 minutes. The transmittance was noted for 10 min and again exposed to laser beam. Surprisingly it was found that the initial transmittance increased during each exposure. We monitored the transmittance by keeping the sample in the threshold region. This refreshing process was repeated a number of times. It was observed that the transmittance remains the same after a few exposures. Figure 3.9 shows the gradual change in transmittance after each exposure, leading to a permanent change. Numbers 1-9 in figure 3.7 indicates the number of times the process was repeated.

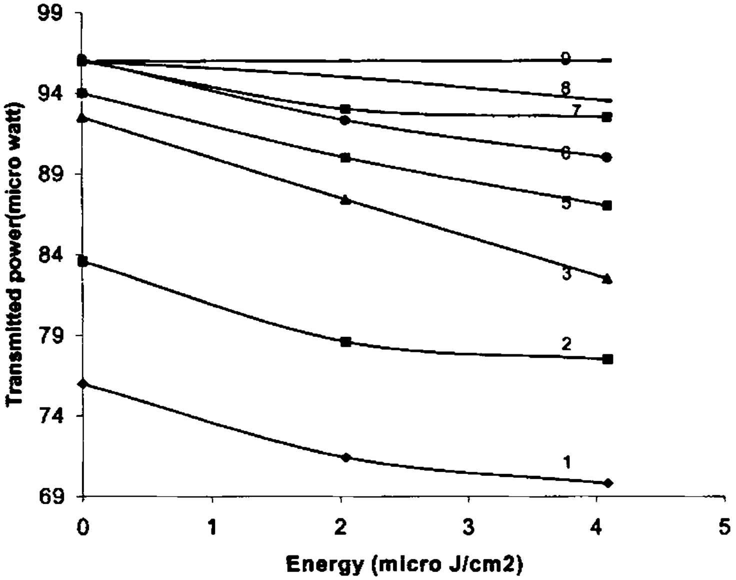


Fig. 3.9. Recyclability of the material

e) Importance of pH control

It has been found that pH greatly influences the efficiency of a hologram recording material. In methylene blue sensitized dichromated gelatin holograms, electron donors like 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 was observed [16]. Hence a control on pH was essential to make a high sensitive recording material. In the case of dichromated gelatin holograms, an optimum pH of 6.2 gives maximum efficiency [17]. To prepare spotless methylene blue sensitized dichromated gelatin plates a high pH of 11 for the photosensitive medium is necessary [18]. The effect of pH of the coating solution on the diffraction efficiency of dichromated poly (vinyl alcohol)(PVA) holograms have been studied by Mannivannan[19] and has reported that the pH variation of the coating solution plays an important role on the diffraction efficiency. It is reported that the diffraction efficiency of MBPVA shows an increasing trend with an increase in pH.

As such it appears that a very thorough understanding of pH, on bleaching properties of complexed methylene blue sensitized poly (vinyl chloride) matrix might put us in the right direction before using the material for hologram recording.

f) Effect of pH variation

The effect of pH was studied for an optimum sensitizer concentration of 1.27 x 10^{-3}mol/l. On absorbing the light of a He-Ne laser beam (632.8nm) a large part of the dye molecules 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 [20]. 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.

It was observed that CMBPVC films of different pH when exposed to He-Ne laser irradiation, the dye molecules get bleached. Hence real time transmission studies were carried out to find 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 substrate is taken as T^0 and the transmittance value obtained for the exposed film is taken as T. In the transmission measurements their ratio (T/T^0-relative transmittance) is used for standardization. Figure 3.10 shows the variation of relative transmittance with time at different pH. In all the cases the relative transmittance increased slowly and then reached a stage of saturation with 120 sec for a laser power of 5mW. CMBPVC films thus exhibit high sensitivity. We studied the rate of bleaching at different pH by finding the slopes at different time. 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 at a pH 4.5. A Plot of rate of bleaching vs. time for different pH is shown in figure 3.11.

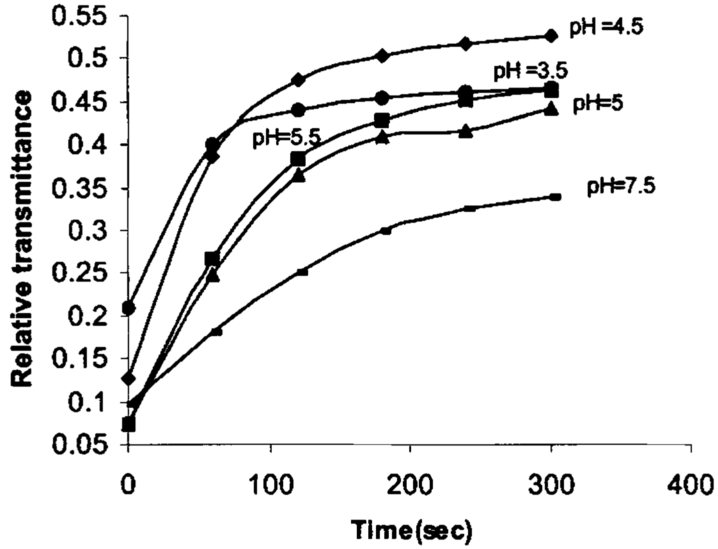


Fig. 3.10.Variation of relative transmittance with time for different pH

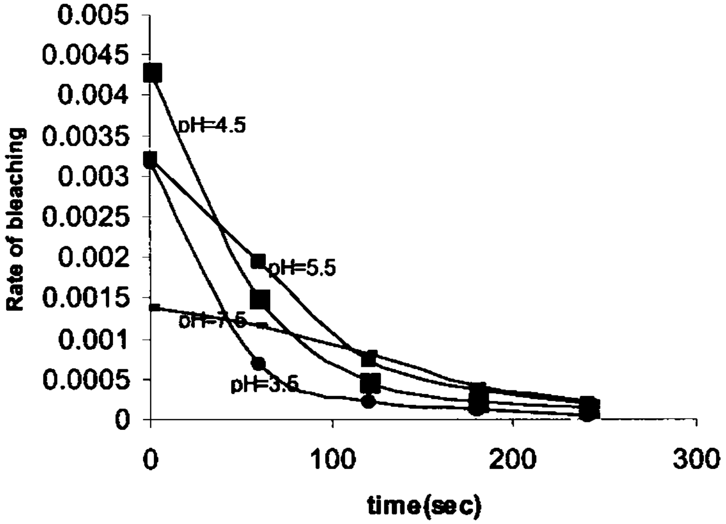


Fig.3.11.Variation of rate of bleaching with time for different pH.

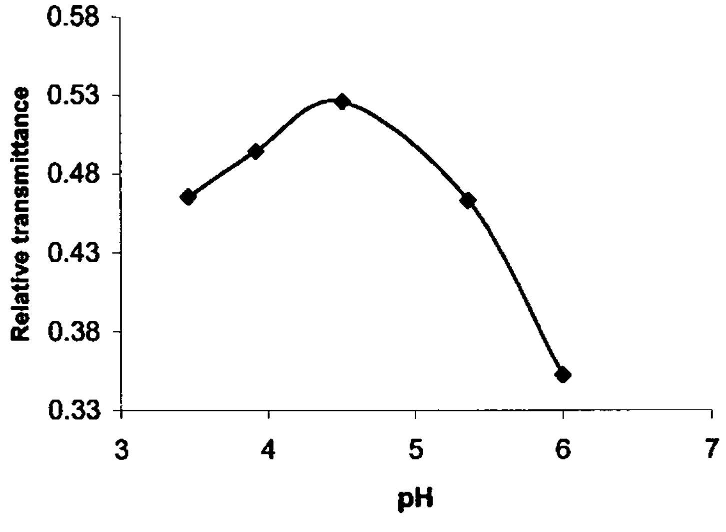


Figure 3.12. A plot of relative transmittance at fixed time for different pH

To find the optimized pH of CMBPVC films, relative transmittance at 600 sec is plotted for different pH. The data in the figure 3.12 demonstrated that very fast bleaching could 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. This is because at high pH the leuco form is unstable. It is already established that there is an equilibrium existing between methylene blue and its leuco form.

$$MB + H^{+} + e^{-} \rightleftharpoons \text{Leuco } MB$$

At high pH, the concentration of H^+ ion decreases, then according to LeChatliers principle the equilibrium is disturbed and the forward reaction takes place with less vigour. Also due to common ion effect the dissociation of methylene blue to its leuco form will be restricted. Hence the rate decreases. The lower rate at low pH can be attributed to the ion association.

It could be concluded that the best film for optical recording is one that prepared around a pH of 4.5 and having a dye concentration of 12.8×10^{-4} mol/l .

g) Direct Imaging

An attempt was made to do direct imaging on the optimized CMBPVC films. The medium consists of an inert polymer 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 red 632.8nm line of He-Ne laser. Hence an expanded beam of 10 mW He-Ne laser was passed through a transparent sheet on which letters were written and the transmitted beam was allowed to

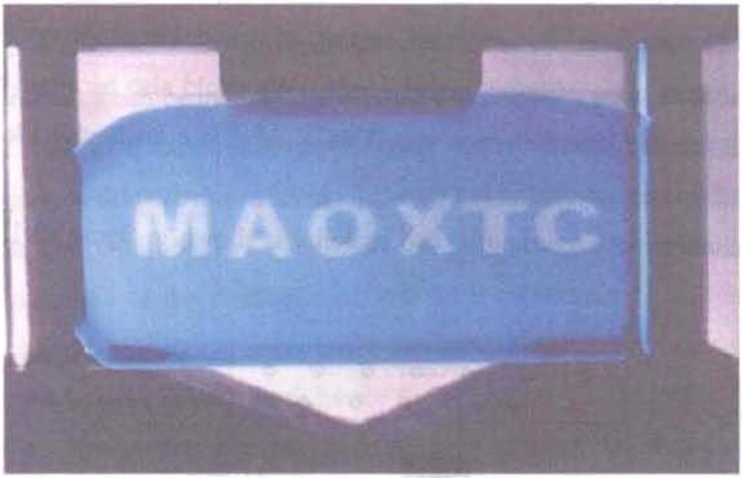


Fig. 3.1 3.A photograph of few alphabets recorded on CMBPVC film

Figure 3.14. A photograph of small words recorded on CMBPVC film

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 centers (figure 3.13, 3.14) were found in the exposed region. 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.

The mechanism of recording in this material is shown in figure (3.15) given below.

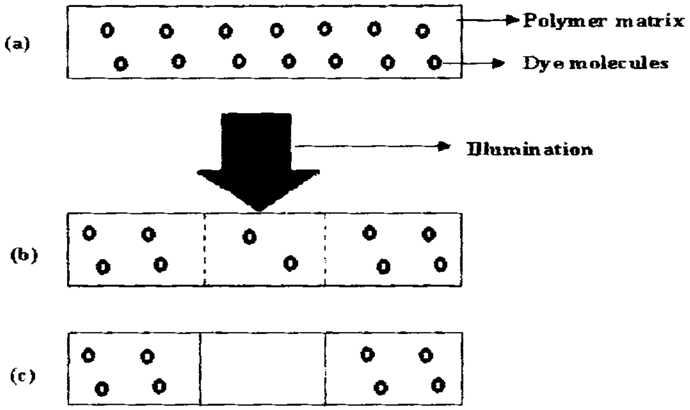


Fig. 3.15. Mechanism of imaging done on CMBPVC films.

a) Medium with a uniform distribution of the dye molecules

b) Illumination starts the conversion of the dye molecules to its leuco form

c) After irradiation the bleached area remains unchanged

Before recording the complexed dye molecules were evenly distributed through out the medium; on illumination from one side, normal to the surface of this material, 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. 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 is less in PVC since the monomer is a gas and its concentration is very low in the polymer and hence the chance of polymerization of the residual monomer in the illuminated area is negligible. So a change in refractive index is not expected. No change in absorption at the unexposed part was observed; hence the migration of dye molecules to those areas on illumination can be ruled out. Complexed dye molecules that are converted into the leuco form in the polymer matrix will become fixed in their location, resulting in a concentration gradient of the free dye molecules in the material. Thus the recorded images were permanent. Materials that operate in a principle similar to that described here have also recently been developed for holographic memories [6]. 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 in the case of other methylene blue sensitized conventional polymer systems.

h) Interferometric studies

The diffraction efficiency of a volume holographic grating was determined by measuring the intensity I_1 available in the first diffraction order and the total intensity I_T of the transmitted light. The light intensity was measured using a power meter. Interferometric experiments were performed to characterize this photosensitive medium; by recording interference gratings and measuring the diffraction efficiency on the CMBPVC films. The photograph of the first order-diffracted pattern on CMBPVC film is shown in figure 3.16

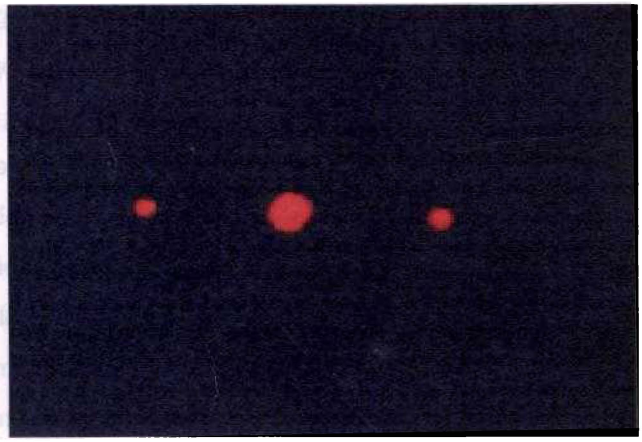


Fig. 3.16 The photograph of the first order-diffracted pattern on CMBPVC film

The set up for recording the interference pattern is shown in figure 2.6. 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/mm only in the range of 193 to 720 for a particular mirror.

Diffraction efficiency measurements on these films at different angles showed a maximum at 10^0 and 40^0. Diffraction efficiency decreased initially and then showed a small increase at 40^0 (figure 3.17). So a detailed study was done at these two angles for this material. The results are shown in the graph (figure 3.18, 3.19). Maximum diffraction efficiency of about 4.46% was achieved on this material for an angle of 10^0 (193 lines/mm) and the beam is allowed to fall

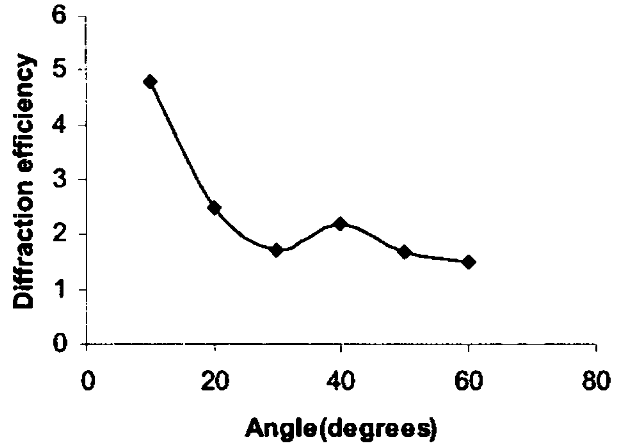


Fig. 3.17. The Variation of diffraction efficiency (D.E) with different angles for CMBPVC films

on the film for a fixed time. The experiment was repeated by changing exposure time. In each case exposure energy was calculated. In all the cases diffraction efficiency were measured as before. It was observed that at lower exposure energies diffraction efficiency was low, then it gradually increased with exposure energy, and reached a maximum value and then decreased. This was true for the angle 10^0,40^0 that we studied. 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. But when the energy increases there is a chance for the dye molecules to 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 for the diffraction efficiency observed at high exposure energies. The variation of diffraction efficiency with exposure energy for these two different angles is plotted as shown in figure 3.18 & 3.19 respectively.

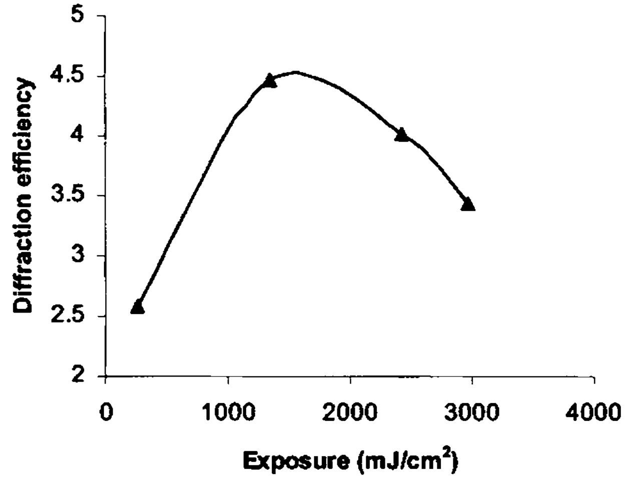


Fig 3.18. Variation of diffraction efficiency with exposure energy at an angle of 10^0

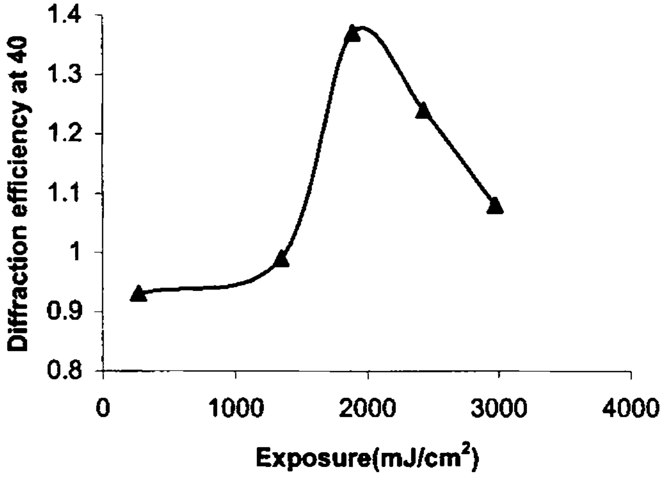


Fig. 3.19. Variation of diffraction efficiency with exposure energy at an angle of 40^0

i) H&D Curves

The response of photosensitive materials to light is normally represented by H&D curves (known as the Hurter and Driffield), in which the optical density of the material, after it has been developed and fixed is plotted against logarithm of the exposure given to it. A typical H&D curve for CMBPVC film is shown in the fig (3.20). Although H&D curve is used almost universally for photography, it is not 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 preferable and the variation of amplitude of transmittance with exposure is shown in fig (3.21). The curve is in good agreement with the conventional system.

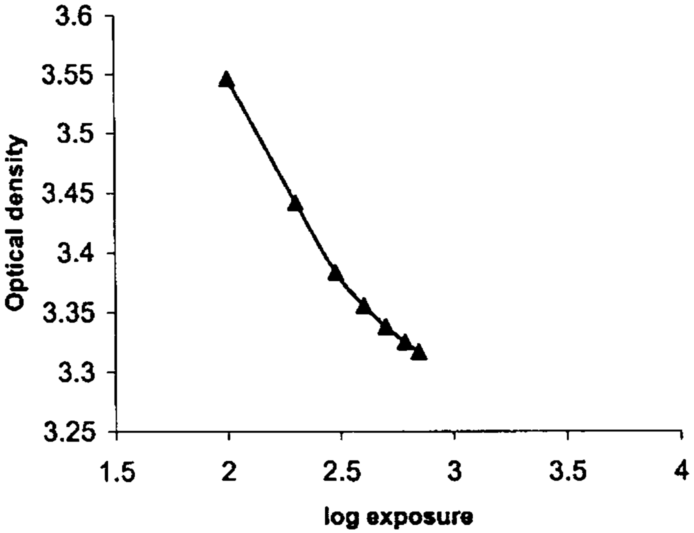


Fig. 3.20. Variation of optical density with log exposure

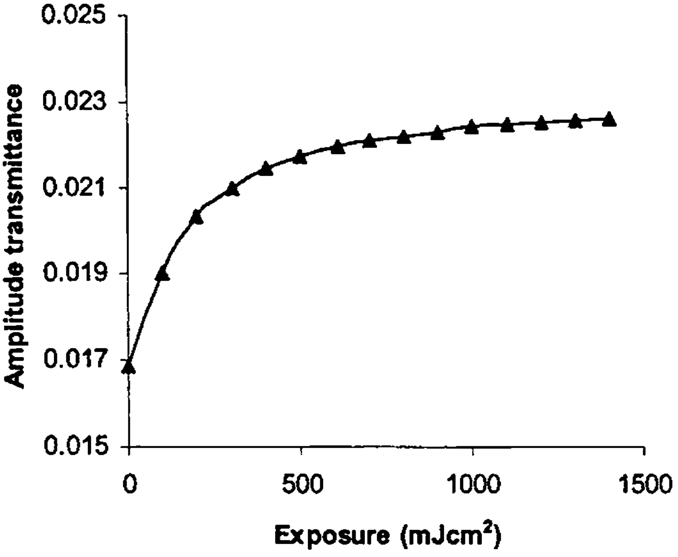
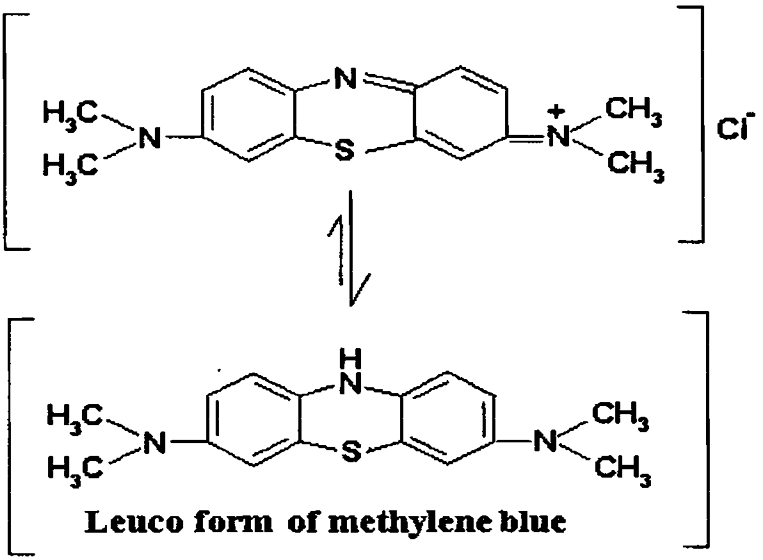


Fig.3.21. Variation of amplitude transmittance with exposure.

j) Dye behaviour

The photosensitizing action of the dye results from the ability of the dye to act either as a strong oxidizing or as a strong reducing agent in the presence of reducable or oxidisable substances, with subsequent regeneration and returning to the normal state. Moreover in many reactions, dyes are predestined sensitizers; because the chemically more reactive triplet state is produced in dyes with high efficiency by inter system crossing from the first excited singlet state [22]. In addition, aggregated or complexed dye molecules are able to react in the excited state with contacting systems and thereby induce important physical and chemical processes, which could not start without dyes under the influence of light.

Chemically methylene blue is 3,7- bis (dimethyl amino) phenantholinium chloride. The structure of methylene blue and its leuco form is shown below



Leuco form of methylene blue

Methylene blue (MB) is a basic dye of the thiazine group and is analogous to the osazones, an atom of sulphur replacing oxygen in the heterocyclic ring. These dyes have phenazonium nucleus as chromophores with amino group para to the ring nitrogen as auxochromes. It accounts for the high colour value of methylene blue, including their ability to form leuco form on reduction [21]. The stability and colourfastness of MB could be improved by complex formation (using copper acetate). In the absence of complexing agent very high exposure energy was necessary for the excitation of dye molecules. Copper acetate was chosen as the complexing agent since it has almost the same absorption as that of the dye and the wavelength of laser used. MB when irradiated with red light, gets excited to MB* where it is converted to a stable leuco form. The role of copper acetate may be that of an activator to speed up the bleaching process.

$$\mathrm{MB} \rightleftharpoons \mathrm{MB}^* \longrightarrow \mathrm{MB}^1 \longrightarrow \text{Leuco MB}$$

According to the mechanism, the photoexicted dye (in the (n, π^*) triplet state) is reduced by transfer of electron or hydrogen. The semi-reduced dye radical is either reoxidised to the ground state by oxygen or is not regenerated, but is transformed to the leuco dye, i.e. photobleached [22]. This sensitized oxidation can also lead to a sensitized photodestruction of the dye. In these cases MB serves as oxidisable substrate as in bleaching of aerated chlorophyll by high intensities of light.

The triplet excitation transfer may be efficient in many photobleaching processes of methylene blue, but only a few studies have been made so far. In most of the studies with MB in different polymer matrices, it is observed that the exposed part of the plate can recover its original colour after some time [1] and chemical or thermal treatment is necessary for fixing the data. In our previous work methylene blue sensitized gelatin (MBG) and methylene blue sensitized poly (vinyl alcohol) (MBPVA) the dye returned to its original colour after 12h and 36 h respectively. In the case of MBG, chemical methods are employed to convert it 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 [22]. In the present work on CMBPVC, the conversion of leuco form back to the original form was observed to be a much slower process and the information stored could be retained for several months without much deterioration. The role of copper acetate and glacial acetic acid in fixing this dye to its leuco form in this polymer matrix can be ruled out because in a similar experiment done on complexed methylene blue sensitized poly (vinyl alcohol) showed that the dye recovered to its original color after 24 hours. Hence the role of PVC in this dye behavior is prominent. No degradation product was formed at the irradiated area. This was confirmed by dissolving the irradiated portion in cyclohexanone. The exact role of PVC in this dye behaviour is not fully known.

3.4.2. Mecahnical properties

No change in mechanical properties like tensile strength was observed when methylene blue was doped in poly (vinyl chloride) matrix. The tensile strength and elongation at break of PVC, both doped and undoped is given in table 3.1.

Table 3.1. Comparison on the mechanical properties of undoped and methylene blue doped PVC

PVC	Tensile strength (N/mm^2)	Elongation at break (mm)
Undoped PVC	35	46
Doped PVC	34.5	44

3.5.CONCLUSIONS

- CMBPVC can be used as a high sensitive medium for optical recording.
- This material is insensitive to humidity unlike other methylene blue sensitized polymer films.
- Copper acetate can be used a sensitizer for methylene blue in this matrix
- The change of state occurring for methylene blue on laser irradiation is permanent in this matrix; hence it can be used as a permanent recording material.
- Less than 5 sec was necessary for bleaching when a 10 mW He-Ne laser was allowed to fall on the film.
- This material has excellent shelf life and storage life.
- Thick CMBPVC films can be fabricated in the laboratory, so it can also be used as a volume recording material.
- Very fast bleaching was observed for an optimum dye concentration of 1.28×10^{-3} mol/l and pH 4.5.
- Diffraction efficiency of 4.8% was obtained.
- Direct imaging was done.
- The major attractions of this material are the low cost, ease of recording and environmental stability.
- There is no change in the mechanical properties of the film before and after doping.

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Chapter 4

PART 1

4.1. STUDIES ON METHYLENE BLUE SENSITIZED POLY (VINYL ALCOHOL) IN WATER FOR OPTICAL RECORDING

4.1.1. INTRODUCTION

Since Gabor's first demonstration of reconstructed wave fronts, holographic techniques have proved to be useful in many applications. At present the future of holography is strongly dependent upon developing new types of holographic recording media, because most of the limitations associated with today's holographic techniques and applications are attributed to the non-availability of good recording materials[1-2]. To record high spatial frequencies, new holographic materials should be grainless; this is why we chose particularly photopolymers for our study. However, their holographic sensitivities are many orders of magnitude below those of silver halide emulsion. Dichromated gelatin[3-6] films have excellent properties for permanent recording but they require chemical development. For these reasons, photopolymers become advantageous in the fabrication of holographic optical elements (HOE). More over, present holographic applications require real time recording materials.

