REVIEW ON PHOTOPOLYMER BASED HOLOGRAPHIC RECORDING MEDIUM

A PROJECT WORK

Submitted by

SUCHITHRA MA

Register No: AM20PHY014

Under the guidance of

Dr. SANTHI. A

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PROJECT REPORT

Name : SUCHITHRA M A

University Register No : AM20PHY014

Year of work : 2021 - 2022

This is to certify that the project "REVIEW ON POLYMER BASED HOLOGRAPHIC RECORDING MEDIUM" was done by Suchithra M A.

Staff Member in Charge

Head of the Department

Submitted for the university examination held in St. Teresa's college (Autonomous) Ernakulam.

Examiners 1) Dr. Issac Paul

2) Dr Gishamol Mathew

Date: 14.06.2022

ST. TERESA'S COLLEGE

(AUTONOMOUS)

ERNAKULAM

CERTIFICATE

This is to certify that the project report titled ***"REVIEW ON POLYMER BASED HOLOGRAPHIC RECORDING MEDIUM"*** submitted by ***SUCHITHRA M A***, towards partial fulfillment of the requirements for the award of the degree of Master of Physics is a record of bonafide work carried out by them during the academic year 2020-2022

Supervising guide

Dr. Santhi. A

Assistant professor

Department of Physics

Head of the Department

Dr. Priya Parvathy Ameena Jose

Associate Professor

Department of Physics

PLACE: Ernakulum

DATE

DECLARATION

I, ***SUCHITHRA M A, Register No.AM20PHY014***, hereby declare that this project entitled ***"REVIEW ON POLYMER BASED HOLOGRAPHIC RECORDING MEDIUM"*** is an original work done by me under guidance of ***Dr. SANTHI. A***, Assistant Professor, Department of Physics, St. Teresa's College (Autonomous), Ernakulam in partial fulfilment for the award of the Degree of Master of Physics, I further declare that this project is not partly or wholly submitted for any other purpose and the data included in the project is collected from various sources and are true the best of my knowledge.

Suchithra

SUCHITHRA M A

PLACE: ERNAKULAM

DATE: 14-06-2022

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ABSTRACT

Holography has become important because of its extended ready applications in many areas, such as hologram-based product labels, optical elements, as a data storage medium, to provide crucial heat-transfer data for the safe design of containers used for the transport/storage of nuclear materials, in bar-code readout systems used in credit cards, and so on. Photopolymers are promising materials for use in holography. They have many advantages, such as ease of preparation, and are capable of efficiencies of up to 100%. Polymer materials have several advantages. Because thick layers can be fabricated, they act as true volume materials giving high diffraction efficiency and good angular selectivity.

Following project give brief review on available literature in polymer-based recording medium for holography. fabrication of methylene blue doped poly vinyl alcohol-polyacrylic acid blended films for holographic recording

CONTENTS

CHAPTER- 1

Review on polymer based holographic recording medium

1.1 INTRODUCTION

The inspiring example of laser technology, Holography is now spreading in data storage and other engineering applications. A brief review on the available literature on polymer-based recording media is given in the context of its contribution towards the realization of theoretical predictions of holography. A general introduction on holographic material is given in this chapter. The requirement of recording medium and the advantage of polymer recording medium are presented.

Photopolymers were first introduced as a holographic recording material by Close et.al in 1969,Since then numerous systems have been examined, but only a small number have become commercially available, Polymer materials have several advantages. Because thick layers can be fabricated they act as true volume materials giving high diffraction efficiency and good angular selectivity. Most of the materials are self–developing or require only some simple post–processing, such as an exposure to light or heat treatment. This eliminates the need for wet chemical development, which makes photopolymers suitable for applications such as holographic embedded photopolymer waveguides,and holographic data storage

1.2 IMPORTANCE OF HOLOGRAPHIC TECHNOLOGY.

Holography is a very useful tool in many areas, such as in commerce, science, medicine, and industry. Holographic technology is on the dawn of quick evolution in various new areas including artificial intelligence, optical interconnects, medical practice, holographic weapon sight, night vision goggles, games etc. So, holograms are not just 3D images!

Storage requirements all over the world are exploding. Making data storage one of the biggest challenges in the expanding multimedia market. For more than 30 years optical storage by a volume holography has been the 'Holy Grail' of photonics. The next generation of data storage system is expected to use optical holography to store information throughout the three-dimensional volume of a material. Combining high storage densities, fast transfer rates, with reliable, low-cost media, makes holography poised to become a compiling choice for next generation storage and content distribution needs. In addition, the flexibility of the technology allows the development of a wide variety of holographic storage products that ranges from hand held devices for consumers to storage products for the enterprises. Optical data storage systems have significant merits over the existing digital system in the level of security achieved.The parallel processing and encryption/ decryption of two-dimensional pages have made secure holographic data bases superior to the existing digital technologies.

Holographic optical elements are diffractive structures that are constructed holographically by the interference of two beams of light. The second beam corresponds to the image beam which is supposed to exit the HOE upon its playback. Optical elements such as lenses, beams splitters, diffraction gratings and filters can be produced by holographic imaging. The HOEs have the advantage of being low cost (small size and light weight) and are easily reproducible by embossing polymer materials. HOEs can duplicate most of the functions provided by glass optics if optical system operates over narrow spectral bandwidth or requires chromatic dispersion. we have realized certain optics that could not be produced with previous optical technologies. Area such as optical sensors, optical Interconnect, optical information processing, fiber optics, optical scanners, optical disc pickup heads, and solar concentrators have benefited from the use of a Hoes. As stated earlier, the advantages of HOEs are multifold. Firstly, since the HOEs are thin and planar, the optical systems can be made more compact. Secondly, several elements performing complicated functions can be integrated into one HOE. The frontline recording materials for the fabrication of HOEs have been the conventional silver halide emulsions, material such as dichromate gelatin (DCG), photoresist and photo polymers etc. have been employed in the fabrication of the HOEs. The most commercially available silver halide materials have faded away from the market. Recently**, Mikhaylova**, introduced the use of photo polymer holographic writing in electronics speckle pattern shearing interferometry

The use of small holograms in credit cards which are made to prevent falsification has made holograms have well known concept. Hologram show up more and more often on tickets and original covers. Important areas of application or barcode readers in shops, warehouses, libraries and so on, which is based on holographic components like optical gratings.

In the aircraft industry head up displays are an important example of holographic technology. Headache this place helps the pilot so they do not need to look down on to the instrument panels,because the instruments are projected on to the wind screen with the help of holographic technology, make flying easier.

The unique advantage of holographic interferometry rises from the fact that holography permits storing a wavefront for reconstruction at a later time. Wavefronts which fare originally separated in time or space or even wavefronts of different wavelength, can be compared by holographic interferometry. As a result, changes in shape of quiet rough surfaces can be studied by interferometric precision. One of the most important applications of holographic interferometry is nondestructive testing. visually reveals structural folds without damaging the specimen. Holographic interprotomer has also proved its utility in aerodynamics, heat transfer and plasma diagnostic etc.

Holography finds Its application in medicine also. Techniques are used by medical doctors. Doctors use three-dimensional holography CAT scans to make measurements without invasive surgery. Holographic interferometric techniques have been widely applied with success for the study of different parts of human body including cornea, tooth mobility, basilar membrane, joint chest and bones. Endoscopic holography is a powerful tool for non-contact high resolution imaging and measurements inside the natural cavities of human internal organs. The internal hologram recording endoscope produces full three dimensionality of the reconstructed image with a large focal depth. This technique can be used for cellular Structure analysis and may even substitute biopsy in tumor diagnosis.

Today there are hundreds of potential applications for holography and it is hard to deny that indeed art is an excellent application. Holography has been used to make an archival recording of valuable and fragile museum artefacts. Holography has been used by artist to create pulsed holographic portraits as well as other works of arts

1.3 CHALLENGES

Although holography was conceived in 1948, it was not considered a potential storage technology until the development of the laser in the 1960 s. While data storage using volume holography has been proposed long ago it has failed to become a commercial technology because of lack of combat laser systems, methods, detectors, input devices and recording medium.

Laser

Though a variety of lasers have been used for holography over the years, a data storage system that is commercially available requires a compact, efficient and ultimately low-cost source. The main requirements are coherence and wavelength compatibility with the material. Conventional semiconductor lasers, through compact and efficient, generally like the coherence length required for holography. Similarly, gas laser light Argon can be used in the laboratory to characterized materials, but they need for external cooling, the large size, and immense power requirements preclude their use in real systems. Now the problems have almost overcome.

Methods

Traditional multiplexing strategies proposed previously result in complex systems which are difficult to implement. More importantly, geometric constraint severely limited the maximum density in the media. The introduction of shift multiplexing, which was conceived at Caltech leave to a paradigm shift in holographic storage system design concepts. The idea of accessing holograms by symbol translation of the media in a manner similar to a conventional disc drives greatly simplified device architecture concepts.

Detectors

Speed and cost are crucial for the output device. Since the last few years several components essential to the development of any viable holographic storage system have been developed. The three ki devices are low cost, highly coherent laser sources, a high-speed height through put input device, and finally high-speed, low-cost output device. Although high speed CCD detectors have been developed; the prospect for low-cost type performance devices is questionable.

Data input devices

SLM is used to display the data to be stored in a two-dimensional page format. Suitable devices developed for the display industry have recently coming into existence. Materials or media: there has been no viable material for this technology. Media for holographic storage has long been one of the primary focus points for researchers.

1.4 MEDIA FOR HOLOGRAPHY

Any material used to record a hologram must respond to exposure to light which cause change in its optical properties. In the absorption or amplitude modulating materials the absorption constant changes as a result of exposure.

