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Photopolymer Holography : Review and investigations

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Dedicated to Padma Shri Prof R S Sirohi, FNAE

Photopolymers are preferred in holography due to their additional advantage of being self-developing along with high resolution. In the present paper, an attempt has been made to review the work relating to the holograms recorded and reconstructed in different types of photopolymers using single/multiple wavelengths. In addition, results of experiments performed on a customized photopolymer with optimized acrylamide concentration and dye concentration for achieving higher diffraction efficiency, are also presented. The results obtained are comparable to the results reported in the literature. A maximum diffraction efficiency of about 88% has been achieved using acrylamide-based photopolymer with Erythrosin B dye

Keywords: Holograms, Photopolymers, Photosensitive Materials, Diffraction Efficiency, Holographic Diffraction Gratings, Diffractive Optical Elements, Holographic Optical elements, Chain Transfer Agent.

1 Introduction

Recording medium (photosensitive material) plays an important role in holography. Various types of holographic recording materials such as photographic plates/films, photoresists, dichromated gelatin, photochromics, photorefractive crystals, thermoplastic-photoconductor combinations, photopolymer plates/films, etc. are generally used in holography. However, photopolymers are preferred in some of the holographic applications because of being self-developing along with high resolution. Close *et al* in 1969 [1] have used the photopolymer for the first time in holography. A typical photopolymer material include monomer(s), polymeric binder, photocatalyst (initiator), sensitizing dye and electron donor, etc. [2-22]. Monomer is considered to be the essential and unavoidable part of a photopolymer material because most of the photosensitive material properties like sensitivity, shrinkage, dimensional stability, dynamic range, environmental stability [23] etc. depend on it. There may be one or more monomer producing constituents in a photopolymer. The monomer may be acrylamide and/or acrylate based, carbazolyl-based, fluorenyl-based, anthracenyl-based [1-22], etc. A combination of lower refractive index methyl methacrylate (MMA) and tridecane acrylate has also been used [24,25]. Further, vinyl acetate and acrylic acid are also commonly used for monomer generation [26,27].

The photopolymer binders used generally, are polyvinyl alcohol (PVA), polymethyl methacrylates (PMMA), poly acrylic acid (PAA), polyvinyl chloride (PVC), epoxy resin (high refractive index), sol-gel, polyelectrolytes,[25, 28] etc. Holograms may be recorded preferably by using any visible wavelength falling in Red and/or Green and/or Blue region(s) of the visible spectrum, and the photoinitiators include Methylene Blue (MB)[1], Irgacure 784j [8,28], etc. dyes for red radiation, Erythrosin B (EB), Yellow Eosin (YE), Rose Bengal (R B) , Phloxine B (P B), etc. (xanthenes) dyes for green radiation [15, 26, 29-36], hexaarylbiimidazolewith p-dialkylaminobenzylidene ketone, etc. for blue radiation, and Fuchin Basic (FB) for green and blue radiation [37-39], along with an electron donor. Cyanine dye can be used at any wavelength within the visible spectrum using corresponding composition/state of dye. Electron donors include ethanolamine (EA), diethanolamine (DEA), triethanolamine (TEA), diethylamine (DETN), triethylamine (TETN), dimethyl formadide, diphenyl iodonium chloride, N-phenyl glycine, [15] etc. Addition of crosslinker has also been reported to increase the life of the recorded hologram. Metallic crosslinkers include ammonium dichromate, cupric chloride, ferric chloride, etc., and organic crosslinkers include gluteraldehyde, N-N'-

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methylenebisacrylamide,[36] etc. In addition, chain transfer agents and stabilizers are used to increase the performance of the photopolymer holograms [37]. Other constituents are sometimes added to control the properties like pre-exposure value, shelf life, viscosity of polymer, stability against environment, [23] etc. Photopolymerization is an irreversible process and photopolymer materials are suitable only for write-once-read-many (WORM) applications.