Like methylene blue sensitized gelatin, methylene blue sensitized poly (vinyl alcohol) is also a latent recording material, which needs development, for high efficiency low noise phase holograms [7]. If no development is performed, the holograms recorded in the red sensitive material will have diffraction efficiency <1%[8]. It has been shown that in dichromated gelatin films, the real time effects of exposure are caused by absorption modulation[9], thus explaining the small amount of diffraction obtained with out development[10-12]. We believe that the causes are same for methylene blue sensitized gelatin and methylene blue sensitized poly (vinyl alcohol), since it is easily noticeable that exposure to light results in a decrease of absorption [13] in both cases. Actually, colour of the film under exposure changes gradually from blue to colourless, the methylene blue molecules transforming from their fundamental state to their leuco form (colourless). Therefore, as in photochromic materials [14] real time modulation is obtained in methylene blue sensitized poly (vinyl alcohol) by bleaching the material. The exact photochemical reactions undergone by the methylene blue molecules are not clearly understood yet. Chankakoti [15] made a detailed study of the effect of amines which act as " external electron donors": ethylene diamine tetraacetic acid (EDTA); Triethanol amine (TEA); N,N,Dimethyl formamide (DMF). The results indicated that the advantages of adding such compounds in methylene blue sensitized dichromated gelatin, were not obvious. Hence we decided that it would be worth searching for related compounds that might be of greater benefit, with the aim of opening up the use of low power lasers to record holograms on methylene blue sensitized poly (vinyl alcohol) plates. Instead of using electron donors, our attempt was to convert the dye to a complexed state, which was more sensitive to red laser. We were able to achieve this through complex formation.

We tried to improve the intrinsic characteristics of methylene blue sensitized poly (vinyl alcohol) used as a latent recording material, such as its sensitivity, rate of bleaching, exposure energy etc by complexing methylene blue with copper acetate. This work was done as an extension of the work done earlier. It was already proved that methylene blue sensitized poly (vinyl alcohol) could be used as a real time recording material at high pH [16]. This is because methylene blue does not separate when it is in the alkaline state because the solubility product in alkaline media is larger than that in an acidic state. Therefore, when the alkaline additive is added to methylene blue sensitized polymer films, the separation of methylene blue is prevented [17]. So in our experiments high pH of 10.2 was maintained through out.

4.1.2. EXPERIMENTAL

Preparation of the methylene blue sensitized poly(vinyl alcohol) films.

The PVA (molecular weight 1,25,000) 7 % solution was prepared by dissolving 7 g of PVA in 100 ml distilled water. Constant stirring was given using a magnetic stirrer. 30 ml of this solution was made basic by adding ammonia solution, so that pH was maintained to be 10.2.

Preparation of the dye solution

Methylene blue (0.15g) and copper acetate (0.3 g) was dissolved in glacial acetic acid (10ml).

30 ml of basic 7% PVA prepared was sensitized with few ml of complexed methylene blue solution. Constant stirring was given using a magnetic stirrer. The solution was kept undisturbed for some time. Their films were prepared with varying dye concentration using gravity settling method [9]. A constant volume of the mixture was poured on a clean micro slide kept on a level surface. It spreads equally on the slide. The plate was kept for 24 hours for drying at room temperature. The dried films were kept in a dessicator. In all cases thickness was maintained to be 0.01mm. For pH measurements, a digital pH meter (systronics 335) was used. pH was increased by adding ammonia solution.

4.1.3. EXPOSURE TO He-Ne LASER BEAM

The exposure beam was derived from a coherent Melles Griot He-Ne laser with emission at 632.8 nm. The laser beam was expanded using a spatial filter arrangement set up in the laboratory as explained in fig 2.5. The samples were placed in the expanded beam. The transmitted intensity was measured using a power meter (OPHIR model 2000). The effects of He-Ne laser irradiation in the absorption spectra of complexed methylene blue sensitized poly(vinyl alcohol) (CMBPVA) films were studied using a Hitachi 330 UV-VIS-NIR spectrophotometer. The absorption spectrum was taken before and after laser exposure and also after 24 h (when the recovery of dye was complete). When the spectrum was taken the position of the sample was adjusted so that the light passes through the same region before and after exposure. The glass plate containing undoped PVA was used as reference. The exposure time was 5min. To determine the power necessary for bleaching, the samples were exposed to varying power from 90μW to 6.4 mW for 20sec and the change in transmittance was observed. To study the effect of complexed methylene blue concentration on real time transmission, samples of nearly same thickness and of 9 different concentration of methylene blue were taken and they were exposed under same laser power of 5mW for 5 min.

4.1.4. RESULTS AND DISCUSSION

4.1.4.1. Optical Characterization

a) Optimization of the amount of complexing agent

The ratio of the complexing agent to methylene blue was varied as 2:1, 1:1 and 1:2. The complexing agent used was copper acetate. Film quality and colourfastness was found to be excellent for the ratio 2:1. In the other two cases the film was discoloured at the center. So through out this study the ratio of copper acetate to methylene blue was maintained as 2:1.

b) Optical absorption studies

The optical absorption spectra of CMBPVA taken before, after exposure and after 12h and 24h (figure 4.1) showed a peak around 655nm which is characteristic of methylene blue. But on exposure the intensity of the peak decreased considerably showing that bleaching occurred on irradiation. But a shift was also observed on this spectrum. The recovery of the dye was almost complete in 24 hours. The shift from 655nm to 635nm shows that the dye recovered to a more stable thionine state, which is indicated by the dark blue colour on the irradiated spot after 24 hours. Thus it is evident from the absorption spectra that there is a change in the absorption property of the material, and optical recording is possible in it.

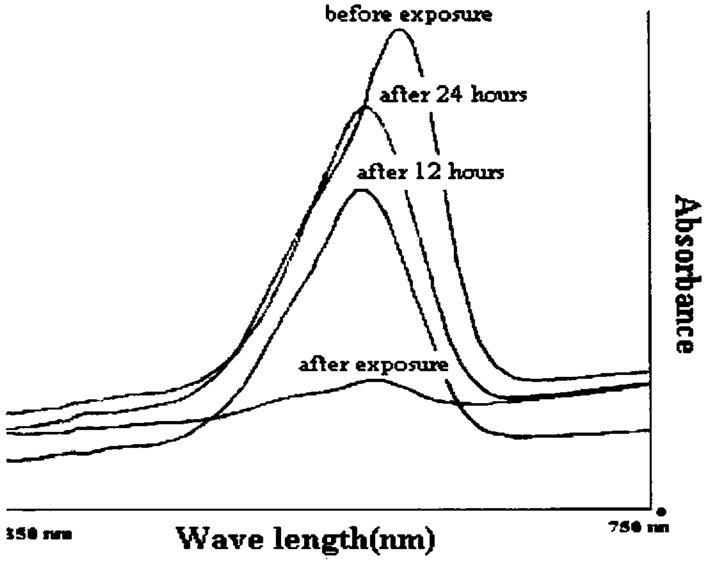

Fig 4.1. The optical absorption spectra of complexed methylene blue doped PVA films before, immediately after, after 12h and 24 h of exposure.

c) *Effect of concentration of methylene blue*

To study this effect in detail the concentration of the dye was varied from 1.156 x10^{-4} to 2.28 x10^{-3} mol/l. The samples were exposed to a laser power of 5 mW for 5 min. The transmitted intensity was measured at regular intervals (at every 20 sec) for 10 min using a power meter. The variation of transmitted power with time for different concentrations was noted and a graph was plotted between relative transmittance and time and is shown in figure 4.2. (The graphs for certain complexed methylene blue concentrations were removed because they are of negligible importance). C1, C2, C3 and C4 in the graph indicate the different concentration of the dye employed (where

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C4>C2>C1>C3). Very fast bleaching was achieved for a sensitizer concentration of 1.27 x10^{-3} mol/l (C1). This is because at high sensitizer concentration more number of molecules will be present in the illuminated area, there by requiring more energy for its exictation on a fixed time.

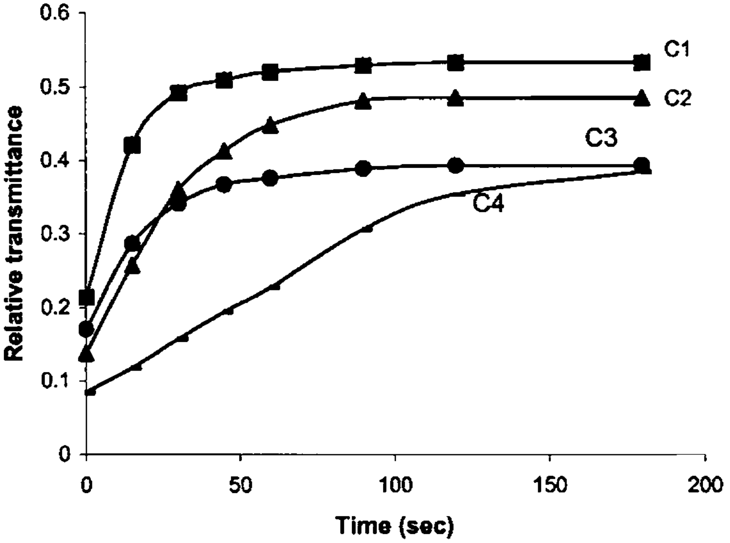


Fig.4.2. Variation of relative transmittance with time for different concentrations of methylene blue.

d) Rate of bleaching

To determine the rate of bleaching with optimum amount of dye, the variation of transmittance in terms of T/T^0 with time was calculated and plotted. The rate of bleaching is found out by finding the slopes at different time. The rate of bleaching with time for the optimized sample is shown in figure 4.3. The rate of bleaching was very fast for CMBPVA films. With in 40 sec the films were totally bleached. By that time most of the methylene blue molecules had absorbed sufficient energy and got converted to its leuco form.

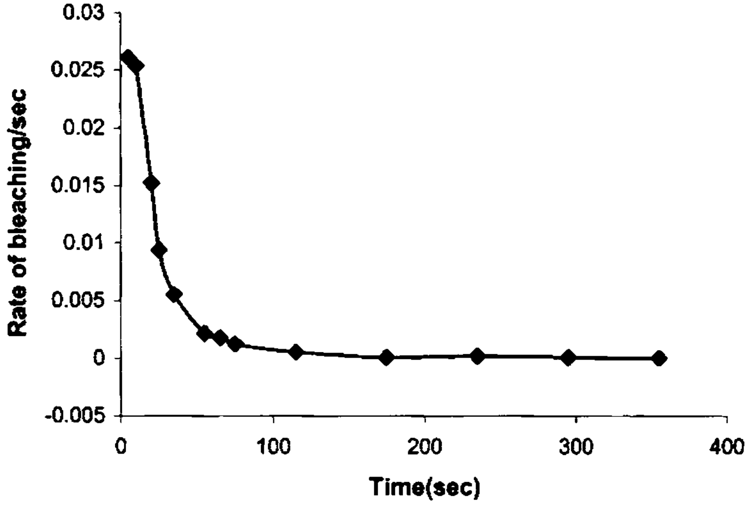


Fig.4.3.Variation of rate of bleaching with time for the optimized MBPVA/methanol films

e) Effect of storage

The study carried out by C.Solano et.al[18] have shown that in conventional MBPVA/water system, the dye that was bleached by laser exposure became colored after 12h and so a permanent grating could not be obtained from this film without any further chemical treatment. The conversion of the dye back to its original form was the mechanism attributed to this observation. So in most of the studies carried out on MBPVA films for permanent storage, the irradiated films were further chemically developed. Almost same observation was noticed when the dye was complexed in PVA/water system. According to the above observation permanent recording was possible only if chemical treatment was given. In the present study, it was observed that the colour of the film regained only after 24 h, and it can be clearly seen that the dye recovered to a stable thionine state which was indicated by the dark blue colour on the irradiated spot. Hence a detailed study on the recovery of the dye on CMBPVA films was done. For this the sample was subjected to a maximum power so as to reach the saturation point. The variation in transmittance of the irradiated sample was monitored as a function of time by sending a laser beam of low power (less than the threshold power). Transmittance at the irradiated spot decreased with time and the variation of transmittance with time was plotted in figure 4.4. The graph showed an exponential behavior and an exponential fitting could be done for figure 4.5. In the case of CMBPVA, very fast recovery was found, it can be due to the transient life of the unstable leuco form of the dye produced during irradiation.

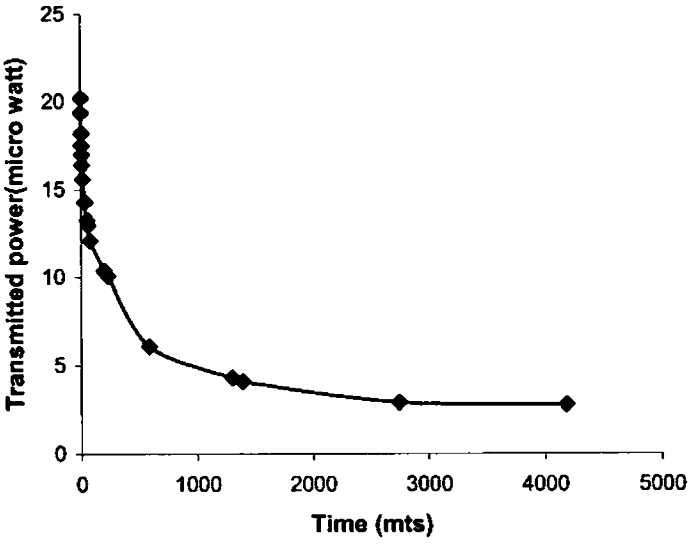


Fig.4.4. Variation of transmitted power with time on storage

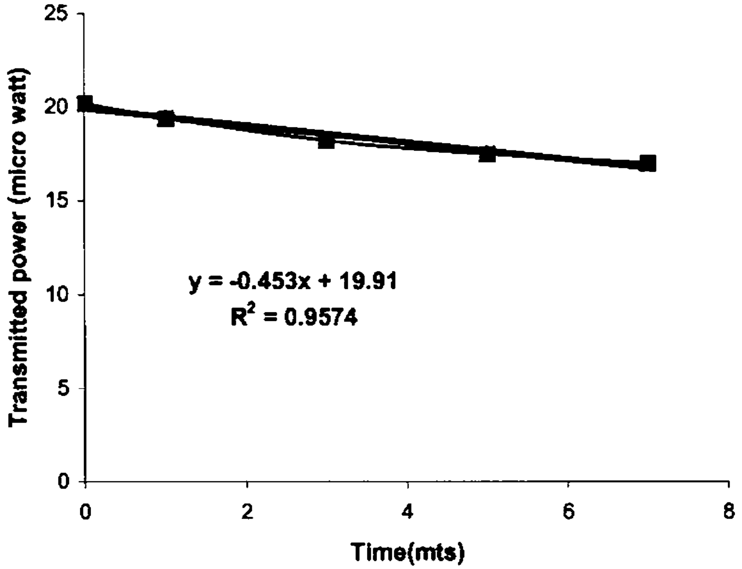


Fig.4.5.The graph showing an exponential behavior with an exponential fitting

The recovery of the dye can be attributed to two reasons (i) high pH (ii) unstable leuco form (due to lack of resonance)

f) Optimization of exposure energy

It was found that only very low energy was necessary for bleaching on CMBPVA films on laser irradiation. After a fixed time of exposure it was found that the change in exposure energy would not bring any changes in the rate of bleaching. Intensity is an important parameter to be optimized, because bleaching of the dye depends on the intensity of laser used. No bleaching was observed when the sample was exposed to an incident power as low as 76μW. It was found that a minimum laser power (approximately 0.186mW) was essential for the photochemical change to take place. From this it is clear that a minimum amount of energy called threshold energy was necessary for the excitation of the dye molecules to the leuco form. Due to very high sensitivity of the sample, threshold energy could not be determined. To determine the saturation energy, different samples of same pH, thickness and concentration were exposed to different laser powers, in each case for 20 sec. A stage of saturation was observed at an exposure of approximately 200mJ. After the threshold region, very fast bleaching was observed with the change in exposure, but after saturation point, no change in the transmitted power was observed with the increase in the exposure (fig 4.6).

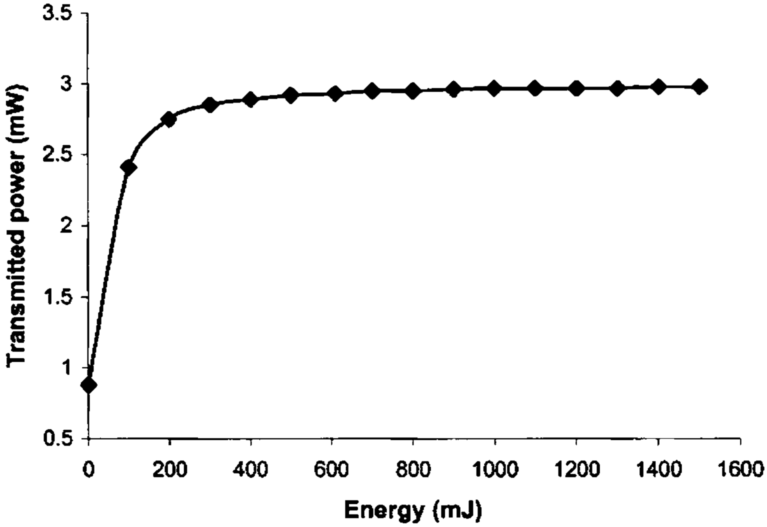


Fig.4.6. Variation of transmitted power with exposure energy till saturation is attained.

g) Diffraction efficiency measurements

Laser beam was expanded and 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 set up for recording the interference pattern is shown in figure 2.6. The angle between the incident beam and the normal was taken as θ. By varying the angle θ it was found experimentally that we could record the number of lines/mm only in the range of 193 to 720 using a single mirror.

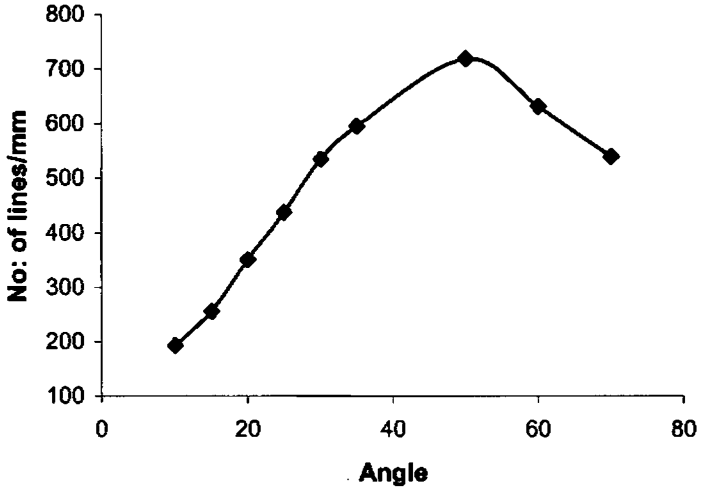


Fig. 4.7. Variation of number of lines/mm with the angle of incidence

Figure 4.7 illustrates the variation of number of lines/mm with the angle of incidence for a fixed laser power. We were able to record diffraction pattern successfully on this sample also but due to very high sensitivity of the sample, the measurement of the intensity of the diffracted pattern was very difficult as the reading beam itself bleaches the material destroying the fringes.

h) H&D Curves

A typical H&D curve for CMBPVA film is shown in the fig 4.8 and a curve

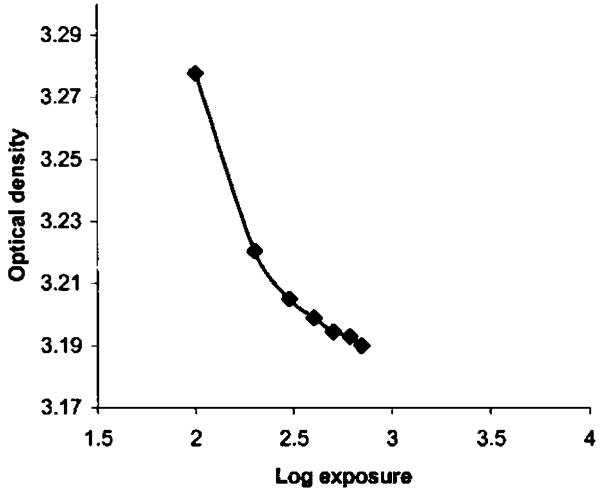


Fig. 4.8. Variation of optical density with log exposure

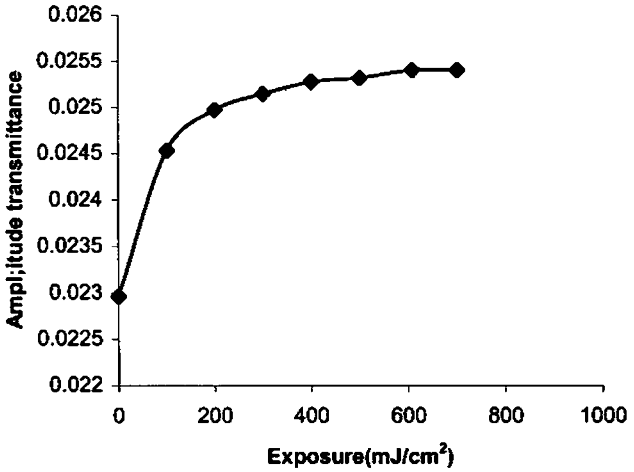


Fig 4.9. Variation of amplitude transmittance with exposure

showing the amplitude transmittance of the material as a function of the exposure is preferable and is plotted in the fig (4.9). The pattern of this graph is in close agreement with the conventional photographic plate. Hence CMBPVA films can be used for real time hologram measurements.

i) Direct imaging

The medium consists of the polymer matrix in which the methylene blue dye molecules are uniformly suspended. The writing wavelength of this material is determined by the photosensitizer (MB), which in this case has an absorption peak close to red 632.8nm line of He-Ne laser. Hence an expanded beam of 10 mW He-Ne laser was passed through a transparent sheet on which letters were written and the transmitted beam was allowed to fall on the CMBPVA film placed on a film holder. The beam was allowed to fall on the material for 5 min. After imaging, it could be observed that the letters were very legible with good contrast and there were no scattering centers. The mechanism of direct imaging is shown in figure 4.10. Before irradiation the dye molecules were uniformly suspended in the medium. On irradiation the dye molecules get bleached i.e. the irradiated part become colorless. But unlike methylene blue in PVC matrix described earlier, very fast recovery of dye was observed in this polymer matrix. It was found that the dye did not return to its original color, but to a different colour with low contrast between the original state and recovered state. This clearly proves the existence of thionine state on the irradiated spot. The photograph of direct imaging done on CMBPVA films is shown in figure 4.11.

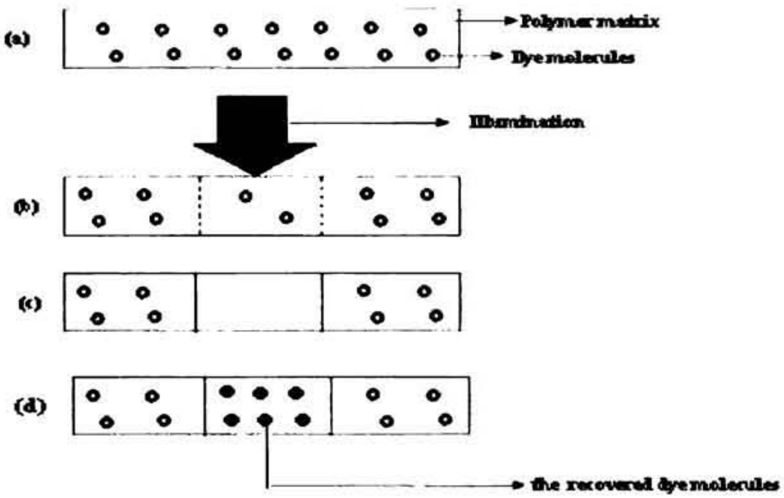


Fig. 4.10. Mechanism of direct imaging on CMBPVA/water films

a) Medium with a uniform distribution of the dye molecules

b) Illumination starts the conversion of the dye molecules to its leuco form

c) After irradiation (bleached area)

d) After the recovery of dye to the more stable thionine state (this area has a dark blue colour than the unexposed area)

Fig 4.11.The Photograph of direct imaging of few letters H,A,T recorded on CMBPVA films

j) Dye Behaviour

The effect of red light absorption on methylene blue was to make it an exicted molecule with a transitory existence as an oxidant seeking electron. It is proved that certain types of amines can provide electrons to photoexicted methylene blue via the transitory formation of a charge transfer complex which is believed to be produced [18]. Similarly the copper acetate may be forming a complex with methylene blue in PVA matrix. The complexed methylene blue is thus turned into a colourless form known as leuco methylene blue on laser irradiation. This is a reactive reducing agent able to gradually return to the original state by reacting with oxygen from the air [19]. When CMBPVA films are exposed to a He-Ne laser, in the exposed area the dye was partially or totally bleached; however the film was kept in the dark after few hours, the dye recovered itself and presented a different colour. More over if the irradiated area was investigated with a red colored beam the diffracted orders were seen. This implies that the dye passed through a transition to the leuco form or excited state, and then decayed to the more stable thionine sate. 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 reduced or oxidisable substance, with subsequent regeneration and returning to the normal state. It was found that the recovery of dye in this matrix is very fast. So the information stored was not stable for a sufficiently long time. It was seen in chapter 3 (CMBPVC) that the complexed dye molecules are held in fixed positions on laser irradiations. The recovery of the dye was not observed in PVC matrix. Whereas in the case of CMBPVA, the recovery was very fast. It is thus evident that the polymer matrix plays the key role in the difference in the behaviour of the dye doped polymer films. Unlike other methylene blue sensitized polymer matrix, CMBPVA has poor shelf life. That is the film had a stability of only 30 days.

4.1.4.2.Mechanical properties

No change in mechanical properties like tensile strength and elongation at break was observed on doping poly (vinyl alcohol) with methylene blue. Table 4.1 shows the value of tensile strength and elongation at break for undoped PVA and methylene blue doped PVA

Table 4.1. Comparison on the mechanical properties of undoped and doped PVA

PVA	Tensile strength (N/mm^2)	Elongation at break (mm)
Undoped PVA	40	89
Doped PVA	39	91

4.1.5.CONCLUSIONS

- Complexed methylene blue sensitized poly (vinyl alcohol) is a high sensitive medium for optical recording.
- Only low exposure energy is necessary for this film for optical recording.
- Threshold energy of this sample is low compared to other methylene blue sensitized conventional polymer films.
- Copper acetate was used as the complexing agent for methylene blue to improve the sensitivity of methylene blue in this polymer matrix.
- Threshold power is measured to be 0.186mW.
- The recovery of dye back to its original form was almost complete in 24 h.
- The saturation energy of CMBPVA films is 200mJ/cm^2.
- Direct imaging was done on this sample.
- Interference pattern was recorded on this sample.
- The shortcoming of this material is the low shelf life, storage life and lack of environmental stability.

c

PART II

4.2.STUDIES ON METHYLENE BLUE SENSITIZED POLY (VINYL ALCOHOL) IN METHANOL FOR OPTICAL RECORDING

Even though numerous studies were done on methylene blue doped poly (vinyl alcohol) using water as the solvent, we are reporting the use of poly (vinyl alcohol) in methanol as the solvent for its use as an optical recording material. Many positive results were obtained when the solvent was changed. Diffracted pattern till sixth order was obtained on this material. In this section we are reporting the characterization of methylene blue doped poly (vinyl alcohol) in methanol for its use as an optical recording material. Finally a comparative study was done on the diffraction efficiency of this system with that of the conventional PVA system in water to explain the superiority of the former over the latter.

4.2.1. EXPERIMENTAL

Preparation of methylene blue sensitised poly (vinyl alcohol) [MBPVA/methanol]

The PVA (molecular weight 1,25,000) solution (10g) was prepared by adding it to distilled water (100 ml). Constant stirring was given using a magnetic stirrer. 20 ml of this solution was mixed with 20 ml methanol. The solution was again stirred till a transparent clear solution was obtained.