In the phase modulating materials, there is no absorption of light and the entire incident light is available for image formation, while the incident light is significantly absorbed in an amplitude modulating material. Thus, a phase material can produce a higher efficiency than an amplitude material. A practical recording media can be considered as a combination of these phase modulating and amplitude modulating material.

The media performance is assessed in terms of parameters like diffraction efficiency (DE), sensitivity, resolution, signal to noise ratio (SNR), temporal stability etc.

For real time applications like digital data storage. For the commercial availability of material, it should be economic with ease of fabrication steps.

Diffraction Efficiency

The diffraction efficiency of a hologram is defined as the ratio of the power diffracted into the desired image to that illuminating the hologram. Diffraction efficiency is proportional to the square of the gradient of the amplitude Transmittance T versus exposure E curve as well as to the squares of input modulation and modulation transfer function. The maximum diffraction efficiency is obtained where the slope of the T versus E curve is steepest. This is usually at a slightly higher exposure than that corresponds to the steepest part of the T versus E curve.

Sensitivity

The sensitivity can be defined in terms of the square root of efficiency in writing plane wave, unity modulation depth gratings with a given fluence It,where I is the total intensity in W/cm^2 and t is the exposure time.

Dynamic Range

It refers to the total response of the medium when divided up among many holograms multiplexed in a common volume of the Material .Though a number of materials were developed, most of the currently available recording media have been optimized for display rather than data storage applications. The requirement for a media for digital holographic data storage arises from the pagewise recording and recovery of digital data and the three-dimensional nature of holography. Media must (i) be optically flat and of low scatter so that pages of data can be imaged through the material, recorded and recovered with low probabilities of error; (ii)have adequate dynamic range to support the overlap of large numbers of holograms, each with sufficiently high diffraction efficiencies to ensure high data read rates; (iii)be thick enough to support the independent storage of large numbers of holograms to yield high densities; (iv) exhibit high photosensitivity to yield high data write rates; and (v) undergo limited changes in their dimensions and bulk refractive index (RI) upon recording to ensure the fidelity of data recovery.

Several holographic recording media are under investigation for last four decades. Silver halide photographic emulsions are still the most widely used recording material for holography, mainly because of its relatively high sensitivity, high resolving power and the commercial availability. Though greater than 70% efficiency could be achieved in Agfa Gevaert 8E75 HD and Kodak 649Fplates, it requires wet chemical development and hence cannot be used in data storage devices and other real time applications. DCG is one of the best holographic recording materials because of its well-known properties: high DE, large capacity for RI modulation, high resolution , high signal to noise ratio, and good environmental stability (with a cover plate or a thin protective coating). A major shortcoming of DCG, limited spectral sensitivity, has overcome by dye doping .

But just like silver halide emulsions, gelatin also require wet developing process and the energy requirement is very high. An alternating material, silver halide sensitized gelatin, combines the relatively high sensitivity of photographic materials and low scattering and high light stability.

Photoresists, light sensitive (UV-500 nm) organic films which yield a relief image after exposure and development, are employed in holography mainly for the production of master plates for embossed holograms and for manufacturing holographic gratings. It requires wet chemical processing and its sensitivity in the blue region is very low. Another class of materials of interest is photochromics. Though the material is reversible, organic photochromics are prone to fatigue and a limited life. Inorganic photochromics are grain free and have high resolution and it requires no processing and can be erased and reused almost indefinitely. But their use has been limited so far by their low diffraction efficeny and low sensitivity.

Photo thermoplastics which are reversible and uses thermal fixing process have reasonably high sensitivity and efficiency. But the equipment required for charging and heating the layer is very expensive and the resolution of the material is limited to 1000 line/mm.

However, the difficult crystal growth and sample preparation required for inorganic crystals has limited the widespread use of these applications. Due to its cost and the impermanence of holograms written therein; it is unlikely to be included in a commercial product.

For a long time, organic materials have found importance in holography. Biological materials like bacteriorhodopsin (photochromic retinal protein), have been used for many applications in optical image processing, such as optical memories and real time holography. Now-a-days the materials include photopolymers, photorefractive polymers, photo addressable polymers, polymers dispersed liquid crystal etc.

Photorefractive Polymers

Rapid advances in the field of Photorefractive polymers and composites have led to the development of high-performance materials with refractive index modulations approaching0.01 and diffraction efficiency is close to 100%. The effect arises when charge carriers, photogenerated by a spatially modulated light intensity, separated by drift and/or diffusion processes and become trapped to produce a nonuniform space-charge distribution. The resulting internal space-charge electric field then modulates to create a phase grating, or hologram, which can diffract a light beam. These types of holograms are dynamic, that is, they may be erased and rewritten.

To produce the Photo resistive effect, the material should consist of a photoinduced charge generator, a transporting medium, trapping sites, and molecules that provide optical nonlinearity.

The first proven polymeric material was made in 1990 and was composed of an optically nonlinear epoxy polymer bisphenol-A-di glycidl ether 4-nitro-1,2-phenylenediamine, which was made photoconductive by doping with 30 wt.% of the hole transport agent diethylamino benzaldehyde diphenyl hydrazone

. The first milestone in this field occurred with the report by the IBM group, having a net gain and Diffraction efficiency of 1% in 125micro meter thick samples of the composite FDEANST: PVK: TNF. Shortly after that Arizona group reported on a composite based on photoconductor PVK: TNF: doped with the chromophore DMNPAA with 6% efficiency. By improving the sample fabrication conditions, enabling higher fields to be applied, these composites exhibited nearly 100% Diffraction efficiency, net gain coefficients of 200cm^{-1} and fully reversible index modulation amplitudes of 0.007 with a response time of 100-500 ms.

The most commonly used polymer binder is poly (vinyl carbazole) (PVK). High-performance material of this class was developed by using inert polymers like poly (methyl methacrylate) (PMMA) and biphenyl-A-polycarbonate. PR polymers are alternatives to their inorganic or semiconductor counterparts owing to their low cost, ease and flexibility of fabrication, large size, and superior performance, one of the limitations is high voltage requirement.

1.5 Photo addressable Polymers

In principle all materials that react to light with a change of specific properties can be described as photo addressable polymers (PAPs). These PAPs are basically azobenzene containing liquid crystalline copolymers. Polyacrylates, polymethacrylates, polycarbonates, polyurethanes, polyimides and aliphatic polyesters have been investigated as the main chain. Azobenzene chromophores exist in two isomeric states: the long rod like trans form and the bent cis configuration. The isomerization can be induced by light in both directions, from trans to cis and from cis to trans, whereas the CIS isomer can also undergo a thermal back relaxation to the thermodynamically more stable trans isomer. Illumination leads to a series of trans-cis-trans isomerization cycles, resulting in a photo-stationary equilibrium that depends on the wavelength of the actinic light and the temperature of the sample. Photoinduced reversible surface-relief-gratings have been well documented as a unique and fascinating property of azobenzene-containing polymers. This is a well-known candidate for both polarization holography and photolithography. Upon exposure to an interference pattern, large surface modulations can be produced on azo polymer films. superimposed inscriptions with beams having different wavelengths or polarization directions.

Polymer Dispersed Liquid Crystals

Liquid crystals (LCs) are an interesting medium for exploring electro-optical effects due to their large dielectric anisotropy and optical birefringence. There has been a fascinating marriage of two polymer-related technologies over the past few years: photopolymer holography and polymer-dispersed liquid crystals (PDLCs) (73-74). The result is a new type of material known as holographic PDLC (H-PDLC). Intriguing features of this material include its high index modulation, true volume hologram character, unique anisotropic nature, and electro-optical behavior. Generally, an H-PDLC sample is made by sandwiching the pre-polymer syrup between two glass slides coated with a transparent conductor. The diffraction efficiency of the recorded hologram can be controlled by applying an electric field across an H-PDLC cell. Pre-polymer syrups are typically a combination of a fast-curing multifunctional monomer, a photo initiator dye, a Co-initiator, a reactive diluent, and a liquid crystal. The choice of a suitable photo initiator dye for free radical polymerization is challenging as few dyes are available for use in the visible region (450-650 nm). Rose Bengal acetate ester has-been found to be useful for writing gratings using Ar laser lines (476, 488, 514nm) or a Verdi laser line (532 nm). Other photo initiators used for making H- PDLC gratings with the Ar laser lines are di bromo fluorescein and diethyl aminocoumarin. There are a number of problems associated with these long wavelength dyes in terms of thermal and photochemical stability and bleaching speed.

Two classes of monomers have been used for H-PDLC formulation, one based on free-radical addition polymerization reaction and the other, a combination of free-radical and step-growth mechanism. Free radical addition polymerization of multifunctional monomers leads to formation of polymer of high molecular weight Urethane resins with functionality ranging from 2 to 6 were also used.

Another class of monomers used in H-PDLC gratings is the commercially available Norland resins. These contain polyfunctional thiols and allenes and undergo a combination of free-radical and step-growth polymerization. widely used resin in PDLC research is NOA 65(Norland Optical Adhesive). Though efficiencies of the order of 70% were obtained, its resolution is limited. There is one report of an H-PDLC reflective display device using a smectic liquid crystal. The efficiency obtained for H-PDLC containing rose Bengal (RB) as photo initiator and n-Phenylglycine as co initiator showed only 12% diffraction efficiency, whereas 18% diffraction efficiency was reported for an azo-dye doped polyimide (20nmthick)

Photopolymers

The term photopolymerization means the initiation by light of a chain polymerization process. In the more general sense, photopolymerization implies the increase of molecular weight caused by light. Photopolymers are photoactive materials capable of recording spatial variations in light intensity through irreversible changes. Both the phase and the amplitude information needed for hologram recreation are stored.