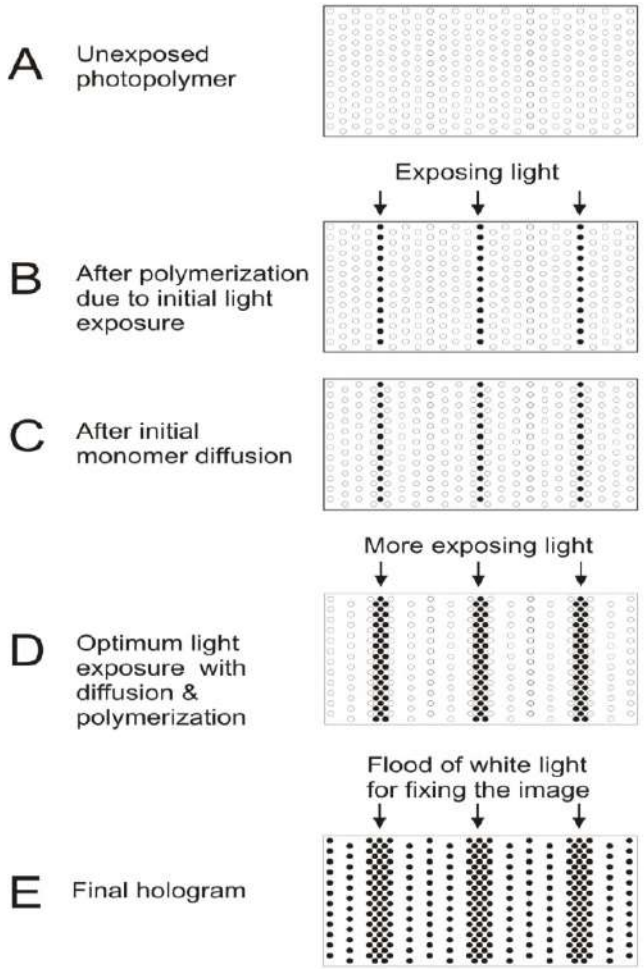

Fig 1. Empty circle shows, monomer (s) and filled circle shows polymerized part for (A) Unexposed photopolymer, (B) After initial exposure and polymerization, (C) After initial polymerization and initial monomer diffusion, (D) After optimum exposure with monomer diffusion, (E) Final hologram

To understand the recording of a hologram in photopolymer it is essential to understand the mechanism behind the image formation in photopolymers. Preparation of polymer, sensitization, drying, hologram recording, image fixing etc. are the steps involved in the recording of hologram in photopolymer [1, 2]. As shown in Fig 1, the photopolymer is illuminated with appropriate wavelength of light. On illumination with light, the photosensitizing dye absorbs photons and the excited triplet state of the dye reacts with the electron donor to produce free radicals (by initiator decomposition) [14]. These free radicals may then initiate local polymerization of the monomer [14]. In case of holographic exposure, the polymerization process lowers the chemical potential of monomers in the bright region, leading to diffusion of monomers

(migration of monomers) from unexposed part (dark region) to exposed part (bright region) during and after (within few milliseconds only) exposure [14]. The changes in density and molecular polarizability which accompany polymerization cause a change in local refractive index and the hologram is thereby recorded as a volume phase hologram [40]. Some time a flood of white light/ultra violet (UV) light is used to fix the image or to polymerize the remaining monomers [1]. Heat treatment or sealing with chemical has also been reported in some cases for stabilizing the grating [9, 41].

The parameters which affect the characteristics of the holograms recorded in photopolymer include wavelength used to record hologram, spatial frequency of interference fringes, power of laser, exposure value, sensitizing dye and its concentration, chemical composition/characteristics of the monomer, refractive index of binder, thickness and/or shrinkage of the photopolymer, absorption characteristics of the photopolymer, chain transfer agent, etc. Various combinations of chemicals for monomers, binders, photoinitiators, other constituents etc. have been reported [1-25]. In addition, many high performance commercially available photopolymers have also been used and the compositions of those photopolymers are proprietary [42-53]. Many authors have published theoretical and/or experimental work explaining the process/mechanism involved in the grating formation in photopolymers. A large number of research papers are available relating to the recording of holograms in photopolymers at wavelengths falling in visible spectrum and it is not possible to include all of them in a brief review. In the present paper, a brief review on the subject is given along with optimized results relating to the acrylamide and EB dye concentrations using acrylamide-based photopolymer. We have included limited number of publications in the review part.