Preparation of the dye solution

Methylene blue (0.3g) was dissolved in distilled water (20 ml)

20 ml of 5% PVA prepared was measured and few drops of methylene blue solution was added. Constant stirring was given using a magnetic stirrer. Then the solution was kept undisturbed for some time. The films were coated with varying dye concentration using gravity settling method. A fixed volume of the mixture was poured on a clean micro slides kept on a leveled surface. It spreads equally on the slide and it was left for 12 h for drying at room temperature. The dried films were kept in a dessicator. In all the cases thickness was maintained to be 0.01mm. For pH measurements, a digital pH meter (systronics 335) was used. pH was decreased by adding hydrochloric acid (35%) and increased by adding ammonia (25%) solution. The absorption spectra of the samples in the visible region before and after exposure are taken using a Hitachi 330 UV-VIS NIR spectrophotometer. To determine the power necessary for bleaching, the samples were exposed to varying power from 90μW to 6.4 mW for 20 sec and the change in transmittance was observed.

The absorption spectra of the MBPVA/methanol were taken before; immediately after, after 12 h and after 48 hours (when the recovery of the dye was complete) exposure.

To study the effect of methylene blue concentration on real time transmission, samples of nearly same thickness and of 9 different concentrations of methylene blue were taken and they were exposed under same laser power of 5mW for 5 min.

To study the effect of pH on the coating solution, samples from coating solution with different pH was prepared as described in section 2.2.11. The pH was varied from 1 to 11. Non-uniform films were obtained at very high and very low pH. So detailed study was done for pH 5, 6, and 7.

To determine the rate of bleaching of the optimized sample, it was exposed to a laser power of 5mW. The transmitted intensity was measured at regular intervals (at every 20 sec) for 10 minutes using a power meter.

A comparative study was done on the methylene blue sensitized poly (vinyl alcohol) in methanol and methylene blue sensitized poly (vinyl alcohol) in water (conventional system) to explain the superiority of using methanol as the solvent. Grating was recorded on these two films at different angles of incidence. In all the cases diffraction efficiency was determined.

4.2.2. EXPOSURE TO 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 using a spatial filter arrangement set up in the laboratory explained in 2.2. The samples were placed in the expanded beam. The experimental set up is shown in figure2.5. The transmitted intensity was measured using a power meter (OPHIR model 2000). The effects of He-Ne laser irradiation in the absorption spectra of MBPVA/methanol (methylene blue sensitized poly (vinyl alcohol) in methanol) films were studied using a Hitachi 330 UV-VIS-NIR spectrophotometer.

4.2.3. RESULTS AND DISCUSSION

4.2.3.1. Optical Characterization

a) Optical absorption studies

The absorption spectrum of the MBPVA/methanol was taken before; immediately after, after 12h and after 48 hours (when the recovery of the dye was complete) and is shown in figure 4.12.

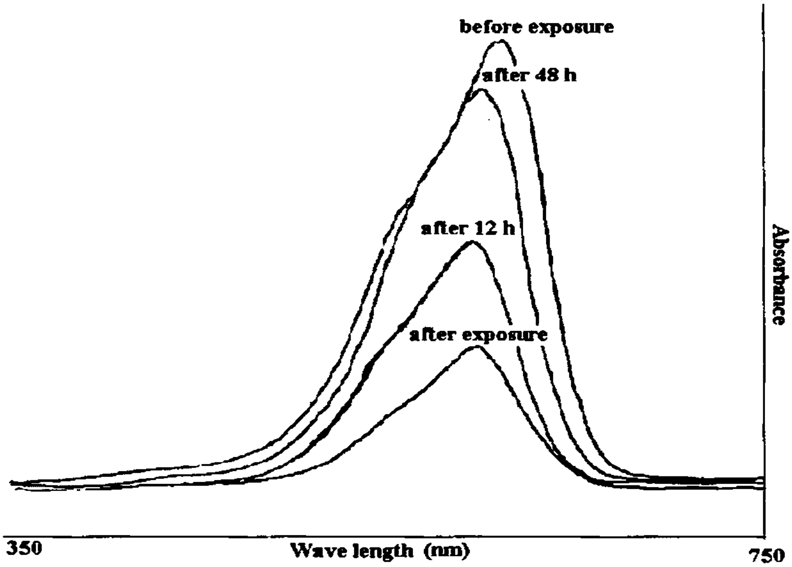


Fig.5.12. The optical absorption spectra of methylene blue doped PVA/methanol films before, immediately after, after 12h and 48 hours.

The spectra showed a peak around 650nm, which is characteristic of methylene blue. But on exposure the intensity of the peak decreased showing that bleaching occurred on irradiation. But a shift was also observed on this spectrum. The recovery of the dye was almost complete in 48h. The shift from

650nm to 635nm shows that the dye recovered to a more stable thionine state, which was indicated by the dark blue colour on the irradiated spot after 48 h. Thus it is evident from the absorption spectra that there is a change in the absorption property of the material.

b) Effect of concentration of methylene blue

The variation of transmitted power with time was noted and a graph was plotted between transmitted power and time for different concentrations and is shown in figure 4.13. (The graphs for certain methylene blue concentrations were removed because they are of negligible importance).

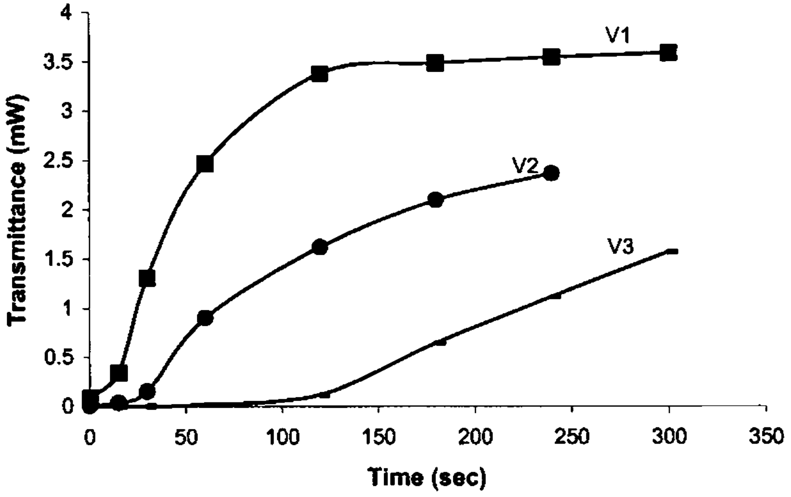


Fig.4.13. Variation of transmittance with time for different concentrations of methylene blue in MBPVA/methanol films.

The concentration was varied from 2.9×10^{-5} to 0.5784×10^{-3} mol/l. and very fast bleaching was achieved for a sensitizer concentration of 2.91×10^{-4} mol/l (V1). This is because at high sensitizer concentration more number of molecules will be present in the illuminated area, there by requiring more energy for its exictation on a fixed time. V1, V2, V3 in the graph indicates the different concentrations of the dye employed.

c) Optimization of pH

Since the rate of bleaching was found to be almost same for the pH 5, 6 and 7, the change in absorbance (it is the difference in absorption of the film before and after a fixed time interval) was monitored for optimizing the pH (figure 4.14). Since the recovery was very fast in almost all the cases, pH= 6 which is the normal pH of the system was taken as the optimum value.

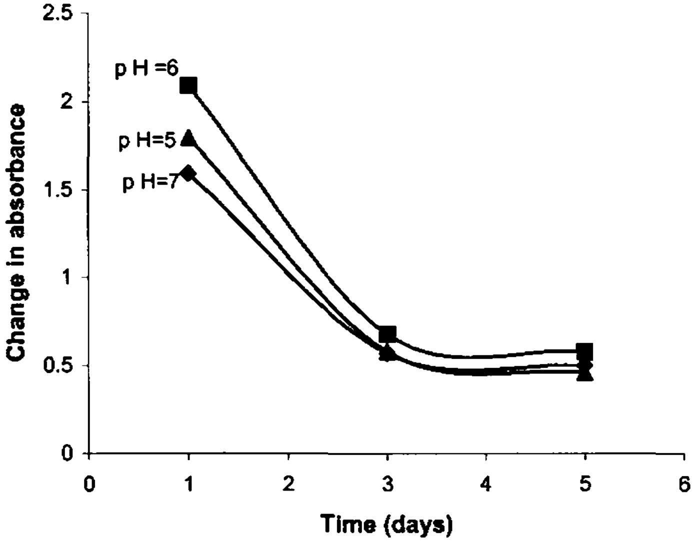


Fig.4.14. Variation of change in absorbance with time for different pH

d) Rate of bleaching

The rate of bleaching with time for the optimized MBPVA/methanol sample is shown in figure 4.15. The variation of transmittance in terms of T/T^0 with time is calculated and plotted.

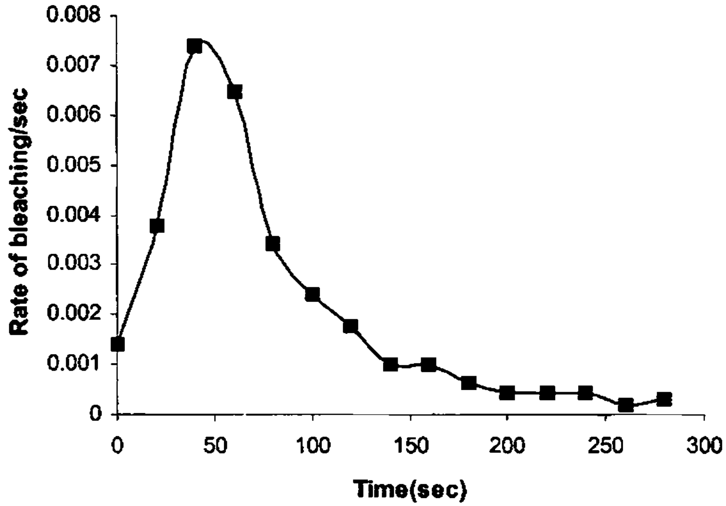


Fig.4.15. Variation of rate of bleaching with time for the optimized MBPVA/methanol films

The rate of bleaching was determined by taking the slopes at different time. The rate of bleaching initially increased rapidly, reached a maximum and then decreased. The rate of bleaching reached a maximum in approximately 50 sec time. By that time most of the methylene blue molecules had absorbed sufficient energy and got converted into the leuco form. Compared to CMBPVC, rate of bleaching was very fast for MBPVA/methanol system and compared to CMBPVA, rate is slow.

e) Effect of storage

In the present study, it was observed that the colour of the film was completely regained only after 48 hours, and it can be clearly seen that the dye recovered to a stable thionine state which is indicated by the dark blue colour on the irradiated spot. The photograph of these two state (bleached and recovered) can be seen in the sections given below. The graph showing the change in absorbance with days is given in figure 4.16.

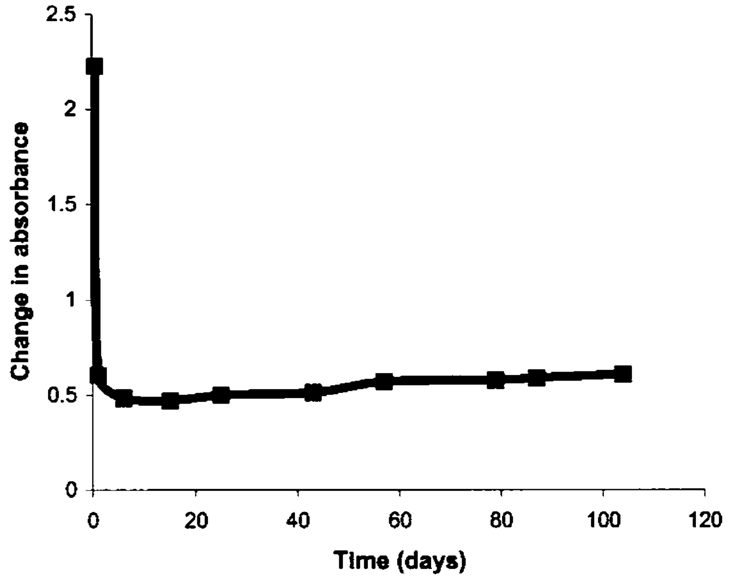


Fig. 4.16. Effect of storage on methylene blue sensitized PVA/methanol film

From the graph it is clear that the change in absorbance (before and after exposure) drastically decreased during the first day itself, showing fast recovery on these methylene blue sensitized PVA films.

f) Optimization of exposure energy

As in the case of the concentration of the dye, pH etc intensity is an important parameter to be optimized, because bleaching of the dye depends on the intensity of laser used. No bleaching was observed when the sample was exposed to an incident power as low as 76μW. It was found that a minimum laser power of approximately 100μW was necessary for the photochemical change to take place.

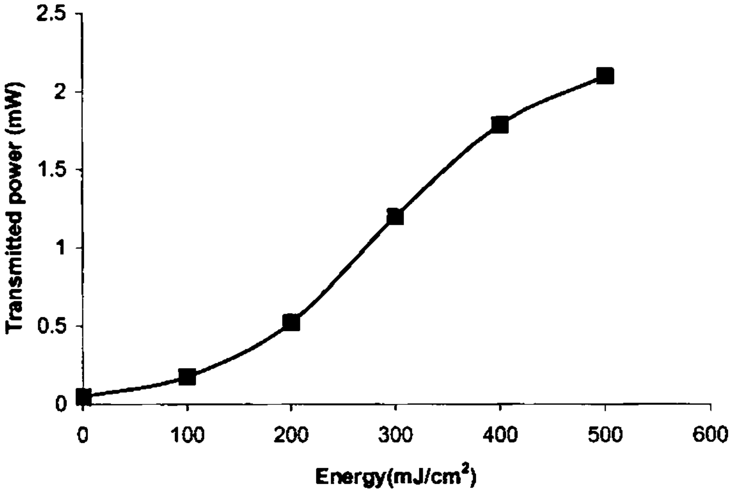


Fig.4.17.Variation of transmitted power with exposure energy for MBPVA/methanol films

From this it is clear that a minimum amount of energy called threshold energy was necessary for the excitation of the dye molecules to the leuco form. The threshold energy of the sample was found to be approximately 200mJ (fig 4.17). To determine the saturation point, different samples of same pH, thickness and concentration were exposed to different laser powers, each case for 20 sec. A stage of saturation was observed at an exposure of approximately

900mJ. After the threshold region very fast bleaching was observed with the change in exposure, but after saturation point, no change in the transmitted power was observed with the increase in the exposure energies (fig4.18)

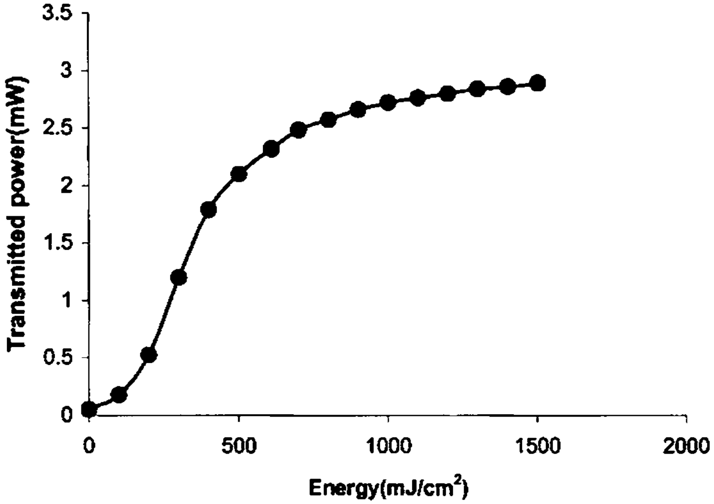


Fig.4.18. Variation of transmitted power with exposure energy till saturation is attained.

g) Diffraction efficiency

The variations of diffraction efficiency with angle for MBPVA/methanol and MBPVA/water films are plotted in figure 4.19. The interesting result observed was that for these two films graph obtained is of similar shape. Diffraction efficiency decreased at first reached a minimum and then increased gradually, reached a maximum value and then decreased. But diffraction efficiency was found to be more when methanol was used as the solvent. It is explained in the literature that high humidity or the presence of residual water in the dye doped polymer matrices especially gelatin and poly (vinyl alcohol), causes instability, which significantly reduces the diffraction efficiency[20]. Hence the low diffraction efficiency in MBPVA/water can be attributed to the presence of water even after the drying process. When methanol was added to MBPVA/water mixture, it forms a binary mixture, which easily removes the residual water. This is because methanol reduces the polarity of water in PVA. Hence the drying process is very fast and diffraction efficiency increases.

Then the gratings were recorded by keeping the number of lines/mm fixed and varying the exposure energy. In all the cases diffraction efficiency was measured. For MBPVA using water as the medium, at lower exposure energies diffraction efficiency was low and then it gradually increased and reached a maximum value and then decreased. This was true for 193 lines/mm (θ-10^0), 605 lines/mm (θ-40^0) and 720 lines/mm (θ-50^0).

But for MBPVA films using methanol as the solvent, diffraction efficiency curve showed two peaks while varying exposure energy. For these two films optimum value observed is for the angle 40^0. Comparisons between two films for three different angles are shown in figure 4.20, 4.21 and 4.22. It was found that at lower exposure energies, there was not much difference in the diffraction efficiency for these two films. Corresponding to exposure energy of the order $2000 mJ/cm^2$ at 40^0 for MBPVA films prepared using methanol as the solvent, we could get up to 6th order of diffracted pattern. But we are unable to photograph it because of its low intensity. The photograph of 3 rd order diffracted pattern obtained on the methylene blue sensitized PVA/methanol films is shown in figure 4.23.

In the present study we obtained a maximum of 20% and 6.6% diffraction efficiency for MBPVA/methanol and MBPVA/water respectively These two films can be prepared in the laboratory conditions with much easiness and can be used for holographic recording. The study of variation of diffraction efficiency with exposure energy also showed an optimum value for the exposure energy. The diffraction efficiency was found to increase with exposure initially, but found to decrease when the exposure energy was increased further. The reason for this may be due to the following facts. When the exposure energy was 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. But when the energy increases there will be a chance for the dye molecules to 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 for the observed diffraction efficiency at high exposure energies.

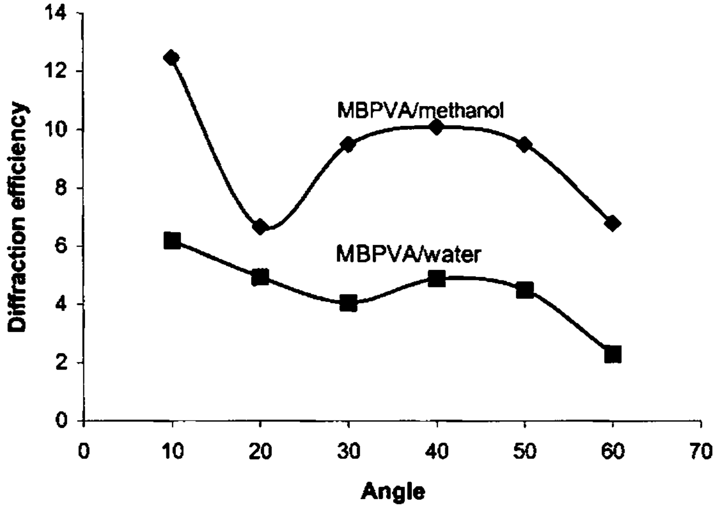


Fig. 4.19. Variation of diffraction efficiency with angle for MBPVA/methanol and MBPVA/water.

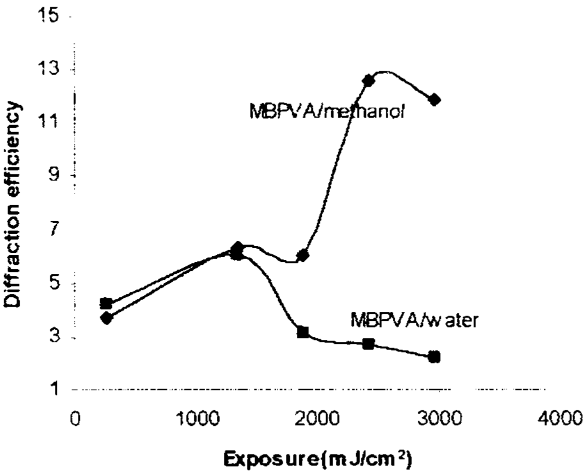


Fig.4.20.Variation of diffraction efficiency with exposure for MBPVA/ methanol and MBPVA/water at an angle of 10^0.

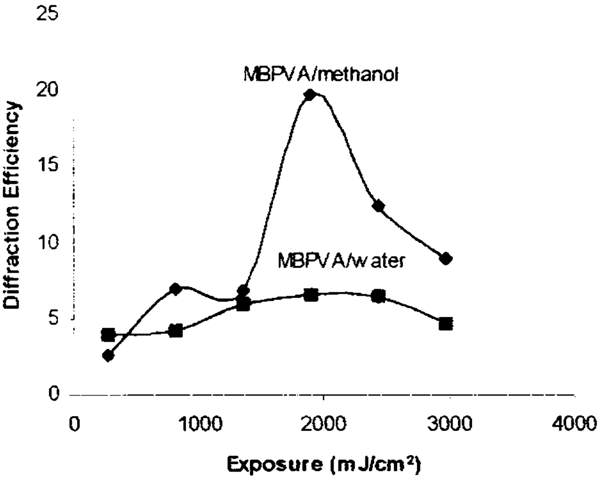


Fig.4.21.Variation of diffraction efficiency with exposure for MBPVA/ methanol and MBPVA/water at an angle of 40^0.

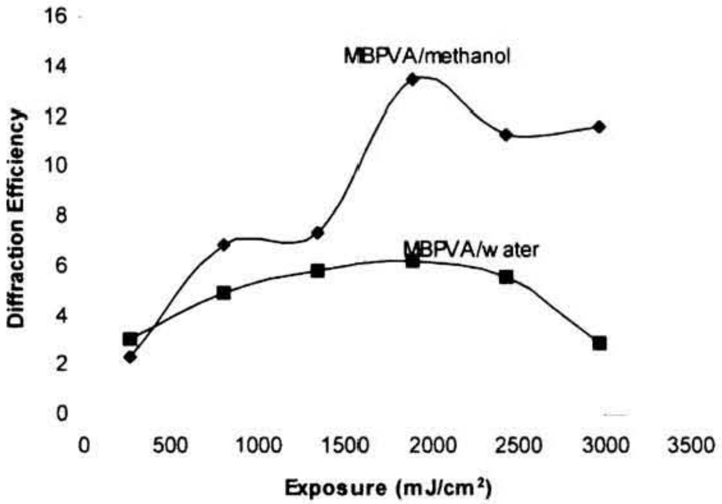


Fig.4.22. Variation of diffraction efficiency with exposure for MBPVA/ methanol and MBPVA/water at an angle of 50^0.

Fig. 4.23. Photographs of the third order diffracted pattern recorded on MBPVA/methanol films

h) H&D Curves

A typical H&D curve for MBPVA/methanol film is shown in the fig 4.24. The amplitude transmittance of the material as a function of the exposure energy is preferable and is plotted in the fig 4.25.

i) Direct Imaging

Direct imaging was done in the same way explained in section 4.1.4(i). The photograph showing the bleached letters A,O,X recorded on MBPVA/methanol film is shown in fig 4.26. On dark room storage the leuco form of the dye was slowly converted back to the ground state (fig 4.27). After 48 h, the dye completely gets converted to the thionine state, which is shown in fig 4.28.

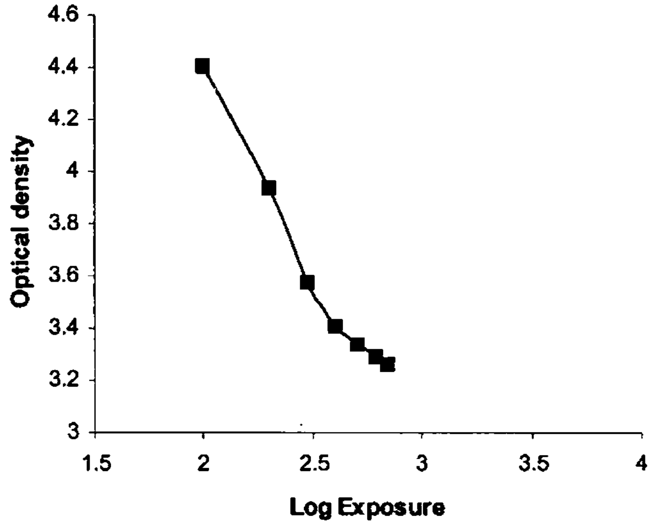


Fig.4.24. A typical H&D curve for MBPVA/methanol film

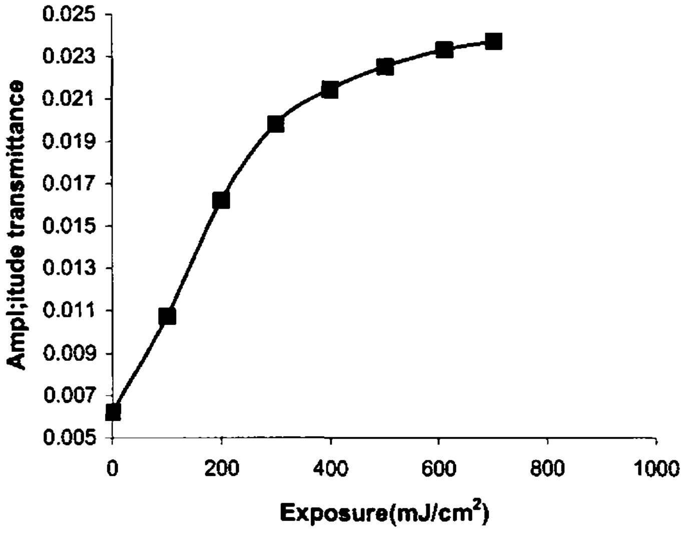
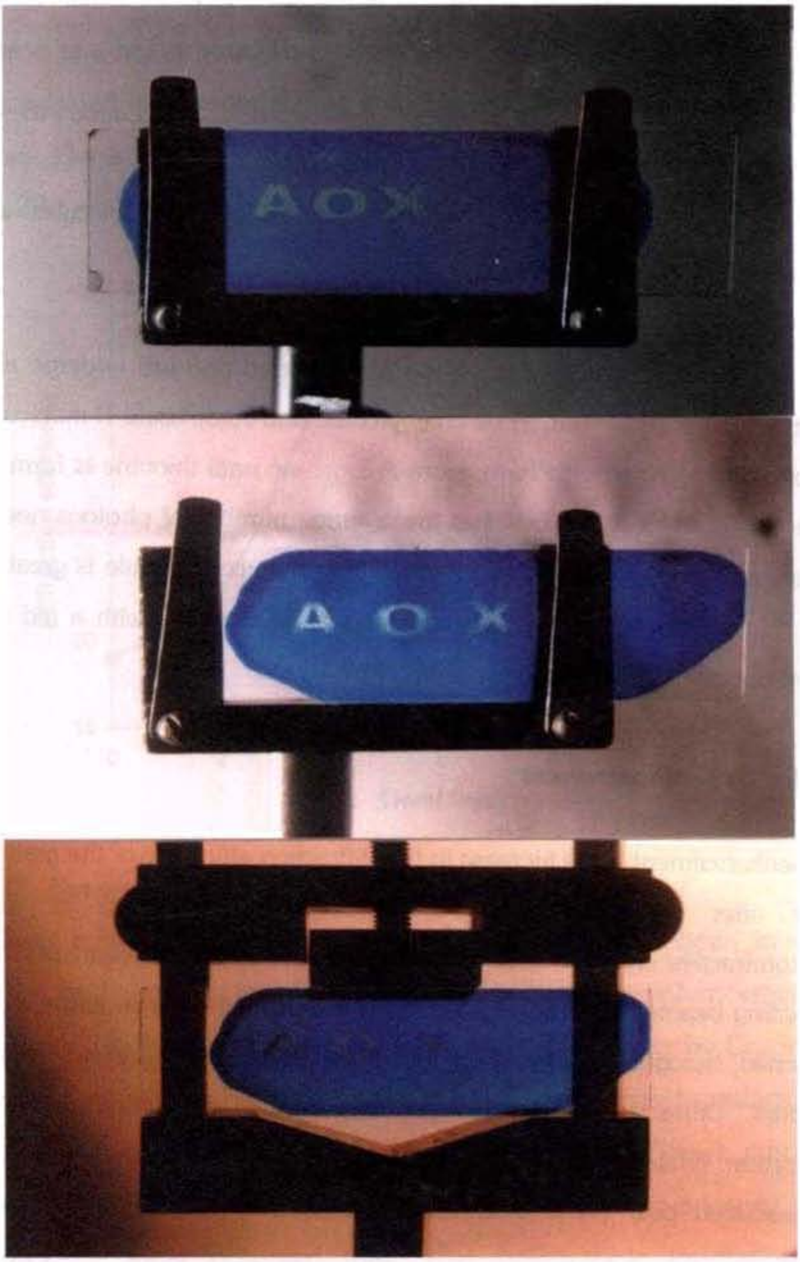


Fig. 4.25. Variation of amplitude transmittance with exposure energy

j) Dye Behaviour

As mentioned earlier the dye used to sensitize the polymer matrix was methylene blue because it presents high absorption at 632.8 nm. Several interesting phenomena were observed after recording the interference pattern. In the exposed area the dye was partially or totally bleached; however when the film was kept in the dark after few hours, the dye recovered itself and presented a different colour. This implies that the dye passed through a transition to the leuco form or excited state, and then decayed to the more stable thionine sate. The expected photochemical reactions that are believed to occur during the bleaching of MBPVA is presented

Photographs showing the gradual recovery of dye in this matrix (fig 4.26,4.27,4.28)



Bleaching mechanism of MBPVA

(1) Photoexicitation

$$MB + hv \longrightarrow {}^1MB^* \longrightarrow {}^3MB^*$$

(2) Redox reaction

$${}^3MB^* + PVA \longrightarrow \text{intermediate products} \longrightarrow \text{Leuco } MB + PVA$$

Other reactions will take place at the same time as

(1b) Photodemethylation: A certain proportion of MB molecules will be demethylated by light.

$$MB^+ + hv \longrightarrow \text{azure B}$$

(1c) Some azure B molecules will be photoexicted and will undergo a redox reaction with PVA to form azure B molecules, and some azure B molecules will be photodemethylated to form azure A ...... etc until thionine is formed and photo reduced. It is obvious that the average number of photons needed to transform one methylene blue molecule into a leuco molecule is greater than one [21]. More over if the irradiated area was investigated with a red colored beam the diffracted orders were seen.

j) Self enhancement

Self-enhancement is the increase in the diffraction efficiency of the grating over time after the recording. Self-enhancement has been reported in photorefractive crystals [22]. in amorphous films [23] and in polymers [24-26] .The recording beams were expanded and the real time diffraction efficiency of the recorded holograms were measured. Fresenel losses were not taken into account. Diffraction efficiency was measured as a function of time. The saturation similar to the earlier studies [25] was observed as in the case of dichromated poly (vinyl alcohol). The maximum diffraction efficiency was found to be 38% for MBPVA grating. The total intensity of the recording beam was 4.5mW.cm^2. After recording was stopped the diffraction efficiency started to increase at a higher rate. The diffraction efficiency was detected for 10 days and it continued to increase during the entire time and saturating at the end of detection. The self-enhancement observed in MBPVA/methanol is shown in figure 4.29.