Photopolymers have been exploited in a variety of applications requiring versatile holographic storage media, such as data storage, HOES, and waveguides. it is widely believed that the high sensitivity, low cost, and versatility of photo polymeric media would enable more widespread commercial applications of holography

Photopolymerization is a chemical process by which small molecules or monomers are combined to make very large molecules or polymers. Photopolymer can be activated through a photosensitizer to exhibit refractive index changes due to polymerization or cross-linking. Photopolymers can be classified into two, photopolymerizable materials and photo-cross linkable materials.

Photopolymerizable Media

Photopolymerizable systems for recording holograms typically comprise one or more monomers, a photoinitiation system, and an inactive component often referred to as binder. The photoinitiation system comprises a photosensitizing dye and a co initiator. The resulting formulation is typically a viscous fluid, or a solid with a low glass transition temperature.

The basic recording mechanism involves several stages: photoinitiation, propagation and termination. The photopolymerization begins by absorption of light by the photo initiator, which results in the formation of primary free amine radicals. A second electron transfer between the amine and the radical and a protonation process give rise to leuco form (colorless form) of the dye.

In the second step of the initiation, cation radical loses a proton to become the c-amino radical. In the second stage (propagation), the c-amino radical is subsequently adding to the carbon-carbon double bonds of the monomer unit to form a growing radical of one repeat unit in length, and thus initiates the polymerization reaction. Monomer depletion in the exposed regions causes a concentration gradient, which then induces monomer diffusion from the unexposed regions.

When the photopolymer is exposed to an interference pattern, the monomers in the constructive interference region get polymerized. Because of the polymerization in the exposed regions, diffusion of monomer occurs from the destructive to constructive interference region.

Two separate paths exist for termination. The first is the normal bimolecular combination, in which two growing macro radicals come together and terminate. The second path for termination is disproportionate, in which a labile atom is transferred from one polymer radical to another.

Binder

Monomers and the photoinitiation system are usually mixed with a third component, binder, to form a photo initiator system. The binder is sometimes a polymer that is included to modify the viscosity of the formulation, to aid sample preparation and to enhance holographic exposure. Though the binder is not directly involved in the photochemical reaction, the selection of binder is an important factor. The binder should be insensitive to humidity and environmental changes.

Polymeric materials such as PMMA, Polydiacetylene, PVK, poly (vinyl alcohol) (PVA), poly (acrylic acid) (PAA). polythiophene, Poly (vinyl chloride) (PVC) etc. have been investigated for holographic applications. Binders can also be small molecules or oligomers polymeric binder. A recording medium of millimeter thickness or more and exhibiting high photoinduced RI change is required to

achieve high storage density by recording multiple volume holograms, separated from each other by the Bragg effect, in the same spatial location. For holographic data storage, the major limitations imposed by organic polymeric binders are the limited thickness of the medium, usually less than 200 micrometers, and temperature and light induced dimensional changes that can distort the holograms and degrade the fidelity with which the stored images can be retrieved. An approach to prepare thicker photopolymers is to use resins consisting of two independents photopolymerizable systems.

To increase the rigidity of the material, higher levels of procuring are required, which decreases diffusional mobility of the monomer in the resin and degrades holographic properties of the photopolymer. The shrinkage observed during UV curing in a holographic solgel material was attenuates with the inclusion of tetra methyl orthosilicate. a photopolymerizable glass can also be used as the binder

Monomer

Monomers are incorporated to the polymerizable recording media to establish high De due to Refractive index modulation. Vinyl monomers such as acrylate and methacrylate esters are used in most photopolymer systems. Vinyl polymerization can be initiated by ionic species as well as free radicals, but almost all examples of photopolymerization are of a free-radical in nature.

Monomers capable of polymerizing by cationic ring opening polymerization (CROP) mechanism have recently been applied to volume holographic recording. The holographic disk developed by Aprilis, Inc. was based on a CROP polymer.

Photoinitiation System

Holographic photopolymer systems typically use at least two different molecules to form a photoinitiation system that is sensitive to the recording wavelength. A photo initiator generally comprises of a photosensitizing dye and a charge transfer agent.

Dye

A dye is a colored substance that can be applied in solution or dispersion to substrate; thus, giving it a colored appearance. The absorption of light by colored substance is due to electronic transitions between different orbital within the molecule and the wavelengths absorbed are determined by a energy differences between the orbitals. Every dye or pigment therefore exhibits a pattern of absorption plotted as ordinate against wavelength as abscissa and this graph is the characteristics of the coloring matters. A structural change which causes the absorption band to longer wavelengths is called bathochromic shift. The reverse shift, towards shorter wavelength is known as a hypochromic effect.

The dye molecule contains two groups: the chromophore and auxochrome. The chromophore is a group of atoms which control the color of the dye. The auxochrome is a salt forming group, which helps to improve the color of the dye. The chromophore is usually electron withdrawing, and auxochromes are normally electron donating. Examples of these include the nitro, nitroso, azo, ethylene and carbonyl groups and it will be seen that all are unsaturated. Compounds containing such groups are known as chromogens and they do not behave as dyes unless they are also substituted by basic or weakly acidic groups such as -NH2. -NH(CH3). -N(CH), or OH.

When the photopolymer material is exposed to laser beam, in addition to the Refractive index change, absorbance modulation also takes place. With the proper choice of photosensitizer, holograms can be recorded throughout the spectral range from 400nm to 650 nm. A variety of dyes have been used as sensitizer which include methylene blue (MB), yellowish cosin , rose bengal (RB), chrysodine, fluorescien,erythrosin B (ErB), methyl orange, mordant yellow, malachite green, brilliant green, riboflavin, rhodamine 6G etc. To form a true molecular dispersion, the dye and other matrix additives must be compatible. Among the different dye doped systems, Methylene blue doped polymers are of special interest owing to its sensitivity to the commonly available He-Ne laser.

Methylene blue is a basic dye belonging to thiazine group. The dye is commonly known as tetramethyl thionine and to an organic chemist it is 3,7-bis-(dimethylamine) phenanthroline chloride and to some histologists it is Swiss blue. It is a dark green colored powder having a molecular weight of 319.86 and the absorption peak, if pure resides at 668nm and 609 nm. The absorption peak at pH values of 0.65,2.10,3,4, 6, 8,2 is at 880,665nm, 880 nm, 880 nm and 840 nm respectively. At neutral pH the absorption peak is at 665 nm. The absorption peak was at the orange red region of the spectrum for a pH value of 2.0. An orange color basic dye is observed in highly basic solution of pH > 13. The photochemical reduction of Methylene blue results in the formation of leuco state through the photoreduction of intermediate state.

Yingjin et al. observed the photoinduced hydride transfer reaction between Methylene blue and leuco crystal violet under steady illumination of visible light and of photosensitization by benzophenone and alpha-nitronaphthalene with UV light. The kinetics and thermodynamics of electron transfer reaction of dye with metal ions are also reported. The free energy for the self-exchange reaction of metal ions as well as the quantum yield for the radical was evaluated.

Somer et al. observed the photoreduction of Methylene blue and thionine in water by red light. Reaction energy consideration requires two photons to reduce each Methylene blue molecule. They also studied the influence of light intensity and Methylene blue concentration on the rate constant, and proposed two photon mechanisms involving a long-lived dimmer intermediate state

Co-initiator

As the direct initiation of polymerization by light is difficult and has a poor yield, the initiation is usually achieved by radical or cationic polymerization and it requires the use of a photo initiator (dye and charge transfer agent). The cation radical of the charge transfer agent (electron donor) produced during laser exposure initiates the polymerization reaction. Electron donors (EDs) like diphenyl iodonium chloride, p-toluene sulphinate, acetylacetone, triethanolamine (TEA) etc. are used as charge transfer agent.

The idea behind the use of these additives is the fact that radicals that are generated by photoexcitation and inhibit the polymerization process interact with introduced additives to form new radicals active in polymerization.

Photo-Crosslinking Polymers

Photo cross linkable systems constitute a major class of materials for many applications like production of HOE, fiber optic couplers, laser scanners and optical interconnects. There are two kinds of photo cross linkable systems: those made of gelatin and those of polymers. These subsystems are also called biopolymers and synthetic polymers respectively, DCG has some limitations such as low environmental stability and rigorous procedures of wet processing.

When the polymer film is exposed to laser beam, the photo initiator undergoes photochemical reactions and crosslinks with the polymer matrix.

Because of their unique properties such as transparency, homogeneity and photochemical stabilities, they constitute important media for non-linear optical devices. In metal ion doped polymers, the first step is the absorption of light by the metallic center. The primary mechanism in most cases is an electron transfer in the excited state.

The accepted scheme is that light irradiation reduces the sensitizer Cr^{+6} to Cr^{+3} first, and then Cr^{+3} cross links polymeric molecules, which enhances the RI, reduces the solubility of the exposed regions and creates the hologram.

It was discovered that polysaccharide polymer of linear structure sensitized with ammonium dichromate possess good holographic properties. The material has useful characteristics such as good environmental stability, simple fabrication, high diffraction efficiency (50% after processing), and high resolution (6000 lines/mm). Other dichromate materials, such as cellulose triacetate, pectin, gum, Arabic, and starch are also good materials for recording holograms.With its special properties, such as strong relief modulation, stratified sensitivity, strong real-time effect, etc., dichromate cellulose triacetate has obtained some preliminary applications in HOEs.

1.6 Literature survey on photopolymer materials for holographic recording

Volume phase holograms in photopolymers have found many potential applications in optical data storage, optical data processing and the production of HOEs. Compared with other holographic materials, photopolymers have the great advantage of recording and reading holograms in real time and the spectral sensitivity could be easily changed by simply changing the sensitizing dye. Also, these materials possess characteristics such as good light sensitivity, real time image development, large dynamic range, good optical properties, format flexibility, and low cost.