2 Holograms recorded on acrylate and/or acrylamide based red sensitive photopolymers

Close *et al* [1] have prepared the photopolymer (liquid state material) by using mixture of barium acrylate (1.6M), lead acrylate (0.5 M) and acrylamide (3.3M) as monomer solution along with Methylene Blue (0.002M) dye accompanied by *p*-tolulenesulfinic acid salt (0.1M) and 4-nitrophenylacetic acid sodium salt (0.1M). The interference between plane reference beam and plane object beam (having 30° angle between two beams), and plane reference beam and diffuse object beam were recorded using Ruby laser. Ultraviolet light exposure was used to fix the image, which converts the dye to a colorless form. They have reported maximum diffraction efficiency of approximately 45% for holograms recorded on 10-20 μm thick photopolmer using 1-30 mJ/cm^2 exposure. They have carried out experiments for both coverplated and uncoverplated polymer materials and analyzed the results using appropriate models. They have provided more detailed analysis of the diffraction process taking place for large period gratings. The life of each of the individual solution was few months, however, the life of the mixed solution was few hours only for unexposed material. It has been observed in similar type of studies that barium and lead acrylate plus acrylamide exhibit higher sensitivity than acrylamide alone [2]. Phase holograms can result from spatial modulation of the refractive index and/or of the thickness of the recording material. It has also been observed that signal-to-noise ratio starts decreasing for spatial frequencies above 1500 lines/mm, and the index modulation depends on the exposing irradiance. Wopschall and Pampalone [3] have studied the diffusion process and pointed out that the diffusion coefficient depends on the recording beams intensity as well as spatial frequency of the interference fringes and the transition from high to low intensity behavior occurs when polymerization time equals diffusion time.

Optimization results and characteristics including the effects of the intensity, the thickness, and the variation of the concentration of each constituents of the acrylamide based photopolymerizable holographic recording material have been reported [10], and a maximum diffraction efficiency of about 80% has been achieved at 35μm emulsion thickness, 1000 line/mm spatial frequency, and 40 mJ/cm^2 energy. The compositions used were acrylamide (3.4×10^{-1}M), TEA 2.0×10^{-1}M), MB (2.4×10^{-4}M), and PVA (10 wt%: Mw ≈ 25, 000). The sensitivity of the acrylamide based material was increased by using new composition of 8 ml of a solution 2.5M of acrylamide, 1.5M of TEA, 2.5ml of MB of 6.25mM, and 50 ml of 10 wt%

of PVA, and adding 0.6M of N,N'-dihydroxyethylenbisacrylamide (DHEBA) and 70% diffraction efficiency was achieved at 5 mJ/cm^2 energy [11]. The holographic method was used to study the photopolymerization kinetics in dry photopolymer with a nonlinear response [12]. A new photopolymer was developed by adding 2-hydroxiethyl-methacrylate (HEMA) to the acrylamide based polymer [13], and diffraction efficiency near 70% with 65 mJ/cm^2 exposure and 1000 lines/mm spatial frequency in 110 μm thick material was achieved. Liu *et al* [14] have presented various studies of the time varying photon absorption effects, which occur during photo-initiation process in photopolymer materials. They have included work relating to absorption, recovery, and bleaching of the dye. They have incorporated a detailed photoinitiation model into the nonlocal photopolymerization driven diffusion (NPDD) model [40], which describes (i) photo absorption behavior and primary radical generation during initiation, (ii) nonlocal macro-radical chain growth propagator, (iii) oxygen diffusion and replenishment for inhibition, and (iv) multiple termination mechanisms. They have experimentally validated the model for high intensity holographic exposure in a PVA/acrylamide based photopolymer.