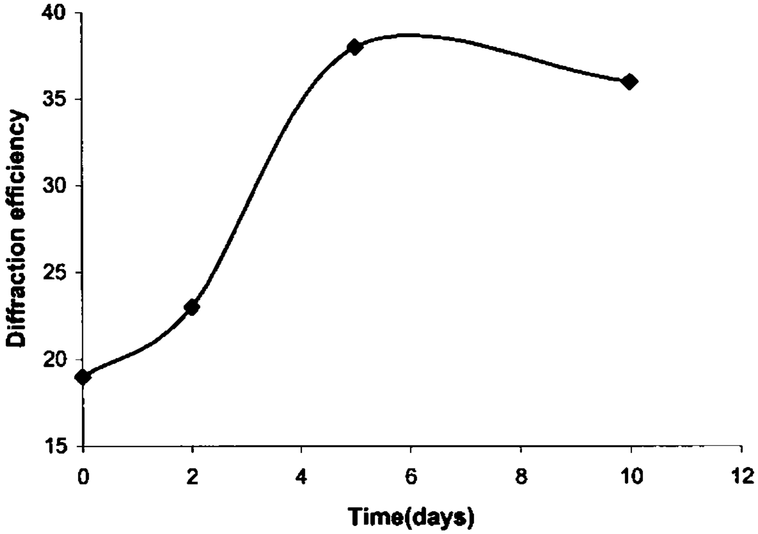


Fig. 4.29. The variation of diffraction efficiency with time

MBPVA as a real time hologram recording material has been investigated during the past decades by many researchers. A strong enhancement effect, reinforcement has been demonstrated in thionine-PVA layers by Caron et al[27]. Ozols et al[23] have reported self enhancement of holographic gratings in As_2S_3 crystals with an enhancement factor 18. Lougnot et al [28] have modeled the hologram formation on photopolymers taking diffusion into account. Lougnot and Turck [24] have observed that, after holographic irradiation of the photopolymer was interrupted at an early stage of conversion, thermal post polymerization enhances the spatial modulation of the segment density. The key phenomenon is the balance between the chemical initiation of the polymerization and diffusion of the unreacted species. A slight enhancement at low energy was observed.

However it should be remembered that these studies were done without any fixing or chemical development process on these dye-sensitized films. The maximum diffraction efficiency for self-enhancement after recording rises in 2 days. A diffraction efficiency of 19% of MBPVA grating at the end of the exposure increases to 38% over 10 days after recording process, the self enhancement gain was thus 2 and the gratings was stored the entire time in the same room conditions that they were recorded. After 20 days the diffraction grating recorded on these samples almost vanished. This self-enhancement may be due to dark reaction or polymerization. Polymerization was not finished during the drying period, it continued bringing new cross-links which are responsible for the grating formation[25].

4.2.3.2. Mechanical properties

No change in mechanical properties was observed on doping PVA in methanol with methylene blue. Even the change of solvent does not bring about any change in the mechanical properties like tensile strength, elongation at break of undoped and methylene blue doped PVA in methanol. Table 4.2 shows the value of tensile strength and elongation at break for undoped PVA and methylene blue doped PVA in methanol.

Table 4.2 Comparison on the mechanical properties of undoped and doped PVA in methanol films

PVA	Tensile strength (N/mm^2)	Elongation at break (mm)
Undoped PVA	39	90
Doped PVA	38.5	95

4.2.4. CONCLUSIONS

- Methanol is a good medium for MBPVA than water.
- Fabrications of the films are easier than the conventional MBPVA/water system.
- Drying period is only approximately 12 h for this film.
- Very fast bleaching was observed for an optimum sensitizer concentration of 2.91×10^{-4} mol/l and pH 6.
- Sixth order-diffracted pattern was obtained on these samples.
- Diffraction efficiency obtained on MBPVA/methanol films is higher compared to the conventional MBPVA/water system.
- Self-enhancement was very prominent in these films.
- Threshold and saturation energy of these samples are 200 and 900 mJ/cm^2 respectively.
- The storage life of this material is high compared to CMBPVA and MBPVA/water system.
- Direct imaging was done on these samples.
- Holograms were recorded on these films.

PART 1I I

4.3. STUDIES ON METHYLENE BLUE SENSITIZED POLYMER BLEND OF POLY (VINYL ALCOHOL)/POLY (ACRYLIC ACID) FOR OPTICAL RECORDING

In methylene blue sensitized PVA films, whether complexed or by using methanol as solvent, the information stored was not found to be stable for weeks. This is due to the reconversion of leuco methylene blue back to its original form. Our attempt was to convert MBPVA matrix to a permanent recording material with out any fixing process. This difficulty was partially succeeded by blending PVA with poly (acrylic acid) and then sensitizing with methylene blue using methanol as the solvent. Close et al [29] mentioned about the use of a polymeric solution formed with acrylates sensitized with methylene blue (MB); exposure energy needed was about 1-30 mJ/cm^2 at 694 nm with diffraction efficiencies of 45%. However, the scattering noise reduced the signal to noise ratio and the mixture had poor shelf life. This rapid decrease of photopolymerizing activity is due to the formation of sulfones in the presence of water [30]. The fixing process was done by optical methods i.e. exposure to ultraviolet radiation which converted the dye to colourless form. Later Jenny [31-33] studied different forms of the above mixture, finding sensitivities of ~0.6mJ/cm^2. Diffraction efficiency of 80% was achieved, but at spatial frequencies>150 lines/mm and the signal to noise ratio diminished considerably. One of the drawbacks of this material was that some of the composing materials were poisonous and volatile. Also the presence of surface grating sometimes out weighed the bulk effects.

Another improvement of the mixture that used acrylamides was presented by Van Renesse[34]. He added methylene-bis-acrylamide to speed up the polymerization reaction. A molecular space lattice of acrylamide chains was formed, and in this the methylene-bis-acrylamide built crosslinks to form a copolymer with transparent and rigid characteristics. The sensitivity of this mixture was ~5mJ/cm^2. The draw back with this material seemed to be the lack of adhesion of the photosensitive material to the substrate and the crystallization of chemicals. The recorded holograms could be kept in good condition for only one week. An improvement of this mixture was cited by Sadlej [35]. Later Sugawara et al [30] reported a method that used a mixture of acrylamide and methylene bis acrylamide with a photoreductant such as acetyl acetone or triethanol amine. Diffraction efficiency of ~65% at exposure of 50mJ/cm^2 were obtained. Photosensitivity was maintained for more than 80 days. No optical fixing of photopolymer was performed during this study.

A different approach was taken by Jeudy and Robillard [36] who used a photo chrome that changed its absorption band when excited by UV light having a wave length of 0.3-0.4μ m. When this material is in its excited state it act as a sensitizer for photo polymerization process in the same way as an ordinary dye sensitizer. In that case the sensitizing action will only exist when irradiation with UV light occurs and a fixing process is not needed. One draw back of this material was that it should be used with in 4-5 days after preparation.

Following the procedure laid by Jenny, Sadlej and Smolinska[38] added a protective polymer to the photosensitive system. In this way they produced stable photosensitive layers, which are used to make diffraction grating and holograms. The protective layers were poly (vinyl acetate), methyl cellulose, poly (vinyl alcohol) and gelatin. To control the rate of photoreaction of methylene blue they used p-toluene sulphonic acid sodium salt. For some mixture they obtained volume effects, but unfortunately diffraction efficiencies of 0.5% could only be obtained. In the case where surface relief modulations were present, diffraction efficiencies of ~4% were measured for sensitivity ~10mJ/cm^2. Thus research in new photopolymeric material is necessary before truly high performance and optical holographic information processing system can be realized. Therefore it is tempting both scientifically and technically to try to develop and study systems for holographic information recording that would posses both the advantages of easily photopolymerisable systems (such as acrylic acid) and the specific positive properties of PVA. The studies reported here include the optimization of the amount of PAA in PVA, sensitizer concentration, pH, behaviour of absorbance, transmittance, storage, rate of bleaching as a function of exposure /time, interferometric studies, dark self enhancement studies, direct imaging etc. It was found that this polymer mixture exhibited outstanding properties than the conventional MBPVA [methylene blue sensitized poly (vinyl alcohol)] system.

4.3.1.EXPERIMENTAL

Preparation of methylene blue sensitized poly(vinyl alcohol)/poly (acrylic acid) blend

Samples were prepared under normal laboratory conditions as follows:

Preparation of 10% poly(acrylic acid) solution.

Acrylic acid was procured from M/s. E.Merk, India Ltd and used as such. Poly (acrylic acid) was synthesized by batch polymerization of acrylic acid using potassium persulphate initiator. A three necked flask fitted with a funnel, reflux condenser, thermometer and a stirrer, was charged with distilled water (90g) and heated to 90^{0}C. Potassium persulphate (0.2 g) was carefully added, followed by acrylic acid (10 ml) slowly but with constant stirring. The temperature was maintained at 90^{0}C and heating was continued for 2-3 hours. The solution obtained was 10% poly (acrylic acid). The molecular weight of poly (acrylic acid) was estimated as 3,34,000 using Ubbelhode viscometer.

Preparation of 10% poly (vinyl alcohol)

PVA (molecular weight 1,25000) (10g) was dissolved in distilled water(100ml).

Preparation of the dye solution

Methylene blue (0.3 g) was dissolved in distilled water(20 ml).

Different proportions of PVA and PAA were mixed and to this methanol were added to get a clear homogeneous solution. The ratio of PVA: PAA was varied from 10:0 to 0:10. A homogeneous solution was obtained by mixing methylene blue with the above solution.

Films of this methylene blue-doped polymer solution were prepared as explained in 2.2.2. The thickness of the film was maintained to be 0.01mm. For pH measurements, a digital pH meter (systronics 335) was used. pH was decreased by adding hydrochloric acid and increased by adding ammonia solution. The absorption spectra of the samples in the visible region before and after exposure are taken using a Hitachi 330 UV-VIS NIR spectrophotometer. To determine the power necessary for bleaching, the samples were exposed to power varying from 90μW to 6.4 Mw for 20 sec and the change in transmittance was noted.

It is very difficult to remove water from poly (acrylic acid). A decrease in film clarity and non-uniformity was observed when a ratio 6:4 (PVA: PAA) or lower than that was used. So a detailed study was done for the ratio 7:3, 8:2, and 9:1. These films were exposed to 5mW He-Ne laser (wavelength-632nm) for 5 min and the change in transmittance was monitored.

To determine the rate of bleaching of the optimized sample, it was exposed to a laser power of 5mW. The transmitted intensity was measured at regular intervals (at every 20 sec) for 10 min using a power meter.

4.3.2. EXPOSURE TO 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 using a spatial filter arrangement set up in the laboratory. The samples were placed in the expanded beam.

The experimental set up is shown in figure2.2.8. The transmitted intensity is measured using a power meter (OPHIR model 2000). The effects of He-Ne laser irradiation on the absorption spectra of MB PVA/PAA [methylene blue sensitized poly (vinyl alcohol)-poly (acrylic acid)] films were studied using a Hitachi 330 UV-VIS-NIR spectrophotometer.

4.3.3. RESULTS AND DISCUSSION

a) Determination of molecular weight of poly (acrylic acid)

The molecular weight of poly (acrylic acid) prepared by bulk polymerization was estimated as 3,34,300 using Ubbelhode viscometer as explained in section 2.3.3.The experimental and calculated data are given in table 4.3.

Table 4.3.Calculated data for viscosity measurements

CONCENTRATION	RELATIVE VISCOSITY	SPECIFIC VISCOSITY	REDUCED VISCOSITY	INHERENT VISCOSITY
0.0741	1.4147	0.4167	5.6235	4.7004
0.1379	1.9167	0.9167	6.6476	4.7179
0.1935	2.8533	1.5833	8.1824	4.9050
0.2424	3.1667	2.1667	8.9385	4.7554
0.2857	3.8333	2.8333	9.9170	4.7032
0.3243	5.0833	4.0833	12.5911	5.0139

Calculation of molecular weight

$[\eta] = K M^a$

$K = 76 X 10^{-3}$, $A = 0.5$

[K, a values are taken from polymer hand book]

$[\eta] = 4.4$

∴ Molecular weight of poly (acrylic acid) prepared in the laboratory = 3,34,300

4.3.3.1. *Optical Characterization*

b) Optimization of PVA/PAA ratio

Transparent films were prepared using PVA/PAA at different proportions. It was found that as the amount of poly (acrylic acid) in the blend increased, the film became sticky and useless for optical recording. This is because it is very difficult to remove water from poly (acrylic acid). A decrease in film clarity and non-uniformity was observed when the ratio 6:4(PVA/PAA) or lower than that was used. So a detailed study was done for the ratio 7:3, 8:2, and 9:1. These

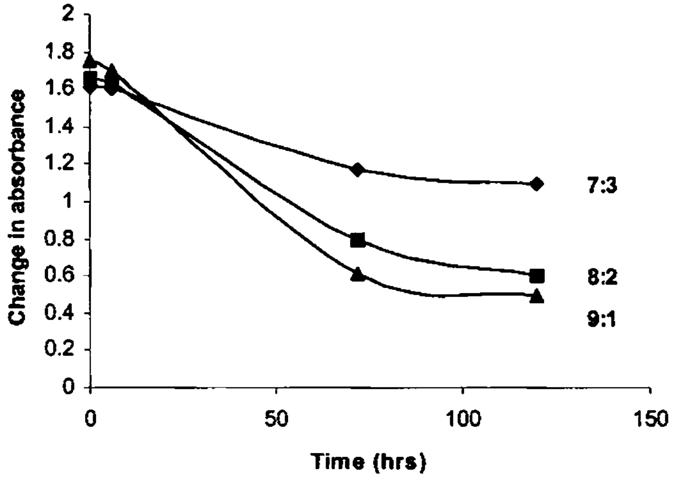


Fig.4.30. Variation of the change in absorbance with time for three different ratios of PVA: PAA.

films were exposed to He-Ne laser (wavelength-632nm) with laser power of 5mW for 5 min and the change in transmittance was monitored. The change in transmittance was found to be almost same in all the three cases. Hence to optimize the ratio, the change in absorbance with time was monitored to find the recovery of dye back to its original form.

Figure 4.30 shows the change in absorbance with time for three different 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 very fast. Since the main motivation behind the study is to develop a new polymeric material, which can be used as a permanent recording medium, 7:3 ratio (PVA/ PAA) was found to be optimum as the recovery of the dye was found to be very slow in this case.

c) Optimization of sensitizer concentration

Keeping the PVA: PAA ratio 7:3, the concentration of methylene blue was varied from 2.9 x 10^{-3} to 2.9x10^{-5} mol/l in the solution. The films thus obtained from this solution were exposed to a laser power of 5mW for 5 min. The

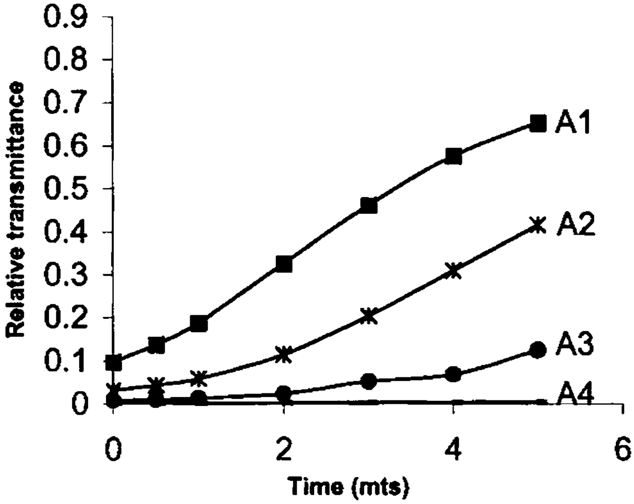


Fig.4.31.Variation of relative transmittance with time for different dye concentrations

change in transmittance was monitored as a function of time. A graph was plotted between relative transmittance (T/T^0) and time. A1, A2, A3, A4 in the graph represents the different concentrations of dye employed. From the graph (figure 4.31) it is clear that the relative transmittance is maximum for a concentration of 1.46×10^{-4} mol/l (A4) and very fast bleaching was observed at this sensitizer concentration. This is because at higher sensitizer concentration more number of molecules will be present in the illuminated area, there by requiring more intensity for its excitation in a fixed time.

d) Optimization of pH.

In order to study the effect of pH it was changed from 1 to 11 in PVA/PAA system. The film prepared at low pH lost its clarity and at high pH the film lost its transparency.

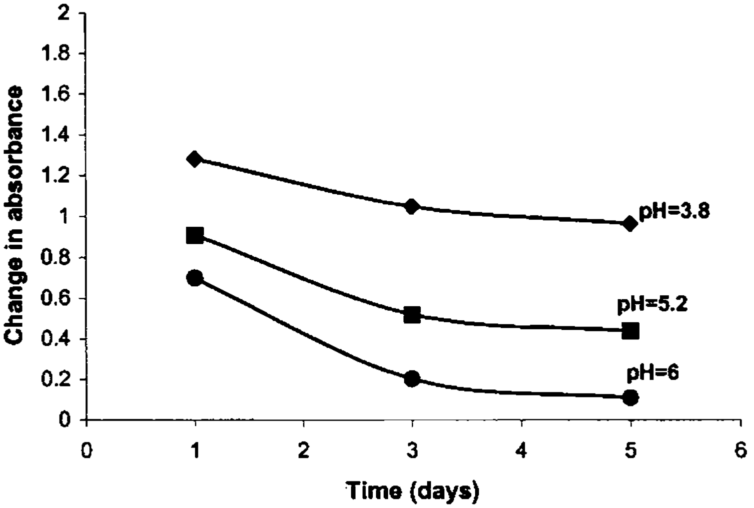


Fig. 4.32. Variation of the change in absorbance with time for different pH

So the experiments were carried out at a pH between 3 and 6. The films prepared at the optimum dye concentration in 7:3 (PVA/ PAA) at different pH were exposed to laser irradiation and the change in absorbance (to note the recovery of dye) as function of time is shown in figure 4.32. It could be seen that as the pH increases the recovery of the dye back to its original form was found to be very fast. At a pH 3.8(normal pH of the system) the recovery was very slow and at pH 6, the recovery was very fast.

Direct imaging was done on all the four samples at pH (3.8, 5, 5.2, 6) to study the recovery of the dye. For this the letter “O” was imaged and the fading was observed. For pH 6 and 5.2, the recovery of the dye was almost complete in 36 and 72 hours respectively and the letter “O” vanished from the film. For pH 5, the recovery was slow and it was almost complete in 8 days. The film of pH 3.8 was found to be very stable for several days and the recorded information’s were found to be long lasting. Hence the pH of PVA: PAA was optimized to be 3.8 for this study. This is because as the pH increases, the solution becomes less acidic and the leuco form becomes unstable resulting in very fast reconversion.

$$MB + H^{+} + e^{-} \rightleftharpoons Leuco\ MB$$

e) Optical absorption measurements

The typical absorption spectra of the exposed and unexposed samples of MB in PVA/PAA are shown in figure 4.33. The exposure time was fixed as 5 min. The spectra showed a peak around 663 nm, which was characteristic of methylene blue. On laser exposure, the material got bleached and the absorption spectrum was broadened. A small shift in absorption spectrum was observed after irradiation. But this shift was not as prominent as methylene blue sensitized poly (vinyl alcohol) in methanol or CMBPVA films. Hence it is evident that there was a change in absorption property of the material on laser irradiation. It is clear from the figure that the recovery of dye in this matrix is

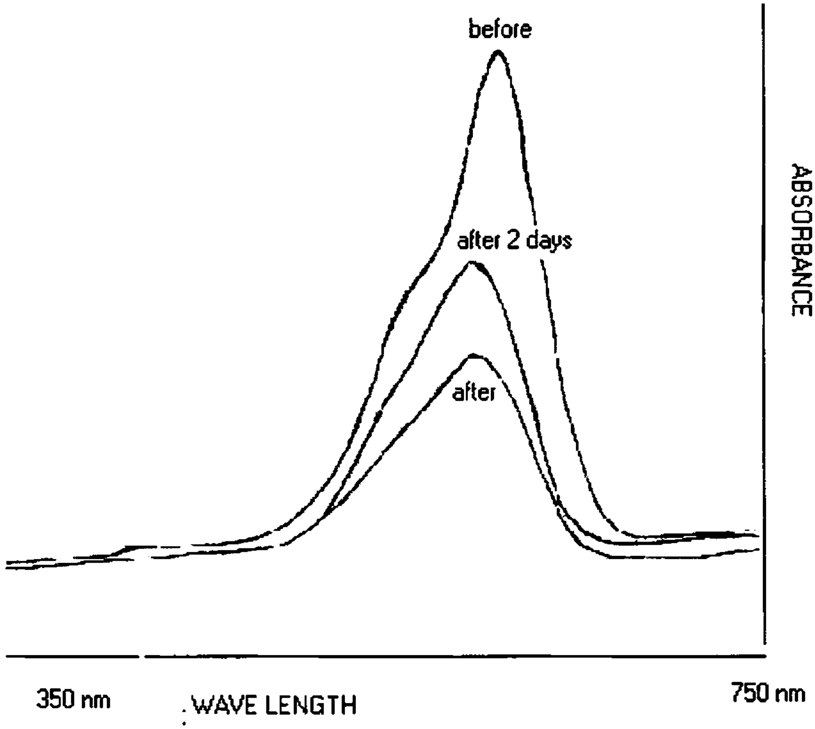


Fig.4.33 The optical absorption spectra of methylene blue doped PVA/PAA films before, after and after2 days.

Very slow even after 2 days, unlike methylene blue in conventional PVA systems. In MBPVA systems the recovery was almost complete in 48 hours. Thus by blending PVA with PAA we can delay the recovery of dye in this polymer matrix.

f) Rate of bleaching

To determine the rate of bleaching the variation of relative transmittance in terms of T/T^0 with time is calculated and plotted. The rate of bleaching was determined by finding the slopes at different time. The rate of bleaching with time for the optimized sample is shown in figure 4.34. The rate of bleaching initially increased slowly and then rapidly, reached a maximum and then decreased. The rate was found to be maximum at 120 sec. By that time most of the methylene blue molecules had absorbed sufficient energy and got converted into its leuco form. In the case of conventional methylene blue doped PVA/water system, the rate of bleaching was found to be very fast initially and no threshold was observed at this laser power. The slow rate of bleaching of methylene blue in this polymer mixture can be due to the higher deactivation energy of PAA in the blend.

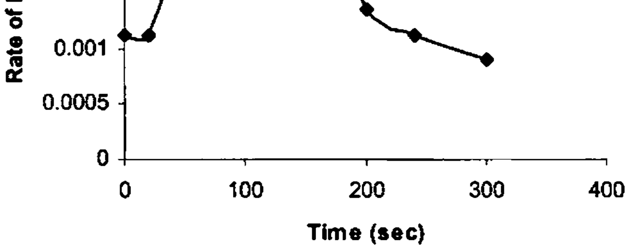


Fig.4.34. Variation of rate of bleaching with time for the optimized MBPVA/PAA films

g) Threshold and saturation energy

As in the case of concentration of the material component, laser 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 118μW was essential for the photochemical change to take place. Figure 4.35 shows the graphical determination of the threshold power of the methylene blue sensitized PVA/PAA blend. To determine the saturation energy of the sample, the optimized sample was subjected to a maximum power of 5mW and the change in transmittance was monitored. The transmittance first increased slowly and then rapidly (Fig.4.36). The threshold and saturation energy of the sample are 300mJ/cm^2 and 2x10^{3}mJ/cm^2 respectively.