The first photopolymer recording systems for holography, as proposed in the late sixties and early seventies, were based on metal acrylate solution contained in recording cells. The photopolymer system developed by Close et al. was based on acrylates solution sensitized with methylene blue, diffraction efficiency of 45% was obtained for an exposure energy of 30 mJ/cm^2 at 643 nm. The recorded holograms were stabilized by post exposure using xenon flash lamp ($3mJ/cm^2$) and thermal fixing. Improvements in the performance of acrylamide (AA m)

photopolymers were achieved by crosslinking with ethylene bisacryl amide and by photoreduction with Triethanol amine, acetyl acetone and hydroquinone. With the incorporation of triethanolamiine, 65% diffraction efficiency was obtained at $50mJ/cm^2$ whereas the efficiency obtained for acetyl acetone incorporated solution was only 20%. A photo polymer consists of liquid acrylic monomer, a cellulosic binder, a photo initiating system and a plasticizer was reported. A liquid photopolymer containing a 1:1mixture of 4,5-diiodosuccinyl fluorescein and MB, which upon visible-light irradiation shows a clear enhancement in the sensitivity and the polymerization rate is also reported.

Dye Sensitized Pol vinyl alcohol

Polyvinylalcohol films has many optical uses, which result from its lack of color, its clarity and its high transmission in the near infrared and ultraviolet. Polyvinyl alcohol films can be oriented to give high degree of birefringence and high tensile strength in the stretch direction. Additional properties which account for its versatility are its hydrophilic character, easy dyeability, ability to be Crosslinked. Polyvinyl alcohol came into use as hologram recording material from late 70's onwards. Its many hydroxyl groups cause it to have high affinity to water, with strong hydrogen bonding between the intra and intermolecular hydroxyl groups, greatly impeding its solubility in water. Aqueous solution of Polyvinyl alcohol is considered as a molten gel.

Aqueous solution of Polyvinyl alcohol of high degree of hydrolysis increase the viscosity with time, and may finally gel. The viscosity of solution increases with concentration and decreases with temperature.

The high viscosity of Polyvinyl alcohol solution enables its use as a binder in the photopolymer system and thick films could be fabricated with Polyvinyl alcohol. Polyvinyl alcohol film is hard and brittle at low humilities, but soft and tough at high humilities

O'Neill et al. have studied the mechanism of hologram formation in acrylamide-photopolymer. Gallego et al. carried out the three-dimensional analysis of holographic memories on Polyvinyl alcohol(PVA) films. Polyvinyl alcohol systems have been reported with different sensitizing dyes and other matrix additives.

Carretero et al. observed a decrease in the transmittance curves as a function of the age of the polymer film consists of MBA.

Blaya et al. described the mechanism of grating formation in MBPVA films and obtained 80% efficiency in their polymer system fabricated using CAMAG scientific thin layer chromatography plate coater.

Blaya et al. presented the holographic characterization of the MBPVA incorporated with a Crosslinker, N,N-dihydroxyethylenbisacrylamide (DHEBA).

The photopolymerizable film used in their experiment was prepared using a TLC coater and the drying period was 20hrs. The gratings recorded using 633 nm He-Ne laser by keeping the beam ratio as 1:1 and spatial frequency as 1100 lines/mm showed 70% diffraction efficiency

Neumann et al. described a simple technique suitable for the direct laser writing of surface relieves in dry photopolymerizable film comprised of Acrylamide, MB, TEA and PVA dissolved in ethanol and water.

Fimia et al. developed holographic photopolymer systems consist of Acrylamide, Zinc acrylate and MBA as monomers, a photo initiator system consist of Methylene blue in 4:1 ratio and p-toluensulfunic acid and they obtained -35%efficiency using He-Ne laser.

Later **Belendez et al.** analyzed the noise gratings formed on MB: RB -acrylamide system. Among the different sources of noise in holography, self-induced noise gratings are due to scattering from inhomogeneities in the recording material and have an important spurious effect on volume holography.

Mallavia et al. reported that an ion pair isolated from Methylene blue acted as the photo initiator in the photopolymer formulation. This photopolymer system showed wide spectral response and obtained 30% diffraction efficiency at 514nm and 60% diffraction efficiency at 633 nm. VA/Acrylamide films were also fabricated with yellowish eosin as sensitizing dye.

Garcia et al. studied the influence of beam ratio and intensity on the optical quality of transmission holograms of diffuse object stored in eosin doped polyvinyl alcohol systems. They used a SNR of 0.94 with a diffraction efficiency of 13% for a beam ratio of 2 0 and intensity of 1.2mW/em .The variation in transmittance produced when a photopolymer is irradiated with a pulsed laser was analyzed and diffraction efficiency is (60%) .

The second order Fourier component of the Refractive index formed in phase diffraction gratings recorded in eosin doped PVA/acrylamide was studied by **Neipp et al.**

Gallego et al. determined the temporal evolution of diffraction efficiency of a hologram stored in an eosin doped Polyvinyl alcohol/Acrylamide /dimethyl acrylamide (DMAA) photopolymer system by measuring the angular response of the hologram immediately after exposure and in subsequent hours.

Gallego et al. proposed several methods to eliminate the residual monomer in eosin/Polyvinylalcohol/Acrylamide m films in order to stabilize the holographic gratings. The residual dye and residual monomer are the main problems in achieving high diffraction efficiency stable under white light.

The surface relief formation in a photopolymer containing AA m is reported by **Boiko et al.**

Jallapuram et al. studied the effect of binder molecular weight. on the Diffraction efficiency and found that it had no substantial improvement of De at higher spatial frequencies.

The spatial resolution of the polymer system was found to be increased with MBA concentration. **Gong et al**. developed a PVA based holographic recording material composed of ErB as dye, TEA as electron donor, AAm and N hydroxymethyl acrylamide as monomers. The recording was obtained by the copolymerization of AAm and HMA and an efficiency of nearly 50% were

Sheriff er al investigated the angular multiplexing in doped PVA/AAm formulated in the Centre for Industrial and Engineering Optics (CIEO) with a view of further optimization for holographic data storage. An investigation of the photoinduced surface relief modulation in thin and thick layers of an AAm based photopolymer system developed at the CIEO was reported. Post-exposure of the gratings

PVA/AAm films sensitive to 500-630 nm was fabricated with methyl violet as photo initiator. The recording characteristics of the holographic film were examined and the compositions were optimized. Only 8% efficiency was obtained and the recorded gratings gradually disappeared on storage.Ability of a diffraction grating recording in photo polymer material was proven at the late 1960 of the last century and it was also show that the grating growth is caused by the diffusion process .

The mode proposed **zhao.et.al describe** the evolution of grating formation in photopolymer using the four harmonic expression of a standard one-dimensional diffusion.

colvin et al. Presented the quantitative model to describe the formation of volume holograms in a polymeric medium containing polymerizable acrylate monomer that undergrowth spatial modulated gelatin as a result of exposure to visible beam.

Sheridan.et.al developed the nonlocal polymerization driven diffusion model, which extended Zhao model to include nonlocal spatial response.

Renotte.et.al applied nonlocal diffusion model to successfully model higher harmonic grating components in polymer materials

Sutherland.et.al examined effect of shrinking and swelling and outlined an extension to the non local diffusion model

Kelly.et.al carried out temporal analysis of grating formation in PAA/PVA films.this is done by analyzing attenuation of light in depth.

The main drawback of an AAm based photopolymer as far as the environment is concerned is the AAm, a substance which has been known to be carcinogenic for many years. So a photopolymer system which is less toxic than AAm system has been developed. The new photopolymer formulation consists of 5'-riboflavin monophosphate as Dye, sodium acrylate as monomer, DHEBA as crosslinker. The new system showed 50% efficiency at 300mJ/cm^2

Azo dyes like chrysodine and mordant yellow 3R on PVA were found to be erasable with Diffraction efficiency of about 27%. A linear polyol incorporated eosin PVA system with 15% Diffraction efficiency was reported by **Ponce et al.**

Metal Ion Doped PVA

Metal ions such as Ferrie (Fe) and Dichromate (Cr+%) have been used in conjunction with PVA for recording holograms in real time. The photochemistry of Cr has been investigated over decades and it has been generally accepted that the photo reduction of Cr leads to Cr+ in the presence of organic-reducing substances like secondary alcohols. From the earlier works done on DCPVA, **Duncalf and Dunn** suggested that the in solubilization of DCPVA after exposure was caused by complex formation between Cr with PVA. **Ziping et al.** recorded holograms of 30% efficiency on DCPVA and developed a technique to fix the holograms by heat treatment. **Lelievre et al.** recorded holograms with polarized light and obtained 30% diffraction efficency **changkakoti. et al.** employed two simple techniques of development using ethyl alcohol and have achieved 60% Diffraction efficiency for fixed holograms.

Maniavannan et al studied the influence of different chemical parameters (e.g:pH and electron donors) on DCPVA and 70% efficiency was obtained using 488 nm Ar laser The EDs influence significantly the Diffraction efficiency of recorded holograms.

The ferric salt photoreduces to the ferrous form as a result of photoreduction of the dye in the presence of an **ED. Sugawara et al.** devised a photosensitive liquid system with a mixture of AAm, MBA coupled with Ferric ion and tert-butyl hydroperoxide. This recording system is sensitive from 200-500 nm and exhibits high diffraction efficiency.

Manivannan et al. presented Fe^{3+} doped PVA systems for hologram recording Although volume holograms recorded in Fe: PVA films exhibited a high peak diffraction efficency of - 80%

Polyacrylic acid

Another synthetic polymer which is very attractive in holography is PAAdoped with metal ions and organic dyes

Photosensitive materials comprising of acrylic acid and catalyst are used to record holograms in the presence of laser beam. Volume transmission holograms have been recorded in polymer films.

Photoinduced holographic surface relief gratings have been fabricated using 442nm laser and they are obtained without any chemical treatment or wet processing.