Lu *et al* [15] have studied the influence of five (TEA, DEA, EA, TETN, and DETN) amine initiators on holographic parameters and on the photobleaching kinetics of the photopolymers and found TEA as the best initiators. Ushamani *et al* [26,27] have fabricated and tested methylene-blue-doped polyvinyl alcohol-polyacrylic acid blend for holographic applications. They have found good characteristics such as easy fabrication, high sensitivity, environmental stability, and long shelf life. They have optimized PVA/PAA ratio, sensitizer concentration, ph, and observed rate of bleaching, effect of storage, threshold and saturation energy, optical absorption, etc. 7:3 PVA/PAA ratio was found to be optimum due to slow recovery of the dye. John *et al* [41] have fabricated Copper-Doped methylene blue sensitized polyvinylalcohol (PVA)/acrylamide films for stable diffraction efficiency and improved storage life of recorded interference gratings. The resolution of the hologram was unaffected with the addition of copper chloride. They have investigated the effect of chromium doping on the diffraction efficiency of methylene blue sensitized PVA/acrylamide films and found improvement in storage life [54]. They have also observed a self enhancement in diffraction efficiency for a particular ratio of methylene blue and ammonium dichromate. Zhu *et al* [55] have improved the spatial resolution of the photopolymer from 1000 lines/mm to 3000 lines/mm by employing low molecular-weight PVA. Photosensitivity of the photopolymer was also increased five times by increasing the ambient temperature during the holographic recording.

3 Holograms recorded on commercially available green and/or blue sensitive photopolymers

Zhao and Mouroulis [5] have solved diffusion equation in the lower-order harmonic approximation for describing the holographic grating formation process and described the influence of the diffusion rate and polymerization rate and ratio between them. Theoretical and experimental results were in good agreement. Holograms recorded on DuPont HRF-600-10 at 514 nm also show that the refractive index modulation decreases with increasing exposure irradiance and fringe spacing. Investigations have been reported using various commercially available (DMP-128,DuPont, etc.) photopolymers also. However, the composition and preparation details are proprietary. Colburn and Haines [46] have made volume holograms in DuPont photopolymer and 10mJ/cm^2 energy density was required for initial exposure at 514 nm. They have achieved 46% diffraction efficiency. Diffusion time of less than 5 ms has been reported. They have studied the mechanism of hologram formation using ultraviolet and blue green radiations. The characteristics of DuPont photopolymer consisting acrylate (monomer) and cellulose polymer binder was studied by Booth [48, 49]. Experimental studies have also been made [47] using DuPont HRF-150-38 photopolymer film and Ar^+ laser (514 nm). The studies included the roles of exposure, processing durations, exposure time variations, emulsion shrinkage, post exposure, and storage. Studies also included diffraction efficiency, thickness changes, and deviation from Bragg angle. A model has been introduced [50] describing real-time grating formation in DuPont HRF-150X001 photopolymer using 514 nm wavelength. It has been indicated that the grating formation time depends sub-linearly on the average holographic recording intensity, and

the beam intensity ratio controls the grating index modulation at saturation. DMP-128 photopolymer (by Polaroid) was studied for recording efficient and stable phase holograms with good signal-to-noise ratios but with lower diffraction efficiencies [51]. Aubrecht *et al* [52] have studied theoretically and experimentally the recording of holographic diffraction gratings in DuPont HRS-150 photopolymers (spin coated at 2500 rpm) using Ar^+ laser at 514 nm wavelength. It has been noticed that the optimum intensity was higher for grating with shorter period, and that the corresponding grating amplitude was also higher.