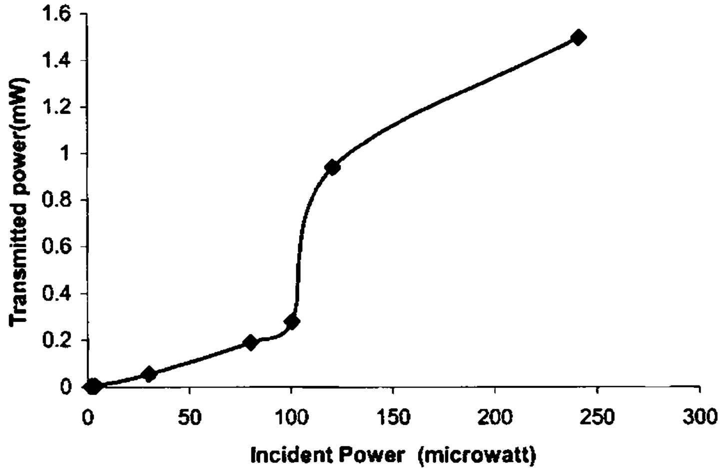


Fig. 4.35. Variation of transmitted power against incident power for MBPVA/PAA films

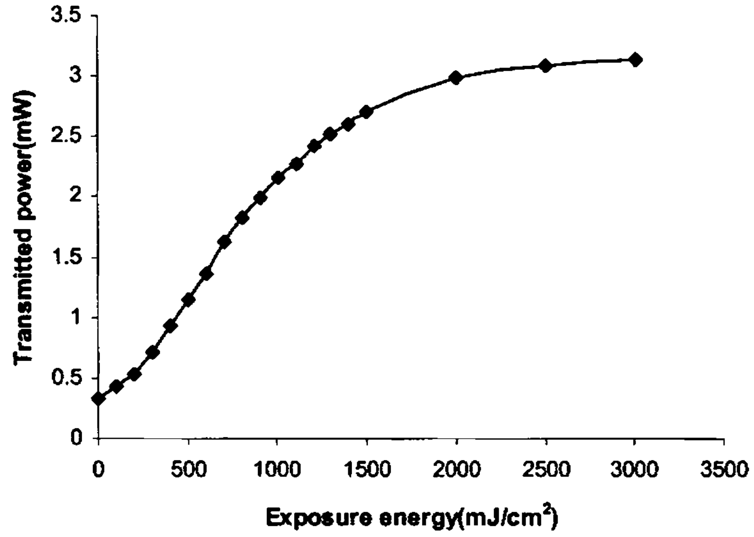


Fig. 4.36. Variation of transmitted power with exposure energy

h) Effect of storage

Even though the possibility of optical recording was suggested by many researchers in methylene blue sensitized PVA, they found that the informations stored were not stable for a long time. The conversion of the leuco form of the dye back to its original form was the reason attributed to this observation.

In the present study on methylene blue in PVA/PAA films, the change in absorption maxima occurred during irradiation remained almost unchanged for a long period of time. To study the effect of storage, the optimized sample was subjected to maximum power so as to reach the saturation point. The transmittance variation of the irradiated sample was monitored as a function of time by sending a laser beam of low power (less than threshold power) and is plotted in figure 4.37. A slight decrease in transmittance at the irradiated spot was observed initially for MB in PVA/PAA film but after that the transmittance remains constant and there was only a slight reduction in transmittance but a sharp decrease was observed in the case of MBPVA/ methanol films, prepared by the same method. Thus it shows that MB PVA/PAA system is more efficient material for storing the information than MB PVA/methanol.

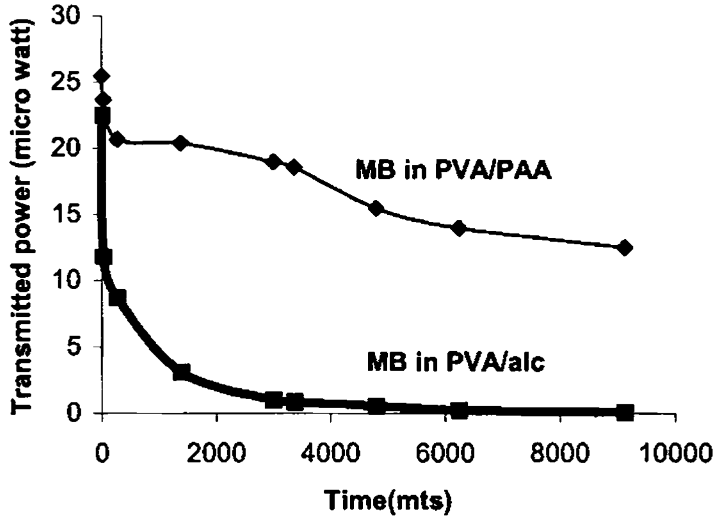


Figure 437. Effect of storage on methylene blue sensitized PVA and PVA/PAA blend

i) Diffraction efficiency

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 photo chemically 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/mm only in the range of 193 to 720 for a particular mirror.

Experimental set up for calculating diffraction efficiency is shown in figure 2.6. The diffracted powers of the diffracted as well as the directly transmitted beam were measured using a power meter. If P_D is the power of the first order diffracted beam and P_T the power of the transmitted beam, then diffraction efficiency is measured using the equation

Diffraction efficiency $= P_D/P_T$

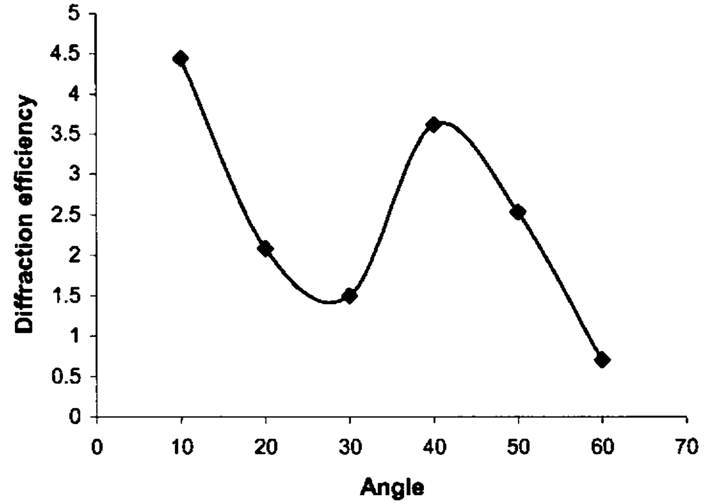


Fig. 4.38. The Variation of diffraction efficiency (D.E) with different angles for MBPVA/PAA films

By varying the number of lines/mm, by adjusting the angle the gratings were recorded on MBPVA/PAA. In all the cases diffraction efficiencies were determined. The diffraction efficiency with different angles for this film is plotted as shown in figure 4.38. The diffraction efficiency decreases at first reaches a minimum, then increases gradually, reaches a maximum value and then decreases. 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. The gratings were recorded by keeping the angle fixed and varying the exposure energy, the power of combined recording beam falling on the film was measured using a power meter.

The beam was allowed to fall on the film for a fixed time. The experiment was repeated by changing exposure time. In each case exposure energy was calculated using the equation

Exposure energy = Power x Exposure time

In all the cases diffraction efficiency was measured as before. It was observed that at lower exposure energies diffraction efficiency was low, then it gradually increased with exposure energy, and reached a maximum value and then decreased. This was true for the angle 10^0,40^0 that we studied. The variation of diffraction efficiency with exposure energy for these two different angles was plotted as shown in figure 4.39 and 4.40 respectively

Variation of diffraction efficiency with exposure energy also showed an optimum value for the exposure energy. The diffraction efficiency was found to increase with exposure initially, but found to decrease when the exposure energy was increased further. The reason for this may be due to the following reasons. When the exposure energy was increased, initially the bleaching process will take place in the exposed regions thus converting the dye to 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

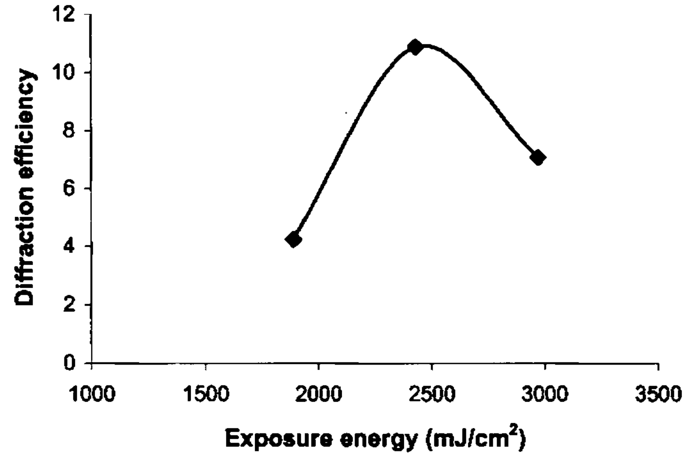


Fig. 4.39. Variation of diffraction efficiency with exposure energy at an angle of 10^0

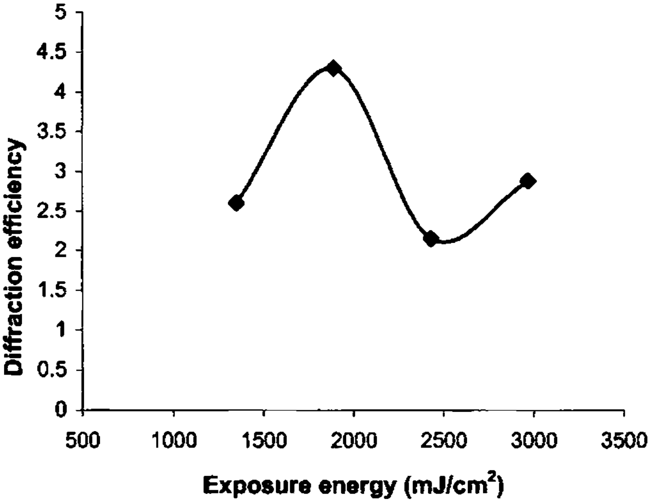


Fig. 4.40. Variation of diffraction efficiency with exposure energy at an angle of 40^0

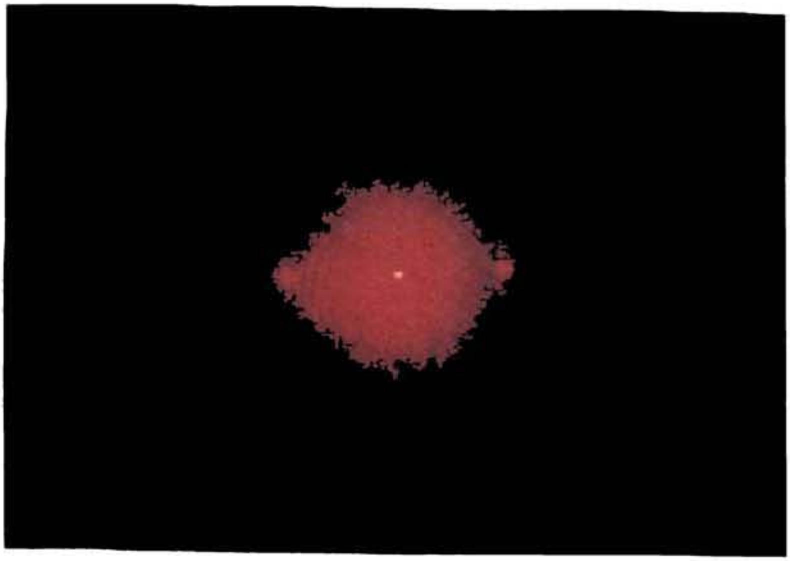


Fig.4.41. Photograph of the diffracted pattern obtained on illuminating the planar MBPVA/PAA films

Fig 4.42.A photograph of the letter 'S' recorded on MBPVA/methanol film

Fig 4.43.The photograph of the alphabets H,A,C,X,O recorded on MBPVA/ methanol film

thionine state, 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 for the diffraction efficiency at high exposure energies. The photograph of the diffracted pattern obtained on this material is shown in figure 4.41. First and second order pattern was obtained on this material.

j) Direct imaging

The medium consists of a polymer blend on which the methylene blue molecules are uniformly suspended. The recording wavelength of this material was determined by the photosensitizer (MB), which in this case has an absorption peak close to red 632.8nm 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 MBPVA/PAA film placed on a film holder. The beam was allowed to fall on the material for 5 min. After imaging it could be observed that the letters were very legible and had good clarity. Before exposure the methylene blue molecules are uniformly distributed through out the medium. However during the imaging process the modulated pattern produces corresponding change in the film. We believe that this change results from the conversion of the dye molecules to the leuco form. Since the reconversion is a slow process in this blend, the concentration gradient developed due to the excitation of the dye molecules as a result of illumination remains fixed in their location. Thus the recorded images are more or less permanent. The photographs of direct imaging done on MB PVA/PAA films are shown in figure 4.42&4.43

k) H&D Curves

A typical H&D curve for MBPVA/ PAA film is shown in the fig (4.44) and the

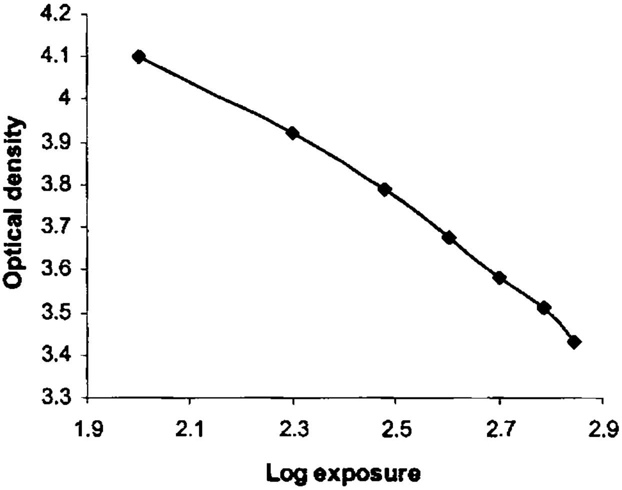


Fig 4.44. Variation of optical density with log exposure.

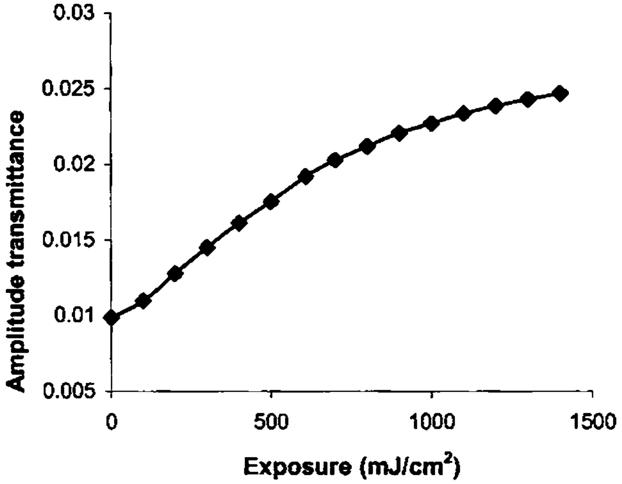


Fig 4.45. Variation of amplitude transmittance with exposure

variation of amplitude transmittance with exposure is shown in figure 4.45. The pattern of this graph is in close agreement with the conventional photographic plate.

l) Self enhancement

A strong enhancement effect, reinforcement, has been demonstrated in this methylene blue sensitized polymer blend. The observed self-enhancement for methylene blue 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 figure 4.46.. However it should be remembered that these studies were done without any fixing or chemical development processes on these dye-sensitized films. In the case of blend the diffraction efficiency of 3.2% (total intensity of the recording beam power was 4.5mWcm^2, which was same as that of MBPVA/methanol) increased to only ~4.5 %, over 15 days, showing that the enhancement process was rather very 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 gratings and the grating was stored the entire time in the same room conditions that they were 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:

a) Dark reaction

b) Diffusion
c) Polymerization
d) Internal stress on the film

Polymerization may be 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. 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 by facilitating shorter exposures than general for these materials and thus vibration free exposures

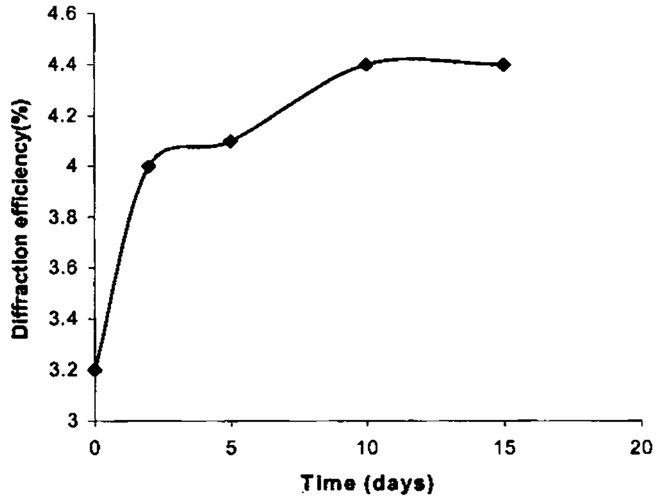


Fig.4.46. Change in diffraction efficiency after exposure for MBPVA/PAA films

m) Dye behaviour

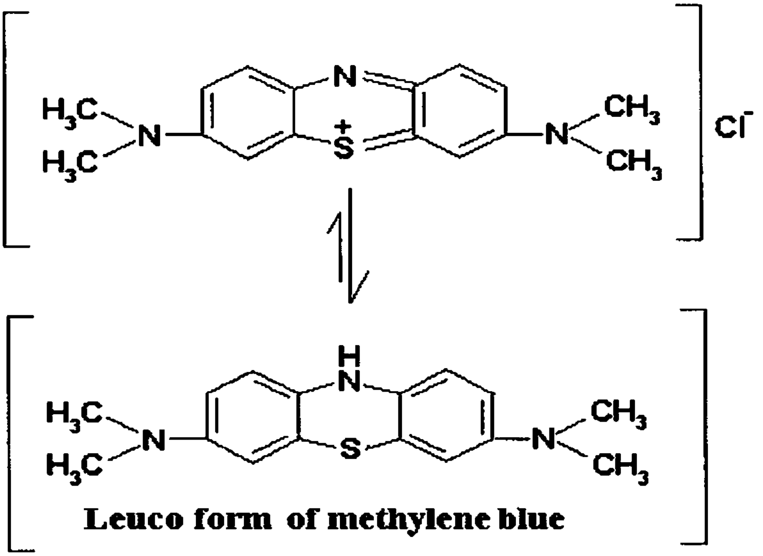
As mentioned earlier the dye used to sensitize the polymer matrix was methylene blue because it presents high absorption at 632.8 nm. Several interesting phenomena were observed after recording the interference pattern. In the exposed area the dye was partially or totally bleached; even though the plate was kept in dark, after few weeks the dye changed itself and presented a different colour. More over if the irradiated area was investigated with a red colored beam the diffracted orders were seen. This implies that the dye passed through a transition state to the leuco form or excited state, and then decayed to the more stable thionine state.

The photosensitizing action of dye results from the ability of the dye to act either as a strong oxidizing or as a strong reducing agent in the presence of reduced or oxidisable substance, with subsequent regeneration and returning to the normal state.

The structure of methylene blue and its leuco form is shown below . Methylene blue is a basic dye of the thiazine group. MB when irradiated with red light, it is excited to MB* where it is converted to a stable leuco form.

$$\mathrm{MB} \rightleftharpoons \mathrm{MB}^* \longrightarrow \mathrm{MB}^1 \longrightarrow \text{Leuco MB}$$

According to the mechanism, the photoexicted dye (in the (n, π^*) triplet state) is reduced by the oxidisable reactant by a transfer of electron or hydrogen. The semi-reduced dye radical is either reoxidised to the ground state by oxygen or is not regenerated, but is transformed to the leuco dye, i.e. photo bleached. This sensitized oxidation can also lead to a sensitized photo destruction of the dye. In these cases MB serves as oxidisable substrate as in bleaching of aerated chlorophyll by high intensities of light.



Leuco form of methylene blue

The triplet excitation transfer may be efficient in many photo bleaching process of methylene blue, but only a few exact studies have been made so far. In most of the studies with MB in different polymer matrices, it is observed that the exposed part of the plate can recover its original colour after some time [38] 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 work on MBPVA/PAA blend, the conversion of leuco form back to the original form was observed to be much a slower process as the information stored could be retained for several weeks without much deterioration. The recovery of dye in the polymer matrix can be delayed more, by increasing the amount of PAA. But PAA cannot be increased in the polymer blend since that make the film less sensitive to laser and sticky. The role of PAA in this matrix is very important and yet to be predicted.

4.3.3.2. Mechanical properties

No change in mechanical properties like tensile strength and elongation at break was observed when methylene blue dye was doped in the PVA/PAA blend. This shows that dye doping does not bring any change in the film. The value of tensile strength and elongation at break of doped and undoped PVA/PAA blend is summarised in the table 4.4

Table 4.4. Comparison on the mechanical properties of undoped and doped PVA/PAA blend.

PVA/PAA blend	Tensile strength (N/mm^2)	Elongation at break (mm)
Undoped PVA/PAA blend	42	120
Doped PVA/PAA blend	41	114

5.3.5. CONCLUSIONS

- MBPVA/PAA in methanol can be used as a permanent recording material.
- Recovery of the dye was found to be very slow compared to methylene blue sensitized PVA films.
- Diffraction efficiency of approximately 11% was attained on this material.
- By changing the pH we can control the recovery of dye in this matrix.
- The information stored was stable for 3 weeks, and did not need any fixing process.
- Direct imaging was done on these samples.
- Very fast bleaching was observed for an optimum sensitizer concentration of 1.46×10^{-4} mol/l.
- The threshold and saturation energy of these samples are 200 mJ/cm^2 and 1800 mJ/cm^2 respectively.
- The role of PAA in fixing the dye in this polymer blend was clearly investigated.
- The major attraction of this material is its excellent optical clarity, shelf life, environmental stability, storage life, low cost etc.
- Self enhancement in the diffraction efficiency exhibited by MBPVA/PAA facilitate shorter exposures than general for this materials and thus vibration free exposures
- Holograms were successfully recorded on these samples

PART 1V

4.4. A COMPARATIVE STUDY ON METHYLENE BLUE SENSITIZED POLYMER FILMS FOR OPTICAL RECORDING

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. Among the great number of photosensitive holographic media, photopolymers that combine considerable sensitivity with high diffraction efficiency and easiness of preparation are of interest. We have introduced a new polymer matrix poly (vinyl chloride) for holographic recording whose characterization is explained in chapter 3. Methylene blue is a common sensitizing dye for polymer matrices like poly (vinylalcohol), gelatin, poly (methymethacrylate), and acrylamide based polymers, because it has the absorption maxima same as that of the wavelength of inexpensive laser diodes and He-Ne laser used. Moreover the spectral region can be extended to 700nm.

Studies on methylene blue sensitized gelatin and poly (vinyl alcohol) (in water medium) possess the shortcomings of shorter storage life, lack of environmental stability, need drying for long time before hologram registration, susceptible to high humid conditions, needs fixing process etc.

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

4.4.1.EXPERIMENTAL PROCEDURE

a) ***Preparation of methylene blue sensitized poly (vinyl alcohol)/ poly (acrylic acid) blend [MBPVA/PAA]***

The polymer films of MBPVA/PAA were prepared as explained in section 4.3.1.

b) Preparation of methylene blue sensitized poly (vinyl alcohol) in methanol [MBPVA/methanol]

The polymer films of MBPVA/methanol were prepared as explained under section 4.2.1.

c) Preparation of complexed methylene blue sensitized polyvinyl chloride in cyclohexanone [CMBPVC]

The polymer films of CMBPVC were prepared as explained under section 3.2.

d) Preparation of complexed methylene blue sensitized polyvinyl alcohol [CMBPVA]

The polymer films of CMBPVA were prepared as explained under section 4.1.2.

Coating was done by pouring a fixed volume of these solutions over clean glass slides, which were kept on a level surface. The thicknesses of all these films were maintained to be 0.01mm. The slides were protected from dust and kept at room temperature for 24 h drying. The optimum concentration and pH of these samples were found out as described in earlier chapters and are given in table 4.5

Table 4.5. A comparison on the optimized concentration and pH of methylene blue sensitized polymers.

Material	Optimum dye concentration	Optimum pH
MBPVA: PAA	1.46 x 10 $^{-4}$ mol/l	3.79
MBPVA/alcohol	2.91 x 10 $^{-4}$ mol/l	5.81
CMBPVC	1.28 x 10^{-3} mol/l.	4.5
CMBPVA	1.27 x 10^{-3} mol/l	10.2

Studies discussed in this section were done on these optimized samples

On irradiating all the four types of samples with an expanded beam of about 5mW, the films were bleached i.e. the samples became colourless. The typical absorption spectra of the unexposed exposed and after 48 h of laser irradiation was taken using a Hitachi 330 UV-VIS-NIR spectrophotometer. The exposure time was kept as 5 min for all the four samples.

To study the rate of bleaching of methylene blue in all the three samples, the optimized samples were exposed under the same laser power for about 5 min.

To study the effect of storage, the optimized samples were subjected to a maximum power so as to reach the saturation point. The change in absorption (difference between the absorption of sample before irradiation and that obtained after exposure for a time t) at the irradiated spot was monitored as a function of time.

To determine the saturation energy, samples were exposed to a laser power of 5mW for 10 min.

4.4.2. RESULTS AND DISCUSSION

a) Optical absorption studies

The typical absorption spectra of the unexposed exposed and after 48 h of laser irradiation of samples CMBPVA, MBPVA/methanol, MBPVA/PAA blend, and CMBPVC, are shown in figure 4.47, 4.48, 4.49, 4.50 respectively. The exposure time was kept as 5 min for all the three samples. In MBPVA/methanol and CMBPVA system the recovery of the dye was almost complete in two days. A broad shift (650 to 635 nm) in absorption spectra of the irradiated sample was also observed. This can be explained due to the conversion of methylene blue molecules to a more stable thionine state. In the case of 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 three weeks. It has been found that as the poly (vinyl alcohol) content in the blend increases, the rate of reconversion of the dye increases. So it is evident that poly (acrylic acid) content in the blend plays a very important role on the recovery of the dye in this matrix. From the figure 4.50 it is clear that no shift in absorption spectrum was found on irradiation on CMBPVC films i.e the leuco form of methylene blue is very stable in PVC matrix and no recovery of dye was observed in this matrix for months

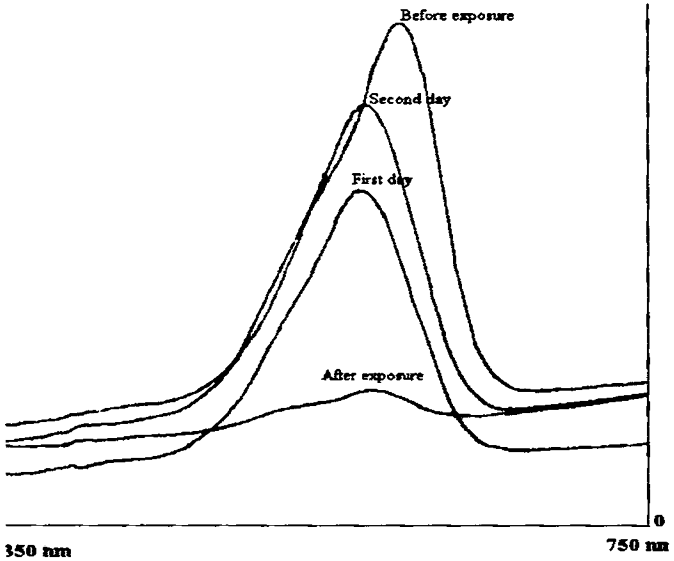


Fig.4.47. Optical absorption spectra of CMBPVA before exposure, after exposure, after 12, 24 hour and 48 hours.

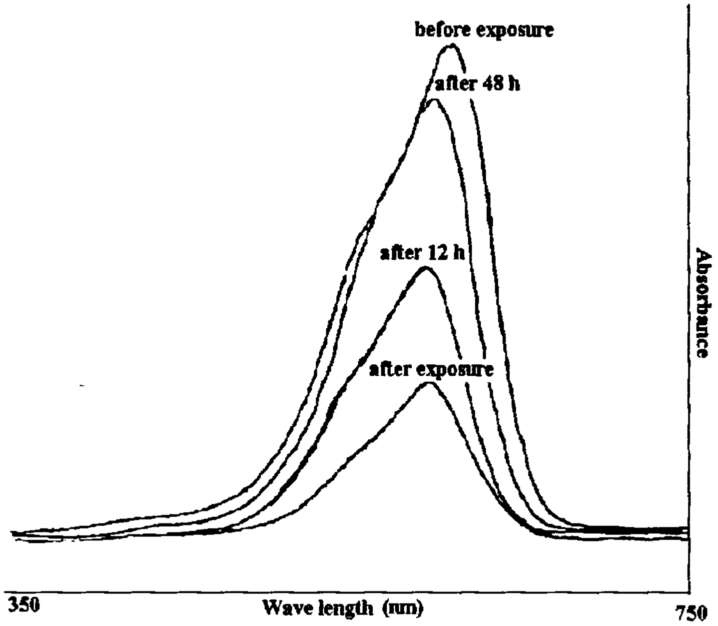


Fig. 4.48. Optical absorption spectra of MBPVA/methanol before exposure, after exposure, after 12 h and after 48 h.