Ushamani et al. fabricated MB sensitized polymer film by blending both PVA and PAA in 7:3 ratio. The storage life of gratings recorded on MBPVA/PAA blend was better than that of MBPVA films. The effect of different EDs on the sensitivity and efficiency of MBPVA/PAA blend also was studied. Later, the development of dichromated blend of PVA/PAA is also reported.

Polyvinyl chloride

Ushamani et al. reported the feasibility of using PVC matrix as an optical recording medium by making it as copper acetate complexed methylene blue sensitized polyvinyl chloride (CMBPVC) films. Later a systematic analysis on the effect of pH on the bleaching property and Diffraction efficiency of CMBPVC were presented. Direct imaging done on pure and CMBPVC films revealed the optical quality of the film.

Unlike in other matrices, the change of state occurring to the dye molecules (MB) on laser irradiation is permanent in PVC and it exists in the leuco form itself. Since the material was not comprised of any monomer or ED as in the conventional photopolymerizable recording medium, the only contribution to the recording mechanism was the absorbance modulation.

The gratings recorded on the CMBPVC films showed an efficiency of 4.46% at 1500 mJ/cm for the intensity ratios of the first order diffracted beam to that of the transmitted beam. Though change in absorbance on storage (after laser exposure) is not observed in this material, the recorded grating vanished within few hours.

Polymethyl methacrylate

Photopolymer comprising PMMA (poly (methyl methacrylate)) as the base is primarily sensitive to some region of the visible spectrum with sensitizers such as p-benzoquinone.

To alleviate the shrinkage effect in thick materials, some techniques for fabricating photopolymer materials have been proposed and demonstrated. Among these recording materials, PMMA is one of the most popular polymer bases for the binder, due to its good dimensional stability and good optical quality. Recent research has shown that PMMA doped with phenanthrenequinone (PQ) could be very attractive for volume holographic recording because it is easy to form in bulk with negligible photochemically induced dimensional change and good optical quality.

Commercially Available Polymers

In order to respond to today's growing demand, a number of photopolymers have been commercialized. It includes photopolymers developed by DuPont, Polaroid, Aprilis etc.

Among commercially available photopolymer materials DuPont's dry photopolymers seem to have gained the highest popularity. The DuPont polymers are coated on Mylar polyester film of Soum thickness. A removable cover sheet of 25um Mylar or 6Oum PVC film is used to protect the slightly tacky photopolymer. The photopolymer thickness typically ranges from 10-50um.

Potential applications for optical storage and interconnection systems have been reported on Dupont's polymer. The commercial photopolymers designed for holographic recording by Dupont have been studied extensively and provide excellent material photosensitivity and Refractive index contrast.

Lougnot et al have developed a solvent-free system with small multifunctional acrylate monomers. As only thin media (<50 μm) can be prepared, these films are unsuitable for high-density data storage.

Aubrecht et al. studied the recording of holographic volume diffraction gratings in Du Pont's photopolymer HRS-150 both theoretically and experimentally.

Moreau.et.al investigated the recording dynamics of omni-Dex photopolymer film from DuPont and different experiments detailed that lead to the determination of material kinetic parameters.it is fully characterized by peritrophic multiplexing. In recent years many photopolymer materials are developed for recording holograms**.**

wang.et.al developed blue sensitive photopolymer system that consist of camphor quinine as photosensitizer.

Yagi.et.al of NIT photonics laboratory proposed thin film multilayer waveguide holographic memory card.**Hirabayashi.et.al** developed a two-color absorption photopolymer in which hologram could be recorded by simultaneous irradiation with a 660nm interference light.

C.S Rajesh et.al portraits the eosin doped polyvinyl alcohol /acrylamide material when another dye methylene blue was incorporated into the photopolymer system by the inclusion of methylene blue it was possible to extend the absorption range.also it enhanced the entire properties of the system.(2018)

Jisha developed selfwritten waveguide in methylene blue sensitized polyvinyl alcohol/acrylamide ph otopolymer material.(2008)

Debopriyo Ghoshal et.al developed methylene blue /PVA composite film for flexible ,wider scale uv –visible cut off filter (2019)

H M Zidan et.al studied photodegradation of methylene blue with PVA/PVP blend under ultraviolet light irradiation.

Beena mary john.et .al reported the efficiency difference between MBPVC and copper acetate doped methylene blue sensitized film (CMBPVC)

The inclusion of nanoparticles also contributes rapid buildup of fixed holograms which give high stability and sensitivity.In order to respond to industrial demand, in application like holographic data storage, display, optical waveguides, much emphasis has to be put on to develop new polymerizable material with high sensitivity and high efficiency.

1.7 Conclusion

Importance of holographic technology in the modern era is presented in this paper description of available recording media with special mention to photopolymer is explained. a detailed review on polymer-based recording is presented.

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CHAPTER 2

Holographic recording films

Introduction

The word Nano is derived from the Greek word 'nanos' meaning dwarf. Nano refers to 10^-9 or 1 billionth. It refers to a nanometer, which is one of the scales of atomic diameters.

Nanotechnology is the study of the controlling of matter on an atomic and molecular scale. Generally it deals with structured sized 100 nm or smaller in at least one dimension. It is very diverse ranging from extensions of conventional device physics to completely new approaches based on molecular self assembly.

The first use of the concepts found in nanotechnology was in "There's plenty of Room at the bottom". a talk given by physicist Richard Feynmann at an American physical society meeting in Caltech in 1959. He described the process by which individual atoms can be manipulated and molecules might be developed using one set of precise tools to build and operate another proportionally smaller set and so on down to the needed scale . Tokyo science University professor Norio Taniguchi in 1974 defined nanotechnology as mainly consisting of the processing of separation, consolidation and deformation of materials by one atom or by one molecule. Nanotechnology and Nanoscience got started in the early 1980s with two major developments; the birth of cluster science and the invention of the scanning tunneling microscope (STM). This development led to the discovery of fullerenes and carbon nanotubes.

Two main approaches are used in nanotechnology : bottom up approach and top down approach. In the bottom up approach materials and devices are build from molecular components which assemble themselves chemically by principles of molecular recognition. In the top down approach, nano objects are constructed from larger entities without atomic level control . Areas of Physics such as nanoelectronics , nanomechanics and nanophotonics have evolved during the last few decades to provide a basic scientific foundation of nanotechnology.

A number of physical phenomena become pronounced as the size of the system decreases. These include statistical mechanical effects as well as quantum mechanical effects. Quantum effects become dominant when the nanometer size range is reached. Additionally a number of physical properties change when compared to macroscopic systems. One example is the increase in surface area to volume ratio altering mechanical, thermal and catalytic properties of materials.

The bottom up approach utilizes the concept of molecular self-assembly and/ or Supramolecular chemistry to automatically arrange themselves into some useful confirmation. The concept of molecular recognition is especially important as molecules can be designed so that a specific configuration is favored due to non-covalent intermolecular forces.

Molecular nanotechnology, sometimes called molecular manufacturing, describes engineered nano systems operating on the molecular scale. It is especially associated with the molecular assembler, a machine that can produce a desired structure or device atom-by-atom using the principle of mechanosynthesis.

APPLICATIONS

With nanotechnology, a large set of materials and improved products rely on the change in the physical properties when the feature sizes are shrunk. Nanoparticles take advantage of their dramatically increased surface area to volume ratio. The various applications of nanotechnology include the following:

Medicine

The biological and medical research community have exploited the unique properties of nanomaterials for various applications. The size of nanomaterials is similar to that of most biological molecules and structures; therefore, nanomaterials can be useful in biomedical research and applications. Nanotechnology can also be used for drug delivery. This is because materials can be synthesized to dimensions fitting the cell, tissues or DNA. If nanomaterials can be functionalized with appropriate functional group they can be directly targeted.

Chemistry and environment

Chemical catalysis and filtration techniques are two prominent examples where nanotechnology already plays a role. The synthesis provides novel materials with tailored features and chemical properties. In this sense, chemistry is indeed a basic Nano science. In a short term perspective, chemistry will provide novel "nanomaterials" and in the long run, superior processes such as "self assembly" will enable energy and time preserving strategies. Some of the greatest potential uses or applications for nanotechnology in the environment are sensors, treatment ,remediation and green nanotech manufacturing and engineering. These applications can be further categorized as either reactive to existing environment problems or proactive in anticipating and preventing future problems.

Energy

The most advanced nanotechnology projects related to energy are: storage, convention, manufacturing improvements by reducing materials and process rates, energy saving and enhanced renewable energy sources. Today's best solar cells have layers of several different semiconductors stacked together to absorb light at different energies but still they manage to use only 40% of solar energy. Nanotechnology could help increase the efficiency of light conversion by using nanostructures with a continuum of band gaps.

Information and communication

Current high technology production processes are based on traditional top-down strategies, where nanotechnology has already been introduced silently. Nanotechnology is being used in the production of novel semiconductor devices and opto electronic devices. It is also used for increasing the memory capacity in devices.

2.2 THICK FILMS

Thin and thick film resistors are the most common types in the market. They are characterized by a resistive layer on a ceramic base. Although their appearance might be very similar, their properties and manufacturing processes are very different. The naming originates from the different layer thicknesses.

Thin film has a thickness in the order of 0.1 um (micrometer) or smaller, while thick film is thousands times thicker. However, the main difference is the method used to apply the resistive film onto the substrate. Thin film resistors have a metallic film that is vacuum deposited on an insulating substrate. Thick film resistors are produced by firing a special paste onto the substrate. The paste is a mixture of glass and metal oxides. Thin film is more accurate, has a better temperature coefficient and is more stable. Therefore, it competes with other technologies that feature high precision, such as wire wound or bulk metal foil. On the other hand, thick film is preferred for applications where these high requirements are not critical since prices are much lower

Whatever be the film thickness limit an ideal film can mathematically be defined as a homogeneous solid material contained between two parallel planes and extended extended infinitely into direction (say X and y (but restricted along the third direction (x) which is perpendicular to the x-y plane. The dimension along is a direction is known as film thickness (d or t).it's magnitude may vary from the limit d to 0 to any arbitrary value or more. But always remaining much less than those along the other directions ie; x and y . A real film ,however deviates considerably from the ideal case since it's two surfaces are never exactly parallel even when format in the best experiment and deposition condition and also the material contain between the two surface are rarely homogenous .neither uniformly distributed nor of the same species a film name also contains some imperfection impurity, dislocation, grain boundaries and various other defect and may also be discontinuous. Some of this can be minimized by appropriate control of deposition condition but cannot all together be avoided.