Colburn and Haines [46] have made volume holograms in DuPont photopolymer and achieved approximately 10% diffraction efficiency. The energy density required at 364 nm was between 1-5 mJ/ cm^2 for initial and 50mJ/cm^2 for complete polymerization. Studies have been made in detail [49] about the behavior of DuPont photopolymer film at different thicknesses, different exposures, different wavelengths, different spatial frequencies, different angles, etc. It has been shown that diffraction efficiency can be varied or pre-adjusted up to 100% by optimum selection of different parameters, and exposure energy between 10 mJ/ cm^2 and 40 mJ/cm^2. Curtis and Psaltis [53] have recorded ten holograms (by angular multiplexing) on the same plate using DuPont HRF – 150 photopolymer at 488 nm wavelength. Pre-illumination (pre-sensitization) pulse was a must for approximately equal diffraction efficiency in each hologram.

4 Holograms recorded on acrylate and/or acrylamide based green and/or blue sensitive photopolymers

A simple diffusion model has been reported [5] describing the properties of volume phase holograms recorded in photopolymer, and later a refined quantitative model was presented [6] describing the volume hologram formation in acrylate based photopolymers. It has been mentioned that the most desirable condition is high diffusion rate relative to the reaction rate. 532 nm wavelength and 0.5 mW/cm^2 to 100 mW/cm^2 beam intensities were used to make the holograms. A maximum diffraction efficiency of approximately 50% has been observed at 514 nm wavelength [4] using acrylate based photopolymer sensitized with Xanthenic dye. Recording and reconstruction has been studied by using photopolymer having pentaerythritol triacrylate (PETA) monomer, methyldiethanolamine (MDEA), and a sensitizing dye (EY, EB, RB, or PB) for real time holographic interferometry [29, 30]. The possibility has been shown of the recording from green region to infrared (850nm) [31], and a maximum diffraction efficiency of about 80% has been reported. Fimia *et al* [32] have developed a photopolymer material based on 2-hydroxyethyl methacrylate (HEMA), ethylene glycol dimethacrylate (EGDMA) and 4, 5-diiodosuccinylfluorescein (2ISF), and achieved 30% diffraction efficiency. A maximum diffraction efficiency of about 80% has been achieved using PETA and HEMA based photopolymer [33].

Boyd *et al* [7] have systematically evaluated the influence of photopolymer (N-vinyl pirrolidone (NVP)) thickness and shrinkage on dynamic range and on diffraction efficiency and approximately 1.5% shrinkage has been observed. The influence of variation in exposure schedule has been investigated for multiplexing holograms in photopolymer with equal diffraction efficiency [8] using angle multiplexing for recording hologram at 532 nm wavelength. Uniformity in diffraction efficiency has been achieved using of epoxy resin (high refractive index) as polymeric binder, and (lower refractive index) methyl methacrylate (MMA) and tridecane acrylate as monomer. Suzuki *et al* [35] have demonstrated and characterized volume holographic recording (at 532 nm wavelength) in ZrO_2 nanoparticle-dispersed acrylate based photopolymer films (with Irgacure 784, ciba dye) with very low scattering. They have observed high refractive index modulation (5.3×10^{-3}) and suppressed polymerization shrinkage at the nanoparticle concentration of 15 vol.%.

Martin [34] has investigated a new photopolymer for holographic applications in the Ph D thesis which consists of a green sensitive dye (erythrosine B), an electron donor (triethanolamine), and a monomer mixture (acrylamide and methylene bisacrylamide) in a polyvinyl alcohol binder. The chemical and physical processes leading to the refractive index modulation caused due to light exposure were investigated in detail. The relative contributions to the refractive index change, density change through diffusion and decrease in

molecular polarizability were discussed. Optimization of chemical composition of the material has been done for sensitivity, diffraction efficiency, shelf life and layer quality. Maximum diffraction efficiency of about 96% was achieved. Investigations have also been made in details the recording characteristics of acrylamide based photopolymer sensitized with EB dye, and the possibility of recording of slanted gratings without distortion as no shrinkage was observed in the material used. Successful recording up