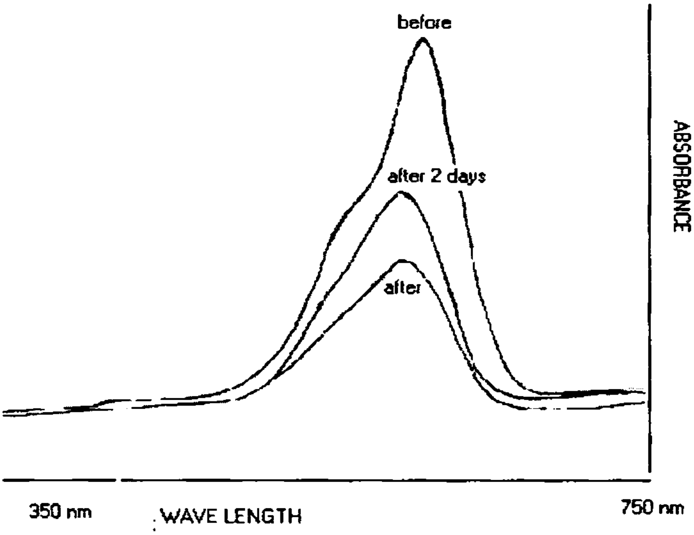


Fig. 4.49 .Optical absorption spectra of MBPVA/PAA before exposure, after exposure, and after 48 h.

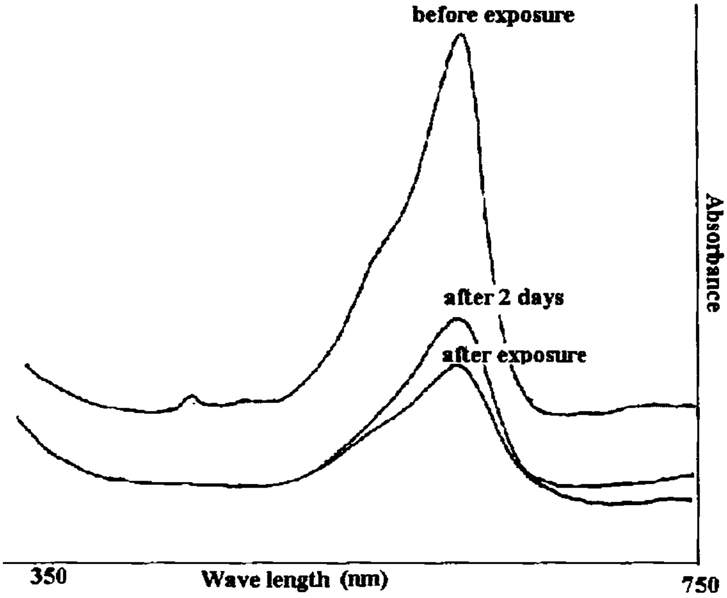


Fig.4.50. Optical absorption spectra of CMBPVC before exposure, after exposure, and after 48 h.

b) Rate of bleaching

The variation in relative transmittance in terms of T/T^0 with time was determined and plotted, from which the rate of bleaching was found out by finding the slopes at different times. The rate of bleaching with time for all the four samples is plotted in figure 4.51. It is very interesting to note that while the rate of bleaching constantly decreases for CMBPVC and CMBPVA, where as the rate increased very fast for MBPVA/methanol, reached an optimum value and then decreased. The blend also showed a similar behavior to MBPVA/ methanol, but the rate increased only very slowly. It is inferred therefore that conversion of leuco methylene blue observed in MBPVA/PAA and CMBPVC

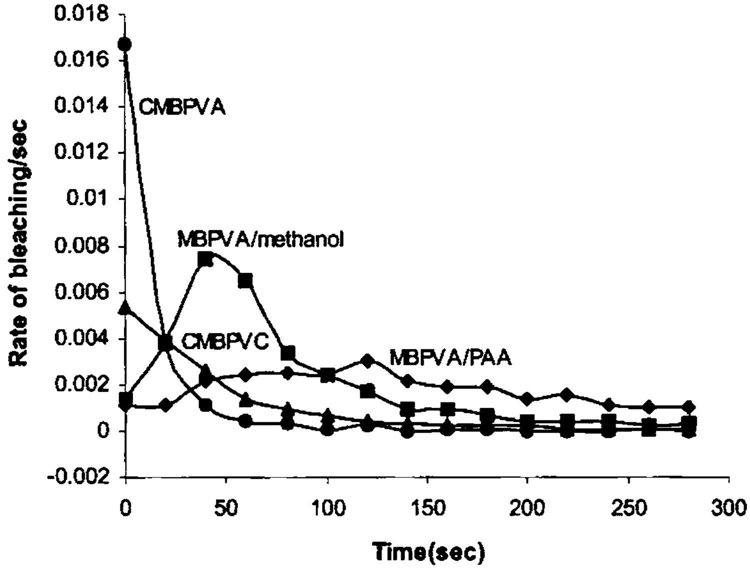


Fig.4.51. Variation of rate of bleaching with time for MBPVA/methanol, CMBPVC, CMBPVA and MBPVA/PAA blend

takes some time where as in CMBPVA and MBPVA/ methanol most of the conversion is finished initially. The rate of bleaching is very high for CMBPVA

c) *Effect of storage*

The change in absorption (difference between the absorption of sample before irradiation and that after exposure for a time t) at the irradiated spot was monitored as a function of time and is plotted in figure 4.52. A small decrease in absorbance change at the irradiated spot was observed initially for MB in PVA/PAA film where as a sharp decrease was observed in the case of MBPVA/methanol and CMBPVA films.

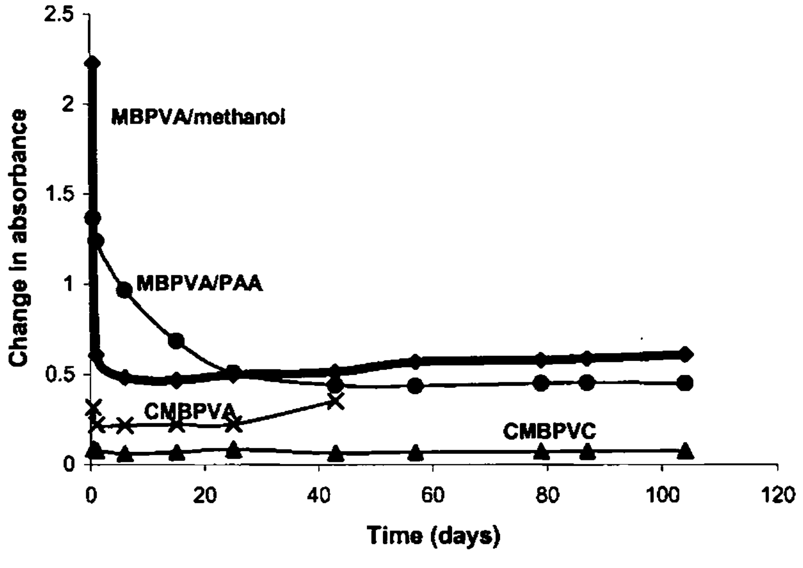


Fig. 4.52. Variation of change in absorbance with time for MBPVA/methanol, CMBPVC, CMBPVA and MBPVA/PAA blend

Where as in the case of CMBPVC films the decrease in absorbance change was found to be very small proving itself to be a permanent recording material. No bleaching was observed in all the samples when exposed to a power as low as 76μ W. It was found that a minimum power of about 100μW, 186μW, 3.8mW and 181μW was necessary for a photochemical change to take place in these MBPVA/methanol, CMBPVA, CMBPVC and MBPVA/PAA blend samples respectively. From this we conclude that a minimum power necessary for the excitation of the dye molecules to the leuco form on these polymer matrices and threshold is more for CMBPVC and minimum for MBPVA/methanol.

To determine the saturation energy, samples were exposed to a laser power of 5mW for 10 minutes. A stage of saturation was observed at an exposure energy of 900mJ, 200mJ, 400mJ and 1200mJ for MBPVA/methanol, CMBPVA, CMBPVC and MBPVA/ PAA blend respectively. Beyond the threshold region very fast bleaching was observed for CMBPVA, MBPVA/methanol, and CMBPVC, but MBPVA/PAA blend showed only a very slow change with exposure energy (figure 4.53). In the case of the blend, it has been found that very high exposure energy was necessary for saturation. This is due to the presence of poly (acrylic acid) in the blend, which delays the excitation of dye molecules.

d) Interferometric studies

Gratings were recorded on MBPVA/PAA blend film and CMBPVC film corresponding to different angle and diffraction efficiencies were measured in all the cases. Diffraction efficiency measurements were not carried out on CMBPVA, due to its high sensitivity.

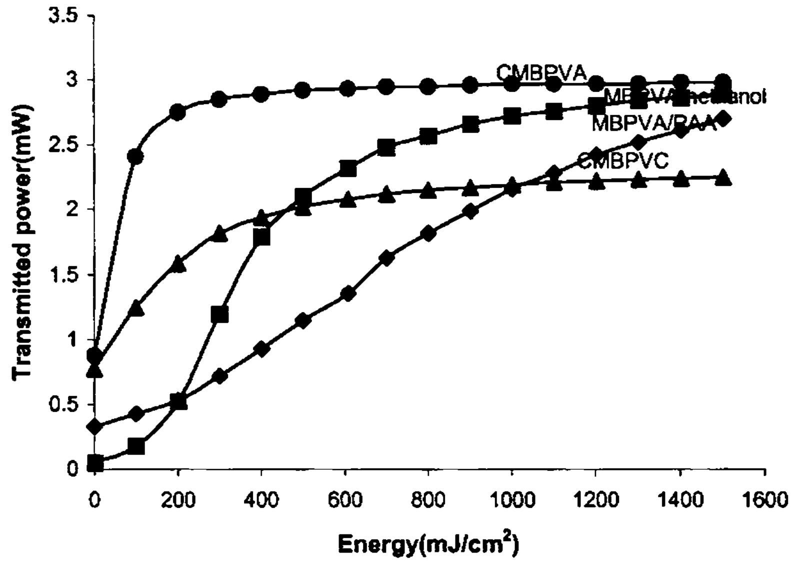


Fig. 4.53. Variation of transmitted power with energy for MBPVA/methanol, CMBPVC, CMBPVA and MBPVA/PAA blend

The diffraction efficiency variations of these two films were then compared with that of MBPVA film prepared in methanol. Interferometric experiments were performed to characterize these photosensitive media. Interference gratings were recorded and the value of diffraction efficiency as a function of incident angle is shown in figure 4.54. It has been found that maximum diffraction efficiency was observed for a fixed exposure at interfering angles of 40^0, 10^0, 10^0 for CMBPVC, MBPVA/methanol and MBPVA/ PAA blend respectively. So a detailed study was done at these angles for different exposures. Maximum diffraction efficiency of about 20%, 4.8%, 10.88% has been achieved for MBPVA/methanol, CMBPVC and MBPVA/ PAA blend respectively. Even though the film property of the polymer blend was not superior to PVA films, a maximum diffraction efficiency of 10.88% was achieved for this polymer blend. These diffraction efficiencies were achieved on all the samples without any fixing or development.

These gratings were also recorded by keeping number of lines/mm or angle fixed and varying the exposure energy. In all the cases diffraction efficiencies were measured. Comparison of variation of diffraction efficiency of MBPVA/PAA blend film, CMBPVC, MBPVA/methanol for three angles(10^0,40^0,50^0) are shown in figure 4.55, 4.56, 4.57. Comparison of the diffraction efficiency in these three methylene blue sensitized polymer matrices is summarized in the table 4.6.given below

Table 4.6.A comparative study on the diffraction efficiency of methylene blue sensitized polymer films

Property	MBPVA/methanol	MBPVA/PAA blend	CMBPVC
Optimum value of number of lines/mm	605 lines/mm	193 lines/mm	193 lines/mm
Maximum diffraction efficiency	20%	10.88%	4.5%

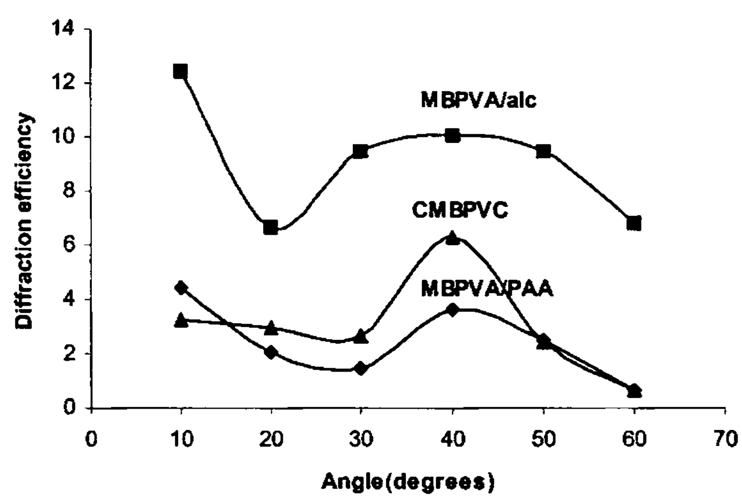


Fig. 4.54. Variation of diffraction efficiency with angle for MBPVA/methanol, CMBPVC and MBPVA/PAA blend

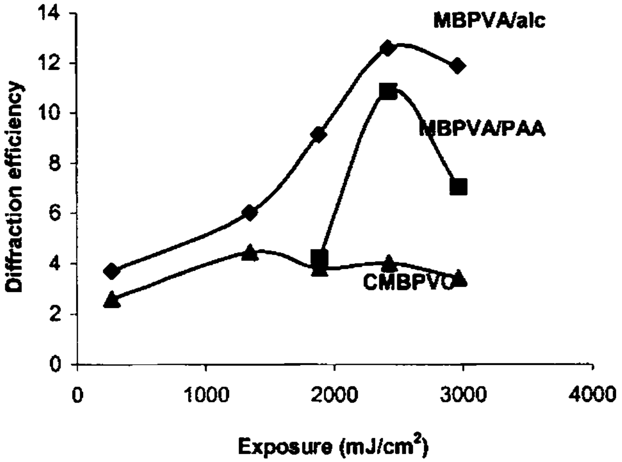


Fig.4.55.Variation of diffraction efficiency with exposure energy at an angle of 10^0 for MBPVA/methanol, CMBPVC and MBPVA/PAA blend

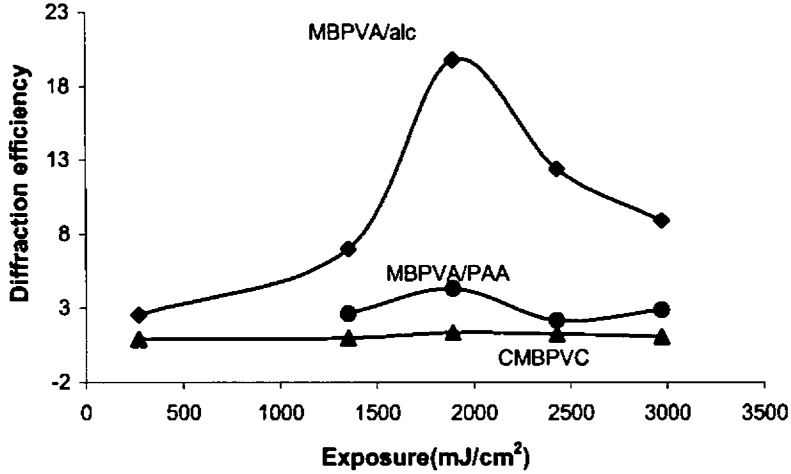


Fig. 4.56.Variation of diffraction efficiency with exposure energy at an angle of 40⁰ for MBPVA/methanol, CMBPVC and MBPVA/PAA blend

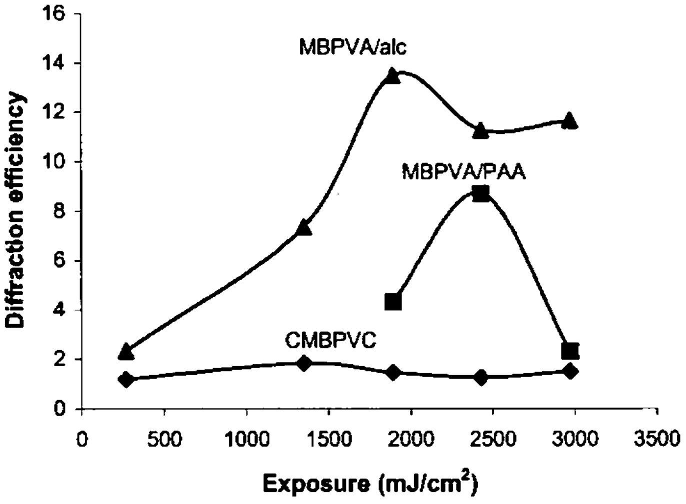


Fig. 4.57.Variation of diffraction efficiency with exposure energy at an angle of 50⁰ for MBPVA/methanol, CMBPVC and MBPVA/PAA blend

The nature of variation of diffraction efficiency was similar for all the three matrices. But methylene blue in PVA system gave maximum diffraction efficiency.

The variation of diffraction efficiency can occur due to the different modes of behaviour of methylene blue in different polymer matrices. In the exposed area the dye was partially or totally bleached, however if the plate was left in a light tight container, after few hours the dye returned to its original colour. This was true in the case of MBPVA/methanol and MBPVA/PAA blend. However, even if the films recovered its original colour, on illuminating the irradiated area with a red coloured beam the diffracted orders can be seen. This implies that the dye passed through a transition state to the leuco form or the exicted state, and then decayed to the ground state. However, the polymerization of the exposed area remained, even though the dye recovered when in the dark. The time taken for the recovery of the dye is different in different polymer matrices. This implies that polymerization in different matrices are different. In the case of CMBPVC, the chances of residual polymerization is very very less, since the monomer is a gas. It may be the reason why the diffracted pattern recorded on CMBPVC films are not stable, even though the irradiated part will not regain colour on standing. This matrix is therefore very much suitable for direct imaging, but not good for holographic applications.

The recording of interference gratings on holographic plates assumes some spatial modulation of the photosensitive medium. For photographic plates a spatial change in the absorbance was observed 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. In the present study the reason for the variation of diffraction efficiency is not very clear as further studies are needed to understand the mechanism involved in the bleaching process. But from the variation of diffraction efficiency with the number of lines /mm it is understood that the resolution of the material is limited as the diffraction efficiency decreases when the number of lines/mm is increased beyond a value. The grating produced may be merging and cannot yield more diffraction efficiency.

e) Dye behaviour

The dye used to sensitize these polymer matrices was methylene blue, because it has high absorption at the red part of the spectrum. Several important phenomena were noticed after the recording of interference pattern on these samples. In the exposed area, the dye gets partially or totally bleached; however if the plate was kept in the dark after a few hours the dye recovered itself and presented a different color in CMBPVA and MBPVA/methanol system. This can be explained due to the conversion of leuco form of the dye to a stable thionine[11], which is clear from the shift in absorption spectra. In the case of MBPVA: PAA blend, this recovery was found to be very slow and the change to leuco form was found to be fixed in the case of CMBPVC. Direct imaging was done successfully on these sample and the recorded images were permanent. Moreover, if the irradiated area was investigated with a 0.6mW He-Ne laser, the diffraction orders were seen.

A strong enhancement effect, reinforcement, has been demonstrated in these methylene blue sensitized polymer films. After the recording was stopped the diffraction efficiency started to increase at a higher rate. A diffraction efficiency of 15% of MBPVA/methanol grating increased to 38 % over 10 days after recording process, the self enhancement gain thus being approximately 2. In the case of blend the diffraction efficiency of 3.2% increased to only ~4.5 % over 15 days, showing that the enhancement process is rather very slow. Where as in the case of CMBPVC films no self-enhancement was observed. It can be due to the lack of residual polymerization on CMBPVC films on laser irradiation. The grating was stored for the entire time in the same room conditions that they were recorded. 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 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 general with these materials and thus enabling vibration free exposures

The conversion of methylene blue to its leuco form could be made fixed by changing the polymer matrix. We have already explained that complexed methylene blue in poly (vinyl chloride) can be used as a permanent recording material for direct imaging. 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 with out any chemical treatment. But the diffraction efficiency was very low. MBPVA/PAA blend gives approximately 11% diffraction efficiency and shows only very slow recovery. This has an intermediate characteristic of MBPVA/alc and CMBPVC. Finally a comparative study is done on the optical properties of all the methylene blue sensitized polymer films fabricated in our laboratory (table 4.6)

Table 4.6.A comparative study on the methylene blue sensitized polymers like CMBPVC, CMBPVA, MBPVA/methanol, MBPVA/PAA is summarized in the following table

Properties	***CMBPVC***	***CMBPVA in water***	***MBPVA/in methanol***	***MBPVA/PAA in methanol***
Solvent	Cyclo hexanone	Water	Alcohol	Alcohol
Dye	MB	MB	MB	MB
Complexing agent	Copper acetate	Copper acetate	-	-
Wave length range of dye	665nm	665nm	665nm	665nm
Laser used	He-Ne	He-Ne	He-Ne	He-Ne
Shift in absorption spectra	No shift	Shift	Shift	Shift
Optimum dye concentration	$1.28x\ 10^{-3}$ mol/l.	$1.27x10^{-3}$ mol/l	$2.91x10^{-4}$ mol/l	$1.46x10^{-4}$ mol/l
Optimum pH	4.5	10.2	5.81	3.79
Recovery of dye	No	Yes, very fast	Yes, fast	Yes, very slow

Threshold Power	3.8milli Watt	0.186milli Watt	100micro Watt	181micro watt
Threshold energy	300 mJ	100mJ	200mJ	200mJ
Saturation energy	400mJ	200mJ	900mJ	1800mJ
Maximum diffraction efficiency	4.8%	Measurements were difficult due to high sensitivity	20%	10.88%
Self enhancement	No	-	Yes	Yes
Variation in Tensile strength on doping	No	No	No	No

4.4.3. CONCLUSIONS

- The recovery of leuco methylene blue to the unexcited state on laser irradiation in different polymer matrices follows the order CMBPVA > MBPVA/PAA in methanol > MBPVA in methanol > CMBPVC.
- For applications like direct imaging, optical memories etc CMBPVC can be used.
- The rate of bleaching of methylene blue in different polymer matrices follows the order CMBPVA > MBPVA/PAA in methanol > MBPVA in methanol > CMBPVC.
- As permanent recording materials for optical recording CMBPVC and MBPVA/PAA are promising candidates.
- For hologram recording MBPVA in methanol and MBPVA/PAA are good candidates.
- CMBPVA is an efficient material for hologram recording, only if a proper fixing method is developed.
- Compared to other methylene blue sensitised polymer films CMBPVA has low shelf life.
- The major attractions of these methylene blue sensititized polymer films, other than CMBPVA are excellent optical clarity, shelf life, storage life, environmental stability, thermal stability, ease of fabrication, low exposure, low cost etc.
- Difference in the behaviour of the dye in these polymer films was investigated in detail.
- Diffraction efficiency obtained on these polymer films follows the order MBPVA in methanol > MBPVA/PAA in methanol > CMBPVC.

- Low diffraction efficiency in CMBPVC can be due to the lack of residual polymerisation taking place on laser irradiation unlike in other polymer systems.
- Self-enhancement was observed on MBPVA/methanol and MBPVA/PAA in methanol films.
- Holograms were successfully recorded on all these methylene blue sensitised polymer films.

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Chapter 5

PART 1

5.1.STUDIES ON EOSIN DOPED POLY (VINYL ALCOHOL) S (BOTH HOT AND COLD) AS PERMANANT RECORDING MATERIAL.

5.1. INTRODUCTION

Poly (vinyl alcohol) is, academically, one of the most interesting among vinyl polymers due to its structural complexity. Poly (vinyl alcohol) has many optical uses, which results from its lack of colour and high transmission in the near infrared and ultraviolet. Films of poly (vinyl alcohol) can be readily prepared, and they can be oriented to give a high degree of birefringence and a high tensile strength in the stretch direction. Additional properties which accounts for its versatility are its hydrophilic character, easy dye doping, ability to be cross-linked and chemically modified. The optical uses of poly (vinyl alcohol) are considered with the retardation, polarization and filtration of light, and with photography and related imaging fields.

Commercially poly (vinyl alcohol) is prepared by the hydrolysis of poly (vinyl acetate). It is possible to control the extend to which acetate groups are replaced by hydroxyl groups by changing the reaction conditions. In particular, the catalyst concentration and the time of reaction have a major role on the degree of alcoholysis. The most common commercial types of poly (vinyl alcohol) are the so called partially hydrolysed grades in which 87 – 89 % of the acetate groups have been replaced and the completely hydrolysed grades in which 99-100 % of the acetate group have been replaced. The degree of alcoholysis has an effect on the properties of the polymer.

Generally speaking, poly (vinyl alcohol) is commercially available in four molecular weight ranges, which are commonly referred to as super-high, high, medium and low viscosity poly (vinyl alcohol)s. The corresponding average molecular weights are 2,50,000-3,00,000; 1,70,000-2,20,000; 1,20,000-1,50,000; and 25,000-35,000 respectively.

Since poly (vinyl acetate) is having atactic structure, the poly (vinyl alcohol) prepared from it is also atactic. However, although poly (vinyl acetate) is amorphous, poly (vinyl alcohol) exhibits crystallinity. The hydroxyl group is small enough to fit into a crystal lattice, which is essentially the same as that of polyethylene.

The physical properties of poly (vinyl alcohol) are somewhat dependant on the degree of alcoholysis. (See table 5.1 for some comparative properties). Thus completely hydrolysed poly (vinyl alcohol) has a higher tensile and tear strength than the partially hydrolysed material, in which crystallinity and hydrogen bonding are less extensive. Physical properties are also affected by environmental humidity. Molecular weight also has an effect on physical properties and the low viscosity grade polymers have appreciably lower tensile and tear strength than the higher viscosity grades.

Table5.1 Comparative properties of typical commercial grades of poly (vinyl alcohol)

	Partially hydrolysed, high viscosity grade	Completely hydrolysed, high viscosity grade
Specific gravity	1.3	1.3
Tensile strength		
(dry)(Mpa)	120	150
(at 50% R.H)(Mpa)	72	83

An important characteristic of poly (vinyl alcohol) is its water solubility. As the acetate groups of poly (vinyl acetate) are replaced by hydroxyl groups the water sensitivity of the polymer increases. Maximum sensitivity occurs at a degree of alcoholysis of about 88% and polymers with degree of alcoholysis in the range 87-89% are readily soluble in cold water. They are called cold poly (vinyl alcohol) or cold PVA. At higher degree of alcoholysis, hydrogen bonding become more appreciable and results in a reduction in the case of solubility. Thus completely hydrolysed grades of poly (vinyl alcohol) are dissolved in water only by heating to above 85°C. They are called hot poly (vinyl alcohol) or hot PVA.

Poly (vinyl alcohol) has an unusual combination of properties. In particular, it has much greater tensile strength than is normally associated with water-soluble materials; at the same time it has out standing chemical resistance. This combination results in a wide variety of applications.