Some of the factors which determine the physical ,electrical, optical and other properties of a thick film are the following :rate of preposition substrate temperature , environmental condition ,residual gas pressure in the system , of the material to be deposited ,inclusion of foreign matter in the deposit etc.

2.2.1 Thick film deposition techniques

Thick films are considered as dispersions, pastes, and inks being conductive, resistive or dielectric; however, for the time being, thick films include a wider group of inorganic and organic materials. Accordingly, the deposition processes can be divided into directed coating techniques, spreading coating techniques, and immersion coating techniques.

Spray coating

Spray coaters are devices that use atomization as the coating method. These devices turn the coating fluid into a mist and spray it onto the target.

Because of their sophisticated and diverse design, spray coaters have been used for a wide range of applications, from thin film coating of flat sheets such as transparent conductive films for touch panels, to solar cell components and semiconductor photoresist.

Spray coaters can be classified into three hu groups according to the spray method: Air spray systems, ultrasonic spray systems, and electrostatic spray systems.

Air spray systems use compressed air to change the coating fluid into a fine mist that is sprayed onto the target. A typical example is an air spray gun, which uses a similar mechanism.

Compressed air applies high pressure to the coating fluid discharged from the nozzle and the fluid then collides at a high speed with the remaining air. The coating fluid is split up and slowed down at that moment due to air resistance, and then changes into a mist before reaching the target

Ultrasonic spray systems are equipped with a chip (atomization surface) at the end of the nozzle. The vibration generated by ultrasonic waves causes the coating fluid to spread over the chip, and ruffling occurs on the surface. When the ultrasonic output exceeds the surface tension, the fluid drops from the surface as a fine mist.

In electrospray systems, the coating fluid is charged with static electricity through the application of several thousands of volts in the nozzle. The fluid is then changed into a fine mist through electrostatic repulsion. The coating fluid mist is attracted to the surface of the target, which sits on a grounded stage. These systems can be used for fluids with varying viscosities as well as pastes, slurries, and fluids containing filler dispersion. The result is a uniform film of even on substrates with uneven surfaces

Aerosol deposition

Aerosol deposition method is a method to fabricate ceramic membranes, in which aerosol, or a mixture of fine ceramic particles with a diameter of around 1 micrometer and gas, is sprayed on a substance at a speed of around 150 to 400 m/sec to form membranes on it.

Typically, fabrication of ceramic membranes requires the ceramic materials, which are the ingredients of the membranes, and the object of membrane fabrication to be kept at a high temperature. In contrast, the aerosol deposition method can form membranes at room temperature, as it makes particles collide against a substance at a high speed and the resulting collision energy is used to form the membranes.

This gives the method an advantage in that the object of membrane formation is not deteriorated by heat.

Research of this method has been under way over recent years, with the theme of reducing costs for practical applications.

Spin coating

Spin coating is a technique used to spread uniform thin films on flat substrates by centrifugal force. The apparatus used for spin coating is called a spin coater, or a spinner. A solution of material is dispensed onto the center of a wafer, which is then rotated at high speed.

Rotation continues until the excess solution spins off the substrate and the desired thickness of the film is left on the substrate. The applied solvent is usually volatile and evaporates during deposition. The two main factors that define film thickness are the spin speed and the viscosity of the solution. Other factors considered include spin time, solution density, solvent evaporation rate, and surface wettability.

Spin coating is arguably the simplest and most commonly used method for solution deposition of metal oxide inks. In the spin process, drops of precursor solution or ink are dispensed on hydrophilic substrate, which then rotates to high angular velocities (hundreds to thousands of rpm) to spin off excess solution, resulting in thin and uniform film. During the spinning, solvent contained in the ink starts to evaporate, which facilitates the formation of solid-like gel film because of dramatically increased viscosity. The thickness (d) of the resultant gel film is mainly determined by the precursor viscosity (η), the angular speed ω (rpm)

The major advantages of spin coating include good reproducibility and easy integration with conventional lithography-based fabrication techniques. However, spin coating is limited in scalability and is not compatible for manufacturing of large area TFT arrays. Moreover, most of the ink ($\approx$95%) is wasted during the spinning process.

Doctor blade / tape casting method

Doctor blade coating is a technique used to form films with well-defined thicknesses. The technique works by placing a sharp blade at fixed distance from the surface that needs to be covered. The coating solution is then placed in front of the blade and the blade is moved across in-line with the surface, creating a wet film. The technique should ideally have solution losses of about 5%; however, practically, it takes time for optimal conditions to be found (Krebs, 2009).

The inks/pastes used in these processes usually require large amounts of binders and thickeners to produce the high viscosities (1000–10,000 mPa s) required for reproducible and reliable production of films

Dip coating

Dip coating is an industrial coating process which is used, for example, to manufacture bulk products such as coated fabrics and specialized coatings for example in the biomedical field. Dip coating is also commonly used in academic research, where many chemical and nano material engineering research projects use the dip coating technique to create film coatings.

The earliest dip-coated products may have been candles. For flexible laminar substrates such as fabrics, dip coating may be performed as a continuous roll-to-roll process. For coating a 3D object, it may simply be inserted and removed from the bath of coating. For condom-making, a former is dipped into the coating. For some products, such as early methods of making candles, the process is repeated many times, allowing a series of thin films to bulk up to a relatively thick final object

The final product may incorporate the substrate and the coating, or the coating may be peeled off to form an object which consists solely of the dried or solidified coating. As a popular alternative to Spin coating, dip-coating methods are frequently employed

Electrophoretic deposition (EPD)

Electrophoretic deposition (EPD), is a term for a broad range of industrial processes which includes electrocoating, cathodic electrodeposition, anodic electrodeposition, and electrophoretic coating, or electrophoretic painting. A characteristic feature of this process is that colloidal particles suspended in a liquid medium migrate under the influence of an electric field (electrophoresis) and are deposited onto an electrode. All colloidal particles that can be used to form stable suspensions and that can carry a charge can be used in electrophoretic deposition. This includes materials such as polymers, pigments, dyes, ceramics and metals

The process is useful for applying materials to any electrically conductive surface. The materials which are being deposited are the major determining factor in the actual processing conditions and equipment which may be used

EPD processes are often applied for the fabrication of supported titanium dioxide (TiO_2) photocatalysts for water purification applications, using precursor powders which can be immobilised using EPD methods onto various support materials. Thick films produced this way allow cheaper and more rapid synthesis relative to sol-gel films, along with higher levels of photocatalyst surface area

The process applies coatings which generally have a very uniform coating thickness without porosity.

Complex fabricated objects can easily be coated, both inside cavities as well as on the outside surfaces.Relatively high speed of coating.,Relatively high purity x Applicability to wide range of materials (metals, ceramics, polymers,)Easy control of the coating composition.

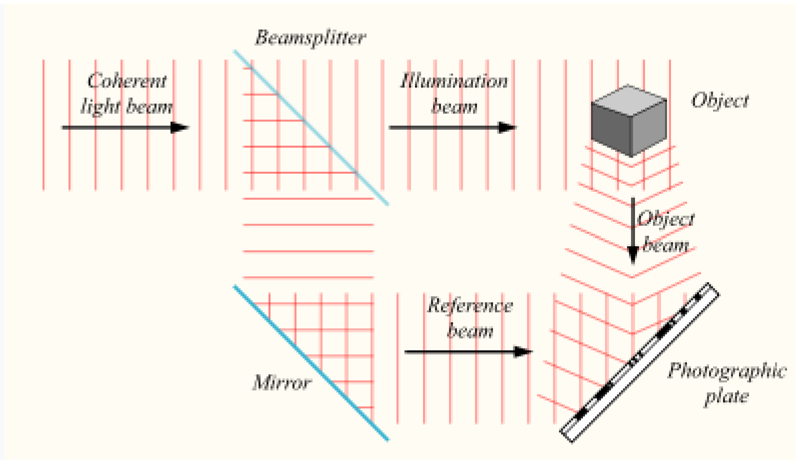
The process is normally automated and requires less human labor than other coating processes,Highly efficient utilization of the coating materials result in lower costs relative to other processes,The aqueous process which is commonly used has less risk of fire relative to the solvent-borne coatings that they have replaced,Modern electrophoretic paint products are significantly more environmentally friendly than many other painting technologies.

In addition to this sedimentation ,texturing ,polymerisation are the techniques used in fabrication of thick film

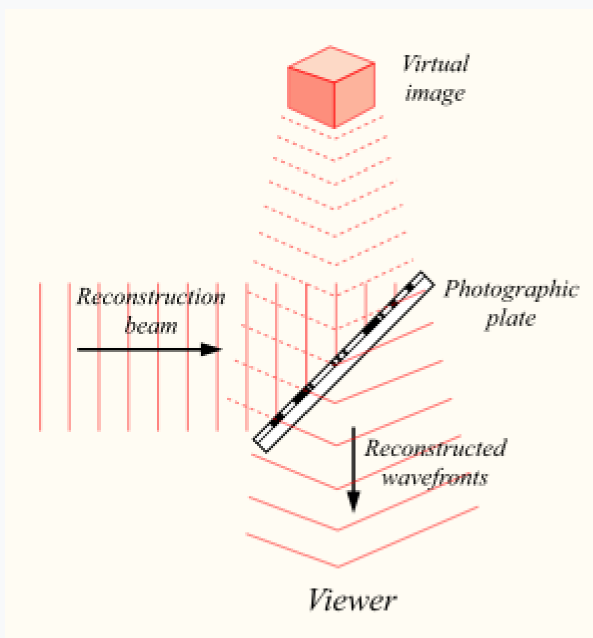
2.3 HOLOGRAPHY

Holography is a technique that enables a wavefront to be recorded and later re-constructed. Holography is best known as a method of generating three-dimensional images, but it also has a wide range of other applications. In principle, it is possible to make a hologram for any type of wave.

A hologram is made by superimposing a second wavefront (normally called the reference beam) on the wavefront of interest, thereby generating an inerferance pattern which is recorded on a physical medium. When only the second wavefront illuminates the interference pattern, it is diffracted to recreate the original wavefront. Holograms can also be computer-generated by modelling the two wavefronts and adding them together digitally. The resulting digital image is then printed onto a suitable mask or film and illuminated by a suitable source to reconstruct the wavefront of interest. Holography is based on the principle of interference. A hologram captures the interference pattern between two or more beams of coherent light (i.e. laser light). One beam is shone directly on the recording medium and acts as a reference to the light scattered from the illuminated scene.



Recording a hologram



Reconstructing a hologram

Holography is a technique that enables a light field (which is generally the result of a light source scattered off objects) to be recorded and later reconstructed when the original light field is no longer present, due to the absence of the original objects. In one common arrangement, the laser beam is split into two, one known as the object beam and the other as the reference beam. The object beam is expanded by passing it through a lens and used to illuminate the subject. The recording medium is located where this light, after being reflected or scattered by the subject, will strike it. The reference beam is expanded and made to shine directly on the medium, where it interacts with the light coming from the subject to create the desired interference pattern.

Like conventional photography, holography requires an appropriate exposure time to correctly affect the recording medium.

A hologram can be made by shining part of the light beam directly into the recording medium, and the other part onto the object in such a way that some of the scattered light falls onto the recording medium. The first element is a beam splitter that divides the beam into two identical beams, each aimed in different directions: One beam (known as the 'illumination' or 'object beam') is spread using lenses and directed onto the scene using mirrors. Some of the light scattered (reflected) from the scene then falls onto the recording medium. The second beam (known as the 'reference beam') is also spread through the use of lenses, but is directed so that it does not come in contact with the scene, and instead travels directly onto the recording medium.

Several different materials can be used as the recording medium. One of the most common is a film very similar to photographic film (silver halide photographic emulsion), but with a much higher concentration of light-reactive grains, making it capable of the much higher resolution that holograms require. A layer of this recording medium (e.g., silver halide) is attached to a transparent substrate, which is commonly glass.

A hologram represents a recording of information regarding the light that came from the original scene as scattered in a range of directions rather than from only one direction, as in a photograph. This allows the scene to be viewed from a range of different angles, as if it were still present . A photograph can be recorded using normal light sources (sunlight or electric lighting) whereas a laser is required to record a hologram. A lens is required in photography to record the image, whereas in holography, the light from the object is scattered directly onto the recording medium. A holographic recording requires a second light beam (the reference beam) to be directed onto the recording medium .A photograph can be viewed in a wide range of lighting conditions, whereas holograms can only be viewed with very specific forms of illumination.

2.3.1 TYPES OF HOLOGRAMS

Unlike ordinary images, holograms are images that resulted from interference and diffraction of light. It is a three-dimensional representation of a person or object used normally in communication or entertainment. In telecommunications, holograms are used mostly as an alternative to screens. A hologram is an image formed when a point source of light (a reference beam) of fixed wavelength encounter light of the same fixed wavelength arriving from an object (the object beam).

There are three types of holograms: the reflection hologram, transmission hologram, and then the hybrid (combination of both).

Reflection hologram

The reflection hologram, in which a truly three-dimensional image is seen near its surface, is the most common type shown in galleries. The hologram is illuminated by a "spot" of white incandescent light, held at a specific angle and distance located on the viewer's side of the hologram. Thus, the image consists of light reflected by the hologram. Recently, these holograms have been made and displayed in color—their images optically indistinguishable from the original objects.

Transmission hologram

The object and reference beam incident on holographic film is on the same side. It is less expensive if mass produced.

The typical transmission hologram is viewed with laser light, usually of the same type used to make the recording. This light is directed from behind the hologram and the image is transmitted to the observer's side. The virtual image can be very sharp and deep. For example, through a small hologram, a full-size room with people in it can be seen as if the hologram were a window. If this hologram is broken into small pieces (to be less wasteful, the hologram can be covered by a piece of paper with a hole in it), one can still see the entire scene through each piece.

Hybrid hologram

There is no need for real object. Interference pattern is calculated digitally using computer algorithms. Between the reflection and transmission types of holograms, many variations can be made. One of such is the mathematics of holography is now well understood. Essentially, there are three basic elements in holography: the light source, the hologram, and the image. If any two of the elements are predetermined, the third can be computed. For example, if we know that we have a parallel beam of light of certain wavelength and we have a “double-slit” system.

2.3.2 Applications of Holography

Holography is not only used to make three-dimensional pictures and it does not confine itself to the visible spectrum. Microwaves are used to detect objects through otherwise impenetrable barriers. X-rays and ultraviolet light are used to detect particles smaller than visible light. This is how holography was discovered. Dr. Dennis Gabor is recognized as the inventor of holography when he used it to aid in his electron microscopy in 1947.

Holography is also used to detect stress in materials. A stressed material will deform, sometimes so minutely that it is not visible. A hologram can amplify this change since the light reflected off of the material will now be at a different angle than it was initially. A Comparison between the before and after holograms can determine where the greatest stress is.In Europe telephone credit cards use holograms to record the amount of remaining credit. Fighter pilots use holographic displays of their instruments so they can keep looking straight up. Museums keep archival records in holograms. One of the best uses for holography is candy. The candy’s surface is etched into tiny prism-like ridges that display 3-D images in brilliant iridescent colors. Holography has even tried to make it into the moviebusiness. Lastly, holography is used in a new kind of computer, an optical computer. Optical computers really are not so new in concept but they are far from perfected and are constantly changing with new technology. They are also far from commercially viable, though they say only in a few more year.

Art

Early on, artists saw the potential of holography as a medium and gained access to science laboratories to create their work. Holographic art is often the result of collaborations between scientists and artists, although some holographers would regard themselves as both an artist and a scientist.

Salvador Dalí claimed to have been the first to employ holography artistically. He was certainly the first and best-known surrealist to do so, but the 1972 New York exhibit of Dalí holograms had been preceded by the holographic art exhibition that was held at the Cranbrook Academy of Art in Michigan in 1968 and by the one at the Finch College gallery in New York in 1970, which attracted national media attention. In Great Britain, Margaret Benyon began using holography as an artistic medium in the late 1960s and had a solo exhibition at the University of Nottingham art gallery in 1969. This was followed in 1970 by a solo show at the Lisson Gallery in London, which was billed as the "first London expo of holograms and stereoscopic paintings".

Data Storage

Holographic data storage is a technique that can store information at high density inside crystals or photopolymers. The ability to store large amounts of information in some kind of medium is of great importance, as many electronic products incorporate storage devices. As current storage techniques such as Blu-ray Disc reach the limit of possible data density (due to the diffraction-limited size of the writing beams), holographic storage has the potential to become the next generation of popular storage media. The advantage of this type of data storage is that the volume of the recording media is used instead of just the surface.

Sensors and Biosensors

The hologram is made with a modified material that interacts with certain molecules generating a change in the fringe periodicity or refractive index, therefore, the color of the holographic reflection

Security

Holograms are commonly used for security, as they are replicated from a master hologram that requires expensive, specialized and technologically advanced equipment, and are thus difficult to forge. They are used widely in many currencies, such as the Brazilian 20, 50, and 100-reais notes; British 5, 10, and 20-pound notes; South Korean 5000, 10,000, and 50,000-won notes; Japanese 5000 and 10,000 yen notes, Indian 50, 100, 500, and 2000 rupee notes; and all the currently-circulating banknotes of the Canadian dollar, Croatian kuna, Danish krone, and Euro. They can also be found in credit and bank cards as well as on electronic products. They often contain textual or pictorial elements to protect identities and separate genuine articles

CHAPTER -3

Preparation and characterisation of holographic recording material using polymer

For the present study, poly vinyl alcohol and poly vinyl chloride were selected as base matrices and methylene blue was used as the photo initiator or dye. The materials used and the experimental procedures adopted in the present investigation are given in this chapter.

3.1 Materials Used

Photopolymer systems for recording holograms typically comprise one or more monomers, a photo initiator system and an inactive component often referred to as a binder. The following section describes the various constituents used for the fabrication of photopolymer films.

Host Matrices

Both poly (vinyl chloride) (PVC) and poly (vinyl alcohol) (PVA) were selected as the host matrices or binder. PVC, the leading plastic material, is a member of the large family of polymers broadly referred to as vinyls, all have the vinyl group ($CH_2=CH-$) in common. It is produced as a result of polymerisation of vinyl chloride. The polymerization of vinyl chloride can result in the formation of molecules with a number of isomeric forms $-(CH_2-CHCl)-_n$.

Dye

The photo initiator system comprises of a photosensitizer dye and a charge transfer agent. here, methylene blue (MB) was used as the photosensitizing dye. MB dye of microscopy grade was supplied by Qualigens. Chemically MB is 3, 7-bis (dimethyl amino) phenantholinium chloride. MB is a basic dye of thiazine group and is also known as swiss blue and tetramethyl thionine The absorption maxima of MB, if pure, reside at 668 nm and 609 nm.