Poly (vinyl alcohol) has found numerous uses in various types of light initiated replicating systems; Kosar [1] discusses many of these. The addition of poly (vinyl alcohol), for example, has been claimed to increase the speed of blue print papers [2]. Poly (vinyl alcohol) films which have been made light sensitive by the addition of dichromates [3-8] and become insoluble after exposure are useful for preparing lithographic plates, photoresists for printing silk screens. Dichromated poly (vinyl alcohol) has also found use in the manufacture of printed circuit boards [9]. Dichromated poly (vinyl alcohol) is preferred as photo resist materials in the Dow etch process for the preparation of etched relief printing plates [10]. The use of dichromated poly (vinyl alcohol) for silk-screening and stencil screening has been patented [11,12]. The mechanism by which poly (vinyl alcohol) containing dichromate is hardened on exposure is discussed by Duncalf and Dunn [13]. These authors have also studied the effect of heat on poly (vinyl alcohol) containing chromium compounds [14]. Poly (vinyl alcohol) has also been suggested as a dye carrier in dye bleach processes [15]. For optical data storage in dye-doped polymers, the combination of guest dye with the solid matrix plays an important role. The action of light on such materials imparts a change in either the absorption coefficient or refractive index. Varieties of dye have been used as sensitizer on PVA for various applications which include methyl orange [16], dichromate [17], thionone[18], fluorescien[19],eosin[19], rosebengal[20,21], methylene blue[22],chrysodine[23] ,mordent yellow3R[24], ferric chloride[25]. In this chapter we report the composition and characteristics of a recording medium based on dye sensitized PVA. We have chosen both hot and cold PVA for our study. The molecular weight of hot and cold PVA are 40,000 and 1,25,000 respectively. The dye used for sensitization is an organic dye, eosin, belonging to the xanthene family of dyes.

5.1.2.EXPERIMENTAL PROCEDURE

Preparation of eosin sensitized poly (vinyl alcohol) [EPVA]

The procedure adopted for the preparation of eosin doped hot poly (vinyl alcohol) and cold poly (vinyl alcohol) are same and is as follows:

a) Poly (vinyl alcohol)(7 g) (molecular weight-1, 25,000) was dissolved in distilled water(100 ml) to yield a poly (vinyl alcohol) (cold) aqueous solution having 10 weight % cold PVA.

b) Poly (vinyl alcohol)(7 g) (molecular weight-40, 000) was dissolved in distilled water(100 ml) to yield a poly (vinyl alcohol) (hot) aqueous solution having 10 weight % hot PVA.

c) Crystals of eosin were dissolved in water to obtain the desired dye concentration.

d) Photosensitive solution was obtained by mixing dye with aqueous PVA solution.

Pouring this solution on a clean glass slide which was kept on a leveled glass substrate resulted in a transparent pink film. The amount of solution that is poured on the glass slide is a function of the desired thickness of the sensitive film. To obtain optically defect free samples it is necessary to eliminate dust particles, which will scatter light. For this after the deposition a cover is placed above the plate. The drying period is a function of the amount of materials used in the photosensitive solution. The size of the glass plate used in the experiment was 75 x 25 x 1.4 mm. The recording sensitivity was measured for different samples of fixed thickness. Thickness of all these samples was maintained to be 0.01mm.

5.1.3.EXPOSURE

The experimental set up used for the characterization of the sample is shown in figure 2.5. A linearly polarized beam from a diode pumped Nd: YAG laser Casix LXD 2000 was used. The laser beam has a maximum power of 30 mW and has a beam diameter 2 mm. The second harmonic out put at 532 nm was used for exposure. This beam was expanded using a spatial filter arrangement set up in the laboratory. For all the experiments, this expanded beam was used. The output from this laser at 532 nm is very close to the center of the absorption band of the dye. The transmitted power was measured using a power meter (OPHIR model 2000).

5.1.4. RESULTS AND DISCUSSION

5.1.4.1. Optical Characterization

a) Optical absorption studies

The spectral absorbance of eosin doped PVA before and after exposure is shown in figure 5.1. The dye was bleached during irradiation. After exposure the magnitude of the peak decreased considerably. There was no shift in the absorption band of EPVA after irradiation. Figure 5.2 shows the variation of absorption for irradiation at different time intervals (5min, 10min, 15min) for a power of 18 mW. As the time of exposure increases more and more dye molecules in the irradiated part gets converted to the leuco form, which results in a decrease in absorption at the exposed area as shown in the graph.

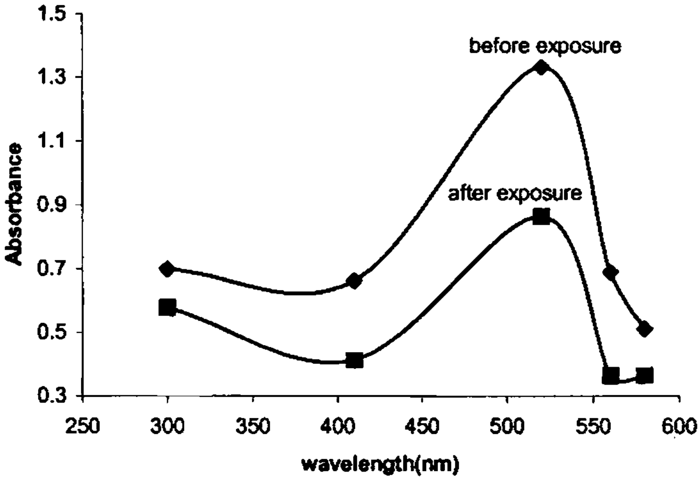


Fig 5.1 shows the variation in absorption of EPVA (both hot and cold) with wavelength, before and after exposure to laser.

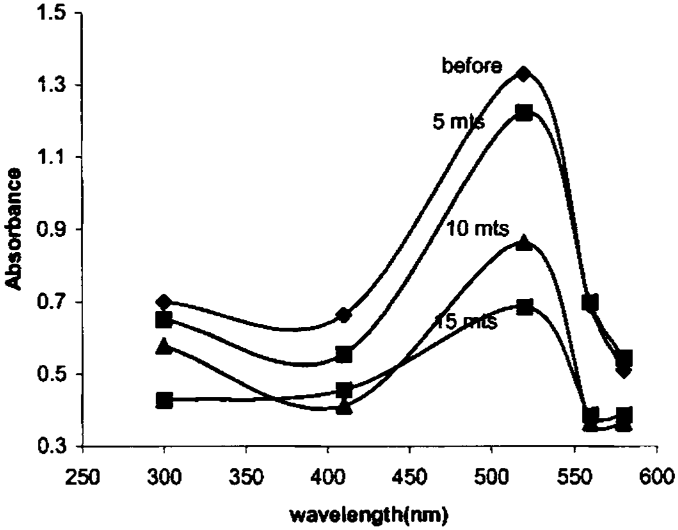


Fig 5.2 shows the variation of absorption on irradiation at different time intervals (5min, 10min, 15min) for a fixed power.

Since EPVA has absorption in the blue region, the storage capacity can be increased by using an Ar^+ ion laser.

b) Optimization of the sensitizer concentration

The components of this photopolymer typically consists of a host polymer PVA, its solvent and the photosensitiser. The dye concentration was varied from 1.44 $x10^{-5}$ g/ml to $2x10^{-4}$ g/ml. The films thus obtained from this solution were exposed to a laser power of 18 mW for 5 min. The change in transmittance was monitored as a function of time. Initially, an increase in the concentration of dye produces high sensitivity. A graph was plotted between relative transmittance (T/T^0) (where T is the transmitted power after a time 't' and T^0 is the initial transmittance) with time for both cold and hot EPVA. Figure (5.3 & 5.4) shows that the relative transmittance decreases with concentrations of eosin greater than 4.67 x 10^{-5}g/ml (C7 and H7) for both cold and hot EPVA and very fast bleaching was observed for this sensitizer concentration. This is because as the concentration of dye in the polymer matrix increases beyond a certain limit, they have a tendency to associate. These associated dye molecules act as a single molecule. Hence relative transmittance decreases with the increase in dye concentration.

c) Optimization of pH

It has been found that pH greatly influences the efficiency of a recording material. So a detailed study was done to predict the effect of pH on both hot and cold EPVA. The pH was varied from 1 to12. Very interesting behavior was observed in both the cases.

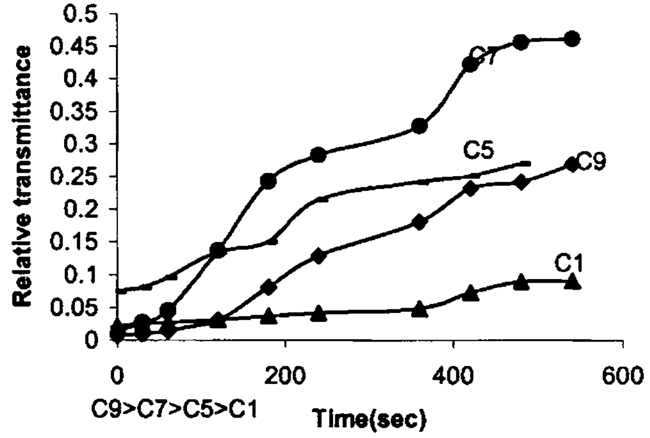


Fig 5.3 Variation of relative transmittance with time for cold EPVA at various dye concentration

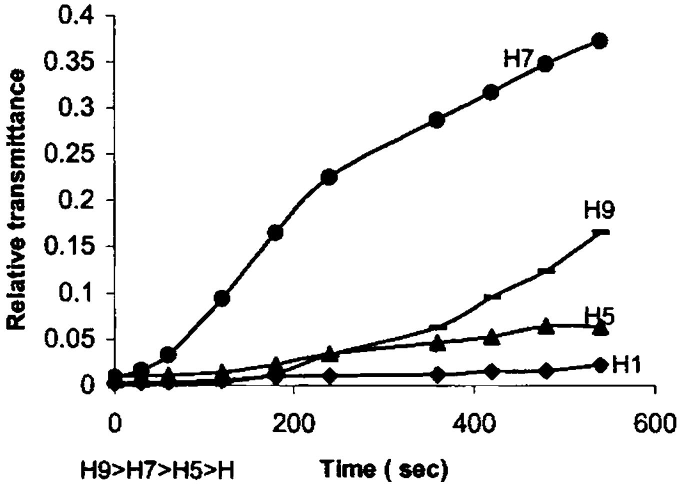


Fig 5.4 Variation of relative transmittance with time for cold EPVA at various dye concentration

In the case of hot EPVA for the optimum dye concentration very fast bleaching was observed for a pH 7 which is the normal pH of the system (figure 5.5). This is because the eosin dye is unstable at both acidic and basic pH. Where as, in the case of cold EPVA, the films prepared at high pH lost its transparency. Between pH 10-11 loss in transparency at the center portions of the film was observed. At low pH the transparency was retained but the film lost its colour. At pH 8.8 gradual loss of colour was observed and the film lost its colour completely on the next day. Hence, characterization of the sample was done at the normal pH of 7.

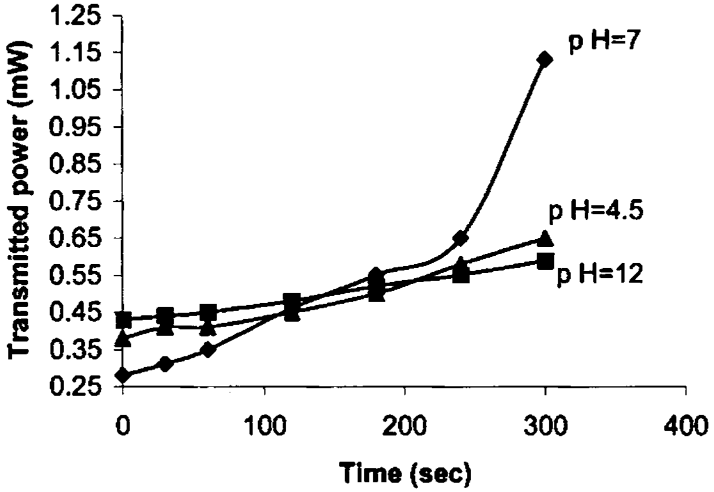


Fig 5.5 Variation of transmitted power with time for different pH for hot EPVA

d) Rate of bleaching

To study the rate of bleaching of eosin in both hot and cold PVA, these optimized samples were exposed under the same laser power for about 7 min.

The variation in transmittance in terms of T/ T^0 with time was calculated and plotted, from which the rate of bleaching was found out from the slopes at different times. The rate of bleaching with time for both the samples are plotted in figure 5.6 & 5.7. It is very interesting to note that the rate of bleaching increases slowly reaches a maximum and then decreases in both the cases. The initial slow rate can be attributed to the attainment of threshold energy by these dye molecules for excitation. Once the threshold energy is attained, the rate becomes very fast, reaches a maximum in 120 sec for both hot and cold PVA respectively. When all the molecules are converted to its leuco form, the rate drops.

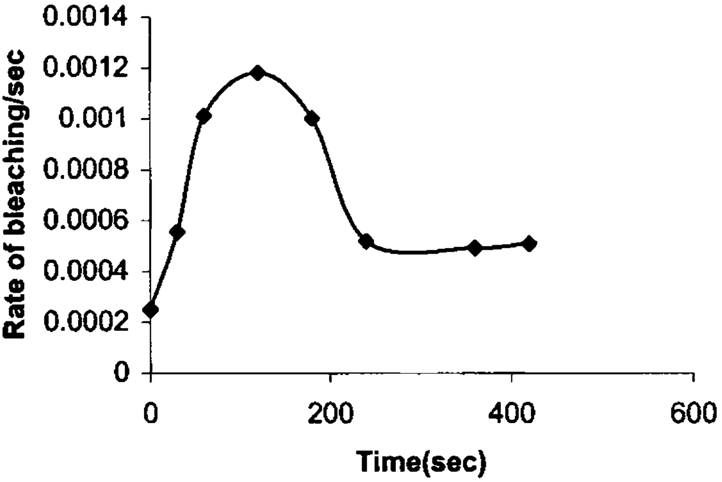


Fig 5.6. Variation of rate of bleaching with time for hot EPVA

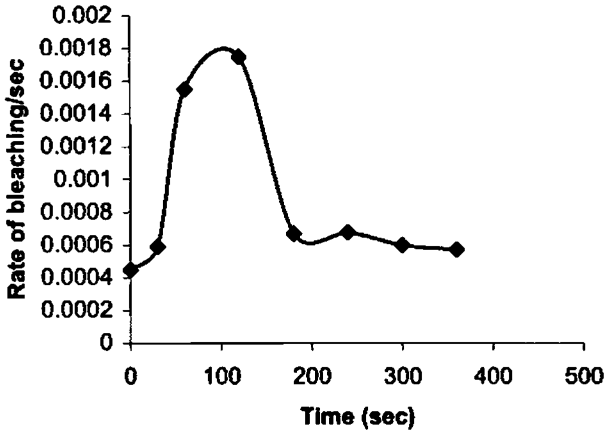


Fig 5.7. Variation of rate of bleaching with time for cold EPVA

e) Threshold and Saturation Energy

Just like concentration and pH, energy is also an important parameter, which should be optimized, since the rate of bleaching depends on the exposure energy. The minimum power necessary for EPVA sample to start bleaching was determined. For this, the optimized sample was exposed to a varying power from 6μW to 135.8mW. It was found that a minimum laser power of 18.5 mW was essential for the photochemical change to take place in both hot and cold EPVA (figure 5.8). This is because these dye molecules possess a minimum amount of energy called threshold energy for the excitation to the leuco form. After the threshold region very fast bleaching was observed with the change in exposure and reaches saturation at an exposure of 6500mJ for cold EPVA and 10,000 mJ for hot EPVA. The threshold and saturation energy of cold and hot EPVA is shown in figure 5.9 & 5.10. From the graph it is clear that hot EPVA needs more exposure energy to reach a stage of saturation.

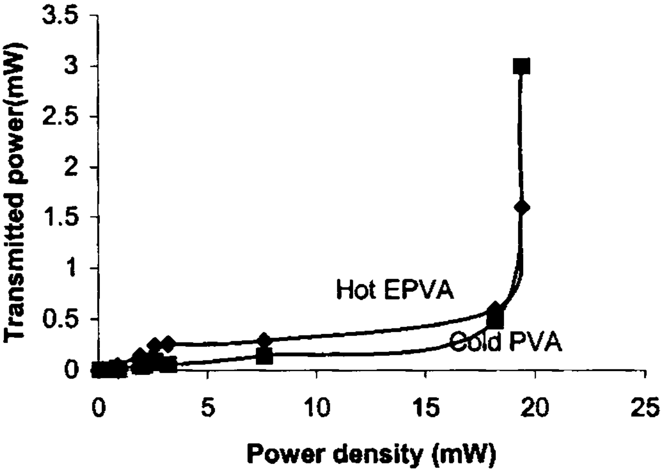


Fig 5.8. Variation of transmitted power with power density for the optimized samples (both hot and cold)

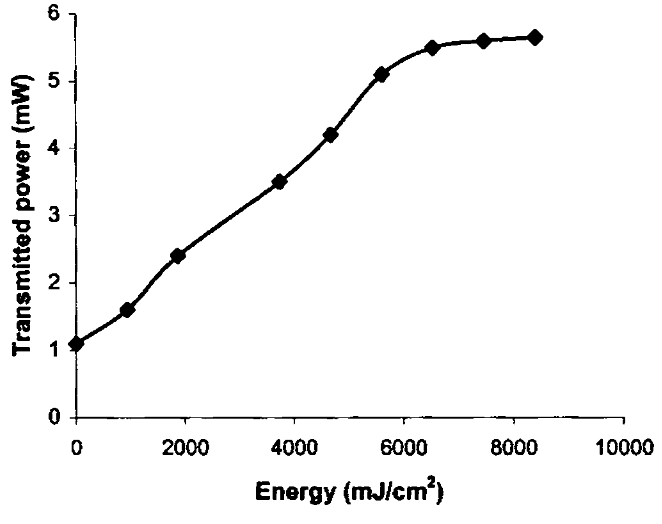


Fig 5.9. Variation of transmitted power with exposure energy for cold EPVA

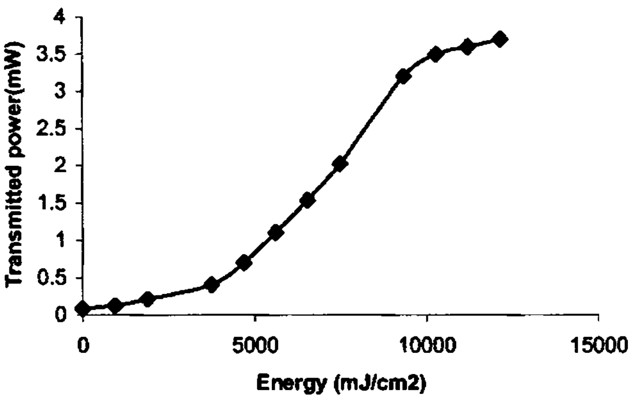


Fig.5.10. Variation of transmitted power with exposure energy for hot EPVA

f) Stability of the material/ Storage life

To investigate the stability of the photochemical changes we measured the absorbance of the spot immediately after exposure and then after each week for approximately 1 year. Neither degradation nor recovery of the absorption occurred in this time interval. Figure 5.11 shows the change in absorption at the irradiated spot with time. From this observation it is clear that eosin doped PVA is a very stable recording material.

g) Transmission Curves

The response of photosensitive materials to exposure of 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 logarithm of the exposure energy given to it. A typical H&D curve for EPVA film is shown in fig 5.12. As

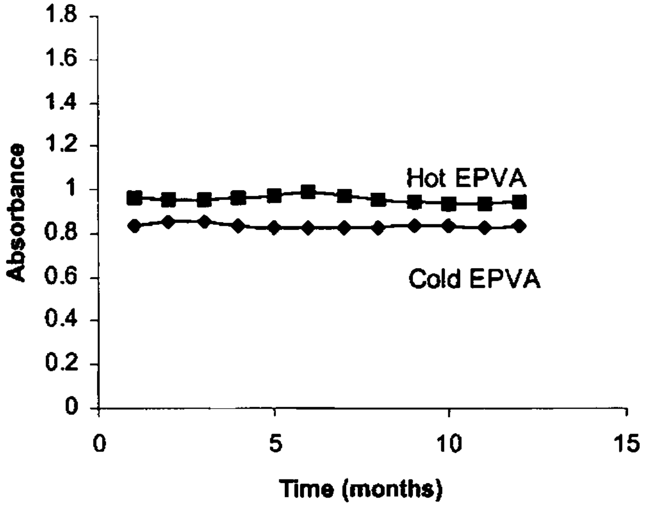


Fig 5.11. Variation of absorbance with time for both hot and cold EPVA

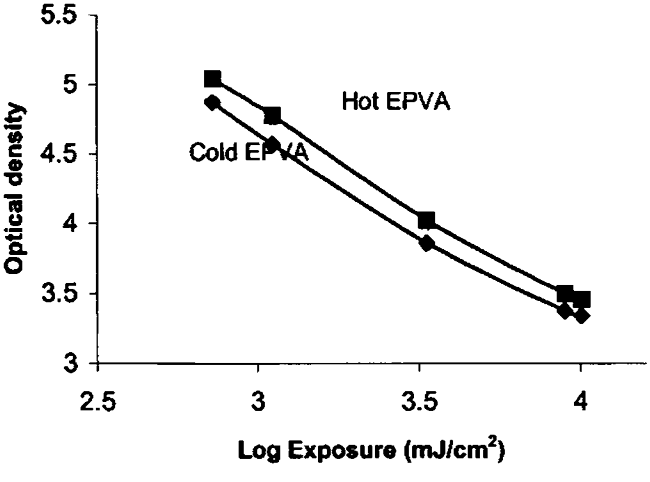


Fig 5.12. Variation of optical density against logarithmic exposure for both hot and cold EPVA

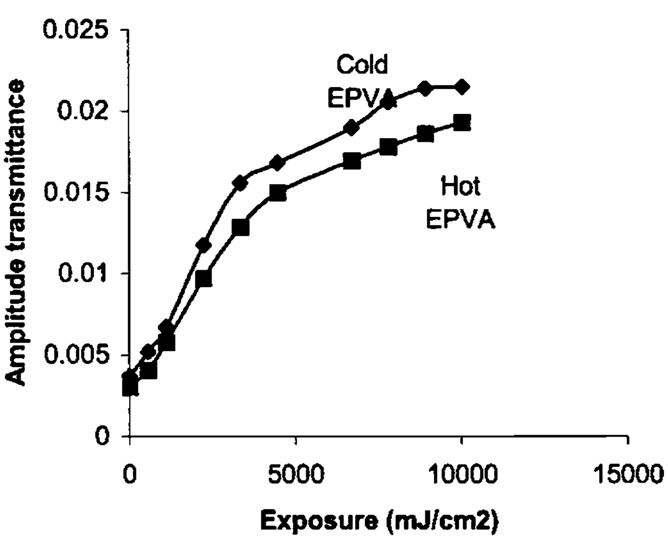


Fig 5.13. A plot of amplitude transmittance against exposure for both hot and cold EPVA.

can be seen the upper portion of the curve is a straight line. To specify the response of material for holography a curve showing *t*, the amplitude transmittance of the material as a function of the exposure is preferable and is plotted in figure 5.13.

h) Imaging

Before exposure the eosin molecules are evenly distributed throughout the medium; however during the imaging process a modulation of the intensity according to the pattern is developed. This may be due to the conversion of the eosin dye molecules to the leuco form. No change in absorption at the unexposed part was observed; hence the migration of dye molecules to those areas on illumination can be ruled out. The dye molecules that are converted into the leuco form on laser exposure in the polymer matrix will become fixed in their location, resulting in a concentration gradient of the free dye molecules in the material. Thus the recorded images are permanent. The photographs of direct imaging done on EPVA samples are given in fig 5.14&5.15.

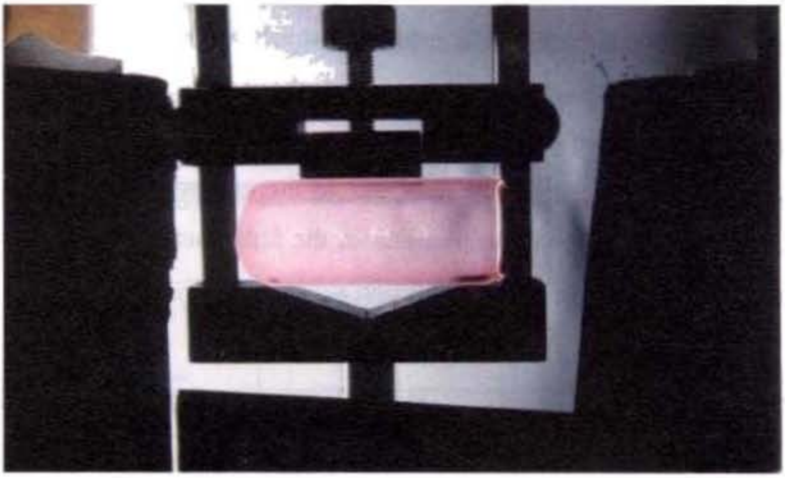


Figure 5.14. The photographs of direct imaging of the alphabets O, X, H, A recorded on EPVA

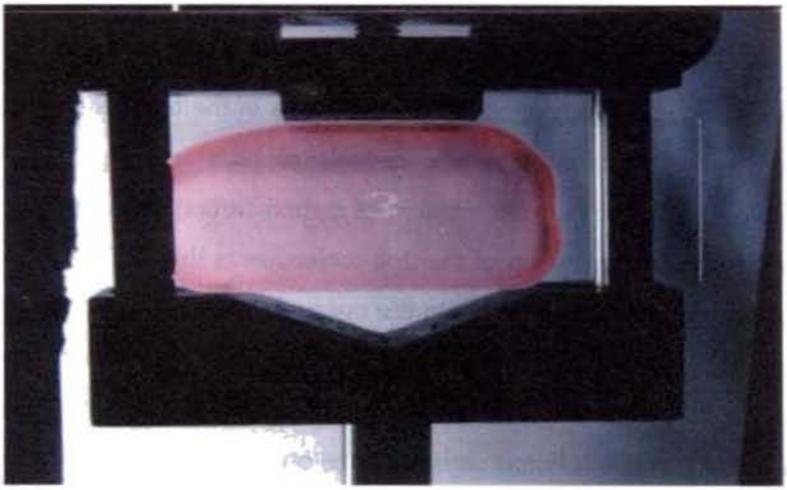
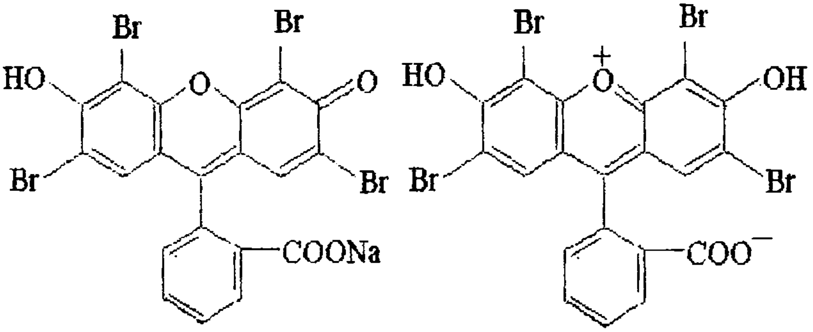


Figure 5.14. The photographs of direct imaging of the number 3 recorded on EPVA.

i) Dye behaviour

Eosin is an acid xanthene dye. It has at least fifty synonyms. Dilute aqueous solution of the dye is pink with a striking greenish yellow fluorescence[26]. The structure of eosin can be represented as shown below. It has a strong absorption at the green part of the spectrum (517nm). When we exposed the EPVA to a diode pumped Nd: YAG laser, in the exposed region the dye was totally bleached. The dye molecules absorb the light energy and are excited to form singlet, which decay rapidly to triplet states.