Monomer

Different monomers were incorporated to the polymer matrices to

establish the grating formation induced by refractive index modulation. MBPVC films were fabricated with vinyl acetate (Lancaster) and butyl acrylate monomer.

3.2 FABRICATION OF FILM

The various techniques for coating polymer solution include dip coating, spin coating, doctor blading, gel casting, gravity settling, spraying etc.

Among these, in the present work gravity settling method was adopted. The method was easy to setup and the procedure was simple. The coating was done by pouring known volume of viscous solution on cleaned glass slides kept on a leveled surface. The solution equally spreads over the slides. The glass slides were covered to protect from dust. The films were fabricated at room temperature under normal laboratory conditions. Depending on the film constituents, the drying period varied from 24 to 48 hours

Sample is prepared under normal laboratory conditions. 10% solution of poly vinyl alcohol(10gram PVA in 100ml) .Filter 45 ml PVA from the above solution .Weigh 1.2 gram acrylamide ,0.3ml triethanol amine .Add it to 45ml PVA stir for 1.5 hours using magnetic stirrer at a temprature 65 degree.Simultenousely weigh methylene blue ,prepare aqueous stock solution in methylene blue dye at 0.006M.Mix 0.1ml of dye solution to the measure TEA and AA.pour it to glass slide allow it to solidfy.

3.3 Optical Absorption Studies

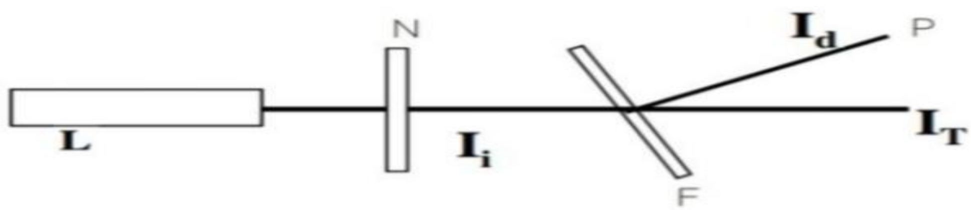
When the polymer film is exposed to suitable wavelengths, the dye molecules in the exposed region are converted to the leucoform and as a result an absorbance modulation occurs in the exposed area. The absorption spectra of both unexposed films and exposed films were recorded using UV-Visible-NIR spectrophotometer. The absorption spectra were taken with the undoped polymer films as reference plate. The absorbance modulation was determined as the difference between absorbance before exposure and that after exposure .The dye molecules could exist in the leucoform itself, it returns to the original state or it is transferred to other states. UV-Visible spectral analysis was done to study the dye behavior on laser exposure in MBPVA and MBPVC films with different matrix additives. To study the stability of this leuco form or the dye behavior on storage, absorption spectra of the exposed regions on storage was recorded.

3.4 Real time transmittance measurements

This is carried out to find out the material sensitivity by exposing the samples to suitable laser for a known time. The transmittance at regular intervals was monitored using a power meter . The relative transmittance T/T0 was determined; where T is the real time transmittance of the sample on laser exposure and T0 is the transmittance of the samples without dye. As the material sensitivity increases the transmittance increases at low exposures. From the relative transmittance, rate of bleaching could be found out by taking the slope of the relative transmittance Vs time curve at different times.

3.5 Diffraction Efficiency Measurements

Unexpanded laser (L) beam was allowed to fall on the grating recorded film (F) placed at Bragg's angle. The diffracted beam was observed on the screen at Bragg angle and its intensity was measured using power meter (P). The intensity of incident beam (Ii), diffracted beam (Id) and directly transmitted beam (IT) was measured. The diffraction efficiency was calculated as the ratio of the intensity of first order diffracted beam to that of the incident beam.



Experimental setup for diffraction efficiency measurements.
Where L-laser, N-ND filter, F- grating recorded film, P-power meter

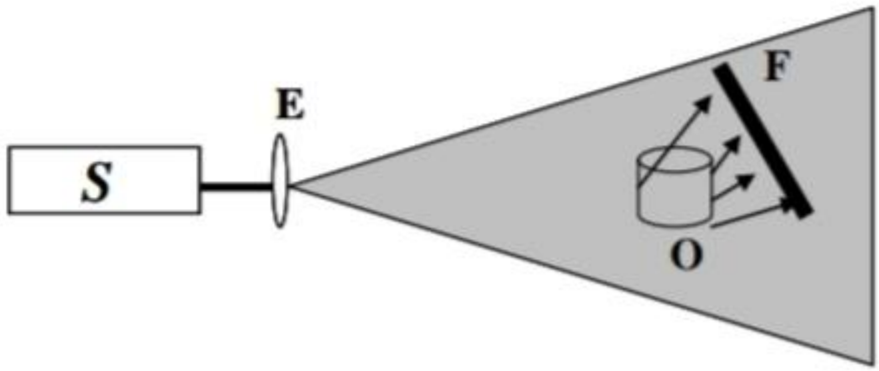
The angular response of the recorded gratings was determined by varying the angle of reconstructed beam and by monitoring the diffracted beam intensity. As it was easier to control, the film was rotated instead of the laser beam. When gratings were recorded with single beam method, diffracted patterns were visible on either side of the directly transmitted beam. As it was not possible to find out the interfering angle from the recording geometry, the spatial frequency was determined from the angle of diffraction. The diffracted pattern is focused to a screen placed behind the film.

3.6 Storage and Shelf Life

In dye doped films, the diffraction efficiency can be reduced or remained unaltered on storage. Storage life gives the idea that how long the material can hold (store) the recorded grating. The storage life of the grating was determined by measuring the diffraction efficiency of gratings after each day of grating formation. Shelf life is defined as the film properties on ageing of the samples. To study the shelf life of the film, gratings were recorded on the film on each day after film preparation and efficiency was determined. It includes optical absorption studies, refractive index measurements etc on each day after preparation of the film. It gives the idea that how long the material can be utilized.

3.7 Recording of Holograms

Transmission holograms were recorded on the polymer film using single beam technique. Laser beam (S) was expanded using a spatial frequency filter arrangement (E). Object (O) is placed in the path of the expanded laser beam and polymer film (F) is placed near the object at an angle. The laser beams scattered by the object act as the object wave and directly transmitted beam act as the reference wave. The position of the film was adjusted to collect maximum object wave. The reference wave and object wave interfere at the film and thus the hologram is created. The hologram was reconstructed by illuminating with an expanded laser beam.



The experimental technique used for recording transmission hologram. where S-Laser, E-beam expander with spatial filter, O-object, F-Polymer film.

So far we have tried to prepare films and obtained various conclusions

1.Procedure: 16 gram of PVA is dissolved in 160 ml of water. The solution was made at a temperature of 70° c. A magnetic stirrer was used for mixing pva in water. It was stirred for one hour.

Observation: The solution had lot of lumps in it.

Conclusion: The solution cannot be used for making a good film

2.Procedure: 10 gram of pva is dissolved in hundred ml water. The solution was made at a temperature of 65 degree Celsius. A magnetic sterer was used for mixing pva in water. It was stirred for 40 minutes. The solution of PVA was of good consistency. 45 ml of PVA was filtered out from the above solution.

1.2 gram of acrylamide and 0.3 ml triethanol amine was weighed out. It was added to the 45 ml PVA and the solution was stirred for 1.5 hours using a magnetic stirrer. An aqueous solution of methylene blue dye at 0.006 M was prepared. 0.1 ml of dye solution was added to the measured AA and TEA.

It was stirred for 1.5 hours using a magnetic stirrer. Then the solution was poured to clean and dry glass slides. It was kept for one day for soldification. A film was obtained. Film was subjected to grating studies

The diffraction efficiency measurements of the PVA-acrylamide dye sensitized photopolymer films were done by recording diffraction gratings on the film using the single beam analysis.The beam from the laser source was expanded using a beam expander and it was split into two by a beam splitter. One of the beam transmitted into a mirror placed in front of the beam splitter in order to make a phase difference and the other beam got reflected and allowed to fall on the photopolymer film. The reflected beam from the mirror was also directed to the film. The superposition of both of the beams created an interference pattern on the photopolymer film, which was the diffraction grating. The film was subjected to the laser beam for 10 minutes to record the diffraction grating.

According to the mechanism of grating formation, on exposing to the interference pattern the MB molecules get excited and electron transfer takes place between MB and triethanolamine that converts MB into leuco MB. Amine radical is also produced in this reaction that initiates polymerization reaction. Polymerization occurs at the region of constructive interference which results in a monomer concentration gradient. This allows the diffusion of the monomer from the unexposed to the exposed regions. Thus, polymerization causes refractive index modulation which leads to the grating formation. The absorbance modulation takes place during exposure and results in the grating formation.

The unexpanded beam from the laser source was allowed to fall on the film on which the grating had been recorded. The beam got diffracted by the grating and the diffracted beam was observed on the screen placed at Bragg angle. The intensity of the diffracted beam was measured using a Field Max II power meter. Diffraction efficiency was calculated as the ratio between the intensity of the first order diffracted beam (Id) and the intensity of the incident beam (Ii).

Observation : The film didn't had diffraction grating.

Conclusion : The film cannot be used as a holographic recording medium

3. Procedure : the above procedure was followed by changing the temperature and amount of PVA. A film was obtained.

Observation: The film didn't had diffraction grating in it.

Conclusion : the film cannot be used as a holographic recording medium

4. Procedure: the above procedure was followed by changing the concentration of dye. The diffraction efficiency of the film was measured.

Observation: the film didn't had diffraction grating in it.

Conclusion: the film cannot be used as a holographic recording medium.

Conclusion

Photopolymer are promising material for use in holography. They have many advantages such as ease of preparation and are capable upto efficiency of 100%.carefull and prominent studies are needed in the preparation of photopolymer material for holographic studies . Suitable temperature is also necessary for the preparation of Holographic photopolymer materials.