Since the energy is high enough, the molecules in the triplet state are further excited and dissociated into free radicals of high volatility [27]. On laser exposure, due to the homolytic fission of carbon-carbon single bond results in a decrease in concentration of the dye molecules in the brighter region. This gives rise to a permanent change in the material. It was necessary to determine the optimum quantity of the dye, since very fast bleaching should be acquired in a short interval of time. Nevertheless, in the case of EPVA no influence of local heating on dye (photodestruction) was observed. This is due to the stable triplet state of the dye molecules in the polymer matrix. Thus, the possibility of permanent recording is suggested.

5.1.4.2. Mechanical Properties

No change in mechanical properties was observed when eosin dye was added to either hot or cold poly (vinyl alcohol). Table 5.1 shows the value of tensile strength and elongation at break for undoped PVA and eosin blue doped PVA

Table 5.1. Comparison on the mechanical properties of undoped and doped EPVA

EPVA	Tensile strength (N/mm^2)	Elongation at break (mm)
Undoped PVA	40	90
Doped PVA	39	80

5.1.6. CONCLUSIONS

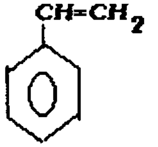
- Eosin sensitized poly (vinyl alcohol) can be used as a permanent recording material irrespective of their molecular weight.
- The information stored was found to be stable for years and does not need any fixing process.
- Storage capacity of the material can be increased due to its sensitivity to blue and green lasers.
- The major attraction of this material is its excellent optical clarity, shelf life, environmental stability, storage life, low cost etc.
- This material does not need any dark room storage.
- Very fast bleaching was observed for an optimum sensitizer concentration of 4.67×10^{-5}g/ml and pH of 5.7
- Very fast bleaching was observed for an optimum sensitizer concentration of 4.67×10^{-5}g/ml and pH of 7
- The rate of bleaching was found to be almost same for both hot and cold EPVA.
- The saturation energy of both cold and hot EPVA are 6500mJ and 10,000mJ respectively.
- Storage life was found to be excellent for both hot and cold EPVA and no change in irradiated spot was observed for years.
- Direct imaging was successfully done on these samples.

PART 11

5.2. STUDIES ON BRILLIANT GREEN SENSITIZED POLYSTYRENE AS AN OPTICAL RECORDING MATERIAL.

5.2.1. INTRODUCTION

Styrene monomer is the most important member of a group of compounds known as the alkenyl benzenes. They are typical aromatic compounds having double bond in the aliphatic side chain. It is a colorless liquid of molecular formulae C_8H_8 and its structure is as shown below.



Styrene is one of the few substituted alkenes that will readily polymerize by free radical, anionic and cationic mechanism. This is a result of the ability of the aromatic ring to stabilize the propagating species, be it a free radical, anion or cation. Free radical initiation is by far the most important industrial method, although anionic initiation has been used in some of the more recently-developed process, e.g. the production of block co-polymers of styrene. Where radical initiation is used, it can be generated by bulk (mass), solution, suspension and emulsion techniques. In practice all the four are used but bulk and suspension process accounts for almost all of the manufactured homopolymers. Styrene polymerizes spontaneously on heating in an atmosphere free of oxygen. Very few other vinyl polymers possess this property.

Bulk polymerization is the simplest process and gives a polymer of high clarity and good optical properties. Although contamination of product is minimum here, the reaction is difficult to control due to its highly exothermic nature - heat dissipation is particularly difficult as the viscosity of the system increases. A wide variety of free radical initiators successfully polymerize styrene and the properties and reactions of peroxides have been reviewed [28-30]. Benzoyl peroxide is particularly useful for polymerizing styrene and thermal decomposition at low temperature proceeds by a first order process. Thermal initiation is used in bulk polymerization where, in order to maintain effective control of the process, only a few radicals are required. Below 90^{0}C the polymerization rates are too low, and the molecular weight of the polymer found is too high to be useful commercially. Since the rate is a function solely of temperature, and the molecular weights are inversely proportional to the temperature, suitable rates and molecular weights are obtained when polymerization is carried out between 120^{0} and 160^{0} C. To complete the polymerization it is necessary to raise the temperature to 180-200 ^{0}C, although this produces less desirable low molecular weight polymer. Using benzoly peroxide it is possible to obtain high rates and complete polymerization at lower temperature. It decomposes to benzoyl and finally phenyl radicals at between 60-90^{0}C.

Polystyrene is a glass clear hard polymer with good electrical properties and easy processing charectarestics. The chemical resistance of polystyrene is dependant on its chemical structure and chemical attack is pronounced at high temperature than at room temperature [31].

Polystyrene in spite of having high clarity, transparency and colorability is seldom used as a hologram recording material. In the present study we have selected brilliant green sensitized polystyrene as the polymer matrix. Brilliant green is a basic dye and has a strong absorption band in the red part of the spectrum. Absorption and real time transmission studies were done on this material. The effect of dye concentration on the photo bleaching was also studied using a 10mW He-Ne laser as the source. It was felt that brilliant green sensitized polystyrene film may open new possibilities for simple and fast formation of holographic films.

5.2.2 EXPERIMENTAL

Preparation of brilliant green sensitized poystyrene [BGPS]

Even though we can prepare polystyrene from styrene monomer by emulsion, bulk, and suspension polymerization, we preferred bulk polymerization technique due to the high clarity the film obtained. The styrene monomer was made inhibitor free and then polymerized in the presence of benzoyl peroxide initiator. The temperature was maintained between 120-140°C. When the solution became partially viscous, antioxidant (2,6 Di-tert-butyl-p-cresol) was added followed by brilliant green in pyridine and glacial acetic acid. Best results were obtained when brilliant green was used in equimolar quantities in two different solvents.

The dye doped slightly viscous polymer solution was casted on thin glass plates of dimension 75 x 25 x1.4 mm. These slides were then covered to protect them from dust and kept at room temperature for about 36 h for drying. To improve the quality of brilliant green sensitized polystyrene a different approach was taken which include the fabrication of thick films. Samples were prepared with varying dye concentration. The thickness of the sample was maintained to be 0 .01 mm

5.2.3. LASER EXPOSURE

The exposure beam was derived from a coherent Melles Griot He- Ne laser with emission at 632.8 nm. The laser beam was expanded and filtered using a spatial filter arrangement fabricated in the laboratory. The samples were placed in the expanded beam. The effects of He-Ne laser irradiation on the absorption spectra of brilliant green sensitized polystyrene films were studied using a Hitachi 330 UV-Vis-NIR spectrophotometer. The experimental set up used for the real time transmission study is as described in figure 2.5.

5.2.4. RESULTS AND DISCUSSION

5.2.4.1.Optical Characterization

a) Optical absorption studies

For optical absorption studies, varying concentration of brilliant green sensitised polystyrene was prepared. It was found that faster bleaching was achieved at an optimum concentration of the dye. The absorption spectra of the brilliant green sensitised polystyrene films before and after exposure to laser irradiation at 632.8 nm are shown in the figure 5.16. The absorption band of the chromophore was bleached during irradiation. The exposure time needed was about 55 min for the sample. The spectra showed two absorption bands (one in the red region and other in the violet region) characteristic of brilliant green. In the unexposed case the peak height at higher wavelength was greater in magnitude than that at the lower wavelength. But after exposure it was found that the peak at lower wavelength became greater in magnitude than that at higher wavelength.

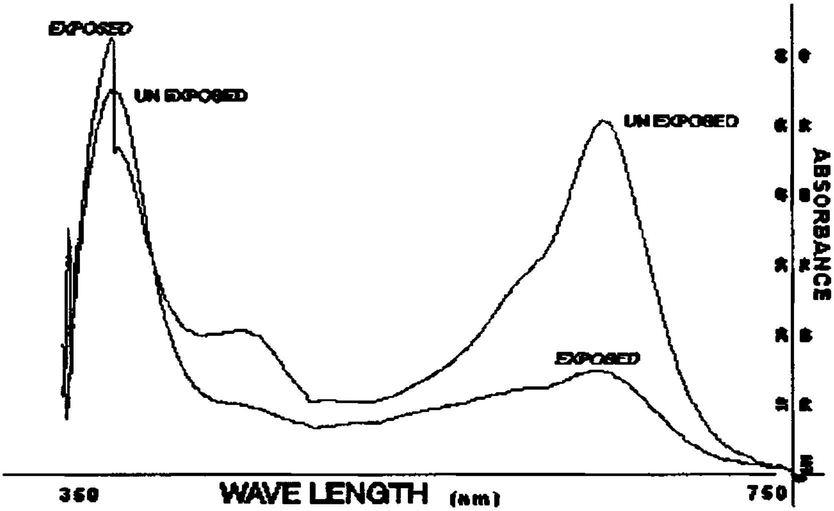


Fig 5.16. The absorption spectra of brilliant green sensitized polystyrene films before and after exposure

In the present study in order to compare the change that has occurred for the absorption spectra due to various effects like dye concentration, exposure energy etc; the intensities of the two peaks were compared for each spectrum and a relative measure of the intensity of the two peaks were taken. The ratio is considered as relative absorbance. So that

$$R_A = \frac{\text{Intensity of the peak around 350 nm}}{\text{Intensity of the peak around 636nm}}$$

It was found that at 4.3×10^{-4} gm/ml concentration, the relative absorbance is more. The absorption properties of brilliant green molecules were thus changed by laser irradiation and proved to be a good candidate for optical recording.

b) Transmittance study

The component of this photopolymer typically consists of photopolymer polystyrene, the residual monomer styrene and the photosensitiser brilliant green. The dye concentration was varied from 1.6085x10^{-4}gm/ml to 4.713x10^{-4}gm/ml. The film prepared under these varying dye concentrations were subjected to He-Ne laser for a fixed power of 5 mW. The change in transmittance at the irradiated spot was monitored as a function of time and graph is plotted between relative transmittance Vs time. Relative transmittance is the ratio of the transmitted power to the incident power. From the graph it was clear that the conversion of dye into its leuco form is very fast for a concentration of 4.36 x 10^{-4}gm/ml (figure 5.17). C1, C2, C3, C4 represents the different concentrations of the dyes employed.

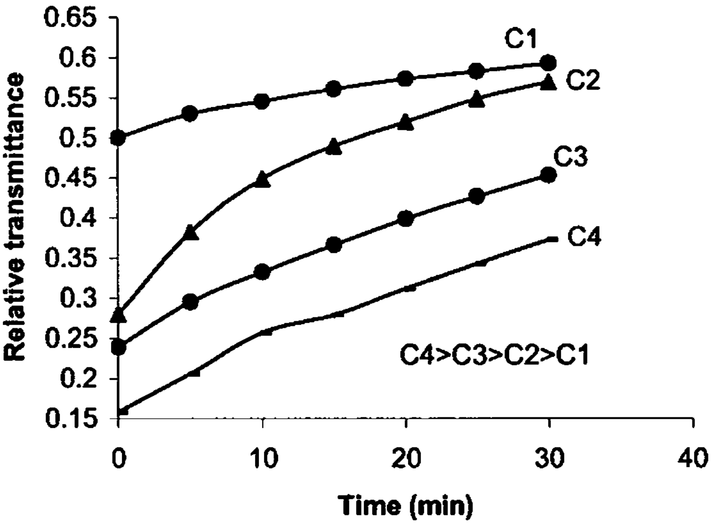


Fig 5.17. Variation of relative transmittance with time for different dye concentrations

c) Rate of bleaching

To study the rate of bleaching of brilliant green in this polymer matrix, the optimized sample was exposed under a fixed laser power for about 5 minutes. The variation in transmittance in terms of T/T^0 with time was calculated and plotted, from which the rate of bleaching was found out by finding the slopes at different times. The rate of bleaching with time for BGPS is plotted in figure 5.18. It was very interesting to note that rate of bleaching constantly decreased with increase in time of exposure. This is because initially large numbers of dye molecules were present in the polymer matrix. On laser exposure these molecules are converted to its leuco form and hence the number of dye molecules in the exposed area decreases with increase in time of exposure, and reaches a constant value after some time.

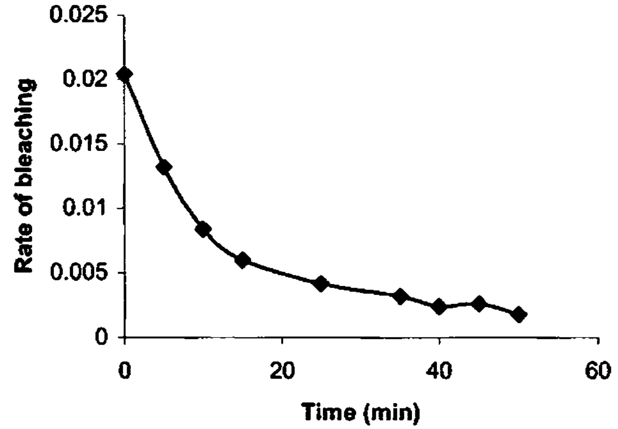


Fig.5.18. Variation of rate of bleaching with time for the optimized sample of BGPS

e) Stability of the material

To investigate the stability of the photochemical changes we measured the absorbance of the spot immediately after exposure and then after each day for approximately 1 month. To study the stability of BGPS for using it as an optical recording material, the optimized sample was subjected to a maximum power so as to reach the saturation point. The change in absorption (difference between the absorption of sample before irradiation and after exposure for a time t) at the irradiated spot was monitored as a function of time and is plotted in figure 5.19. From the graph it was clear that the change in absorbance remained fixed for some time and then increase. This was due to the fading of dye in this polymer matrix observed during the course of time. This can be prevented by using the complexed form of dye. But in the complexed state it is observed that very high exposure energy is necessary for the dye to get converted to the leuco form.

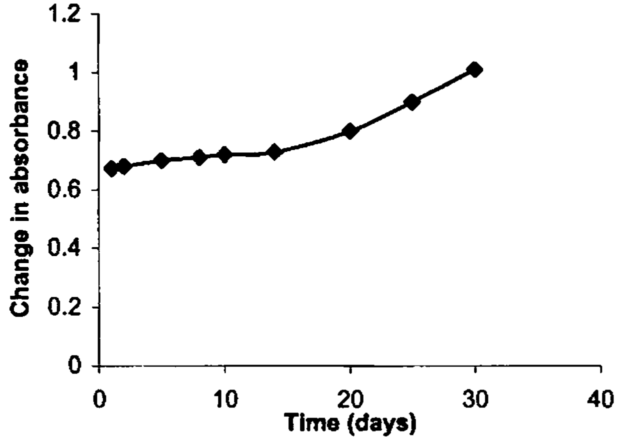
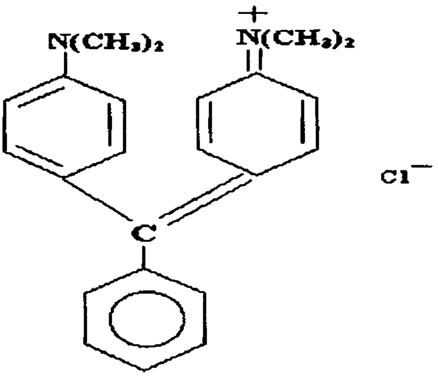


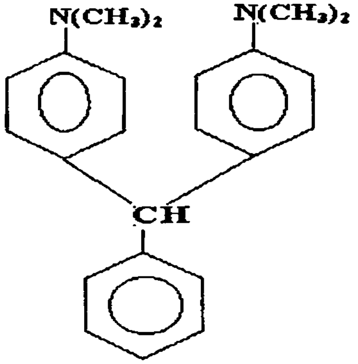
Fig 5.19. Change in absorbance with time at the irradiated spot for brilliant green sensitized polystyrene film.

f) Dye behaviour

As mentioned earlier the dye used to sensitize the polymer was brilliant green because of its high absorption at 636 nm. The structure of brilliant green and its leuco form can be represented as



Structure of brilliant green



Structure of leuco brilliant green

Not many works were reported on brilliant green sensitized polymers. In the exposed area the dye was partially or totally bleached; recovery of the dye to the original coloUr was not observed. So it was expected that there is a possibility of permanent recording in this material. But gradual fading of the dye in the unexposed part was observed during the course of time.

Solutions of cationic dye like brilliant green in certain organic solvents are always unstable. It will fade rapidly in certain solvents. Hence stabilization of this dye in these solvents is a prerequisite for accurate analysis. Kissa has shown that the solvent acidity is a critical variable determining the absorbance and stability of this dye. Accurate results can be obtained by acidifying the solvent to an apparent pH of 1.4-4.0[31]. Brilliant green consists of a colored organic cation and a colourless anion.

(a) Conversion of the dye to a leuco base or loss of proton caused by a pH shift usually causes the fading of this dye in organic solvents.

b) Non photolytic degradation of the dye.

(c) Photochemical degradation of the dye

One drawback observed in these films was the formation of cracks on the film on standing for a long time. This was due to the lower molecular weight of the polymer prepared, which was confirmed by Ubbelhode viscometer study (Table5.2). Crack formation is found to increase at low temperature. But we could overcome this defect by exposing these cracked films to the vapors of dichloromethane. Rapid penetration of vapors through cracks in the dry polymer, that were subsequently sealed up by the penetrant was observed. Even after the penetration of vapors into the cracked film, no change in absorption was seen at the irradiated spot. No crack formation was observed when the commercial polystyrene (molecular weight-1,02,000) was dissolved in toluene and doped with brilliant green. But these films were found to be unfit for optical recording due to surface non-uniformity.

Fading of the dye in solvent devoid of acid was accelerated by traces of water in the solvent. But in our present work we dissolved brilliant green in glacial acetic acid. Very few drops were enough for the doping process. pH cannot be increased beyond a certain limit in the polymer matrix, because it will result in the loss of transparency. Fading of brilliant green in polymer matrix was observed in all solvents like glacial acetic acid, chloroform, pyridine, 2-butanone, ethyl acetate etc.

Table5.1.Determination of molecular weight of polystyrene

CONCEN TRATION	RELATIVE VISCOSITY	SPECIFIC VISCOSITY	REDUCED VISCOSITY	INHERENT VISCOSITY
0.0200	1.3808	0.3808	18.9800	16.0800
0.0171	1.3223	0.3223	18.7490	16.2500
0.0150	1.2936	0.2936	19.5212	17.1160
0.0133	1.2734	0.2734	20.4480	18.0770
0.0120	1.2585	0.2585	21.4870	19.1120

Calculation of molecular weight

$[\eta] = KM^a$

$K = 9.23 \times 10^{-3}$

$a = 0.72$ [K, a values are taken from polymer hand book]

$[\eta] = 22.5$

$\therefore$ Molecular weight of polystyrene prepared in the laboratory = 50,582.

Attempts were done to copolymerise styrene with methyl methacrylate. A 6:3 ratio of styrene and methyl methacrylate was heated to 120 °C. The resulting viscous solution was stirred with brilliant green in acetic acid. These films developed cracks after few days. It was found experimentally that as the amount of methyl methacrylate in the mixture increases, the colour retaining property of the film decreases. Moreover loss in transparency was observed in these films.

Transparent copolymer of styrene and divinyl benzene was prepared in our laboratory and it was doped with brilliant green in pyridine and acetic acid. Fading was obtained in both the cases. Since dichloromethane is a common solvent for styrene and brilliant green, extensive studies were done on these systems to make a stable film, but the film casted became colourless on the next day. Studies are being done to enhance the stability of brilliant green in polystyrene.

5.2.5. CONCLUSIONS

- Brilliant green sensitized polystyrene is a new recording medium, which will respond to He-Ne laser in our laboratory.
- The material is attractive on accounts of its clarity, transparency,
- The shelf life and storage life of this material was very low.

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Chapter 6

SUMMARY AND CONCLUSIONS

Non-linear optical effects in the dye doped polymer systems offer new possibilities for the production of versatile and highly effective optical devices. Such materials will play an increasingly greater part in holography, telecommunications, optical processing etc in future. The primary aim of this work has been to develop new dye doped polymer matrices for optical recording. Attempts were also made to improve the sensitivity of the state of art materials to laser irradiation. Another objective of the work has been to synthesise and characterize new methylene blue doped polymer blends based on poly (vinyl alcohol) and poly (acrylic acid), which can be used for holographic recording. The novel dye doped polymer matrices (photosensitive) developed were found to be of low cost, high sensitivity, low exposure energy, good storage life etc. The content of the various chapters in the thesis are summarised below :

An introduction about the need for developing new optical recording material and the evolution from magnetic disk to holography is given in chapter 1. The essential requirements of a good photosensitive material and the advantages and disadvantages of the various materials used in holography are discussed.

A brief survey of photopolymers and the important polymers used in holography are also given. The objectives of the present study are also listed.

The specifications of all the materials used in the study and different experimental techniques used are described in chapter 2.

The preparation and characterization of copper acetate sensitised methylene blue doped poly (vinyl alcohol) as a hologram recording material is presented in chapter 3. The major advantages of this material are its low cost, ease of recording, insensitivity to humidity, excellent shelf life and storage life, environmental stability, flexibility on storage, no need for dark room storage etc. The state of the dye in the PVC matrix was analysed by using U.V.absorption. Unlike the role of methylene blue in other polymer matrices like gelatin, poly (vinyl alcohol), poly (methyl methacrylate) etc, the change of state of methylene blue was permanent in this matrix i.e. the reconversion of leuco form back to the original form was a very slow process and it could be used as a permanent recording material. Studies on exposure energy reveal that very short exposure is enough for CMBPVC films. Less than 5 sec was only necessary for bleaching when a 10 mW He-Ne laser was allowed to fall on these films. The threshold energy and saturation energy of these samples are 100mJ/cm^2 and 129mJ/cm^2 respectively. Studies on the storage life of CMBPVC films revealed that the change of state occurring for methylene blue in this polymer matrix is fixed and the information stored was stable for months. Very fast bleaching was observed for an optimum pH of 4.5 in this matrix. Direct imaging was tried on this sample and it was observed that the fabricated films were of good quality, which shows the high-resolution capacity of the material. The doping of methylene blue in PVC matrix did not affect the mechanical properties of the polymer. Hologram was recorded on these films.

Chapter 4 is subdivided into 4 parts. Part 1 deals with the characterization of copper acetate sensitised methylene blue doped poly (vinyl alcohol) in water (CMBPVA). Sensitising methylene blue with copper acetate showed remarkable response to He-Ne laser. It was found that less than 40 sec was enough for bleaching when these films were exposed to an expanded beam of 5mW. Characterization was done to determine the rate of bleaching, storage life, saturation energy, etc. Since leuco methylene blue is unstable in these films, recovery is very fast and the information stored was stable for only 24 hours and chemical treatment was necessary for fixing the data. The shelf life of this film was very low (1 month). Part 11 deals with methylene blue sensitised poly (vinyl alcohol) in methanol for holographic recording. Best films were obtained when methanol was used as the solvent. A comparison with the properties of similar films prepared using water as the solvent is also done. Characterization on these films showed that the information stored was stable for 48 hours. The major attraction of this material is the high clarity, transparency, ease of fabrication etc. Diffraction efficiency measurements showed that it can be used to record holograms and diffraction efficiency of about 20 % was obtained with out any fixing process. Self-enhancement behaviour was observed on this material. The diffraction efficiency increased on storage to 35%. Holograms were successfully recorded on these samples. Part 111 deals with the synthesis and characterization of a new polymer blend of poly (vinyl alcohol)/poly acrylic acid sensitised by methylene blue for hologram recording. It was observed that the poly acrylic acid in the blend delays the recovery of dye in this matrix and the information stored was found to be stable for 3 weeks at an optimum ratio of the blend (7:3), concentration of $1.46\mathrm{x}10^{-4}$ mol/l and at 3.8 pH. Characterization was done to determine the rate of bleaching with exposure energy, storage life, diffraction efficiency etc.

Diffraction efficiency of 11% was obtained on this material. Self-enhancement was also observed on this material. Part 1V deals with a comparative study on all the four methylene blue sensitised polymer films namely copper acetate sensitised methylene blue doped poly (vinyl chloride), copper acetate sensitised methylene blue doped poly (vinyl alcohol), methylene blue sensitised poly (vinyl alcohol) in methanol and methylene blue sensitised poly (vinyl alcohol)/ poly acrylic acid in methanol. The different dye behaviour in these different polymer matrices was also evaluated. It is concluded from the above study, that for applications like direct imaging, permanent recording, holographic recording etc CMBPVC and MBPVA/PAA can pose as stiff competitors.

An attempt was also made to develop films with dyes other than methylene blue. Dyes chosen were eosin and brilliant green. Eosin is found to be sensitive to lower wavelengths (green) and hence these plates could definitely be used for increasing the density of data storage. The preparation and characterization of eosin doped poly (vinyl alcohol) as an optical recording film is described in chapter 5. A linearly polarised beam from a diode pumped Nd: YAG laser was used, because its wavelength matched with the wavelength of the dye used. Characterization of these films showed that the changes of state occurring on these films were permanent and could be used as a permanent recording material. Studies on exposure energy revealed that high energy was needed for the excitation of dye molecules. Storage studies revealed that there was no change in absorbance at the irradiated spot for years. Direct imaging was done on these samples. Part 11 in this chapter deals with the preparation and characterization of brilliant green sensitised polystyrene. Only preliminary studies were carried out on this material. Even though the change of state occurring on these films upon He-Ne laser irradiation was permanent, the films develop cracks on storage. Hence the storage life was very less (~1 month). Attempts were also done to copolymerise styrene to improve the stability of the film, but this dye needs long exposure time to get bleached unlike methylene blue

List of publications from the work

- ***Complexed Methylene blue sensitized Poly (vinyl chloride)-A new polymer matrix for hologram recording***
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- ***Photobleaching in Brilliant Green sensitized Polystyrene***
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- ***Characterization and Photobleaching in Eosin doped Poly(vinyl alcohol) for hologapic recording***
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- ***Optimization of pH and direct imaging on complexed methylene blue sensitized poly(vinyl chloride)***
  Ushamani.M, K.Sreekumar, C.Sudha Kartha, Rani Joseph
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  M.Ushamani[1], N.G.Leena Deenja[2], K.Sreekumar[3], C.SudhaKartha[2], RaniJoseph[1]
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- ***Methylene blue sensitized polymers: efficient media for optical recording***
  Ushamani.M, K.Sreekumar, C.Sudha Kartha, Rani Joseph
  Communicated to Kerala State Science Congress, Jan 29-31 (2003)

List of Abbreviations

ASTM	American society of testing materials
NH_3	Ammonia
BG	Brilliant green
BGPS	Brilliant green sensitised polystyrene
CD	Compact disk
CMBPVA	Complexed methylene blue sensitised poly(vinyl alcohol)
CMBPVC	Complexed methylene blue sensitised poly(vinyl chloride)
DCG	Dichromated gelatin
D.E	Diffraction efficiency
^{0}C	Degree celsius
DVD	Digital video disk
η	eta
EPVA	Eosin sensitised polyt(vinyl alcohol)
gm	Gram
h	Hour
He-Ne	Helium- Neon
HCl	Hydro chloric acid
l	Litre
MB	Methylene blue

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MBG	Methylene blue sensitised gelattin
MBPVA/PAA	Methylene blue sensitised polymer blend of PVA/PAA
μW	Micro watt
Min	Minutes
mW	Milli watt
mm	Millimeter
ml	Milli litre
mJ/cm^2	Milli joules per centimetre ^{2}
mol/l	Mole/litre
nm	Nano meter
%	Percentage
PAA	Poly (acrylic acid)
PVC	Poly (vinyl chloride)
PVA	Poly (vinyl alcohol)
PMMA	Poly (methyl meth acrylate)
PVK	Poly (vinyl carbazol)
Sec	Second
θ	Theta
3-D	Three dimension
2-D	Two dimension
UV	Ultra violet
USLV	Ubbelohde suspended level viscometer
λ	Wave length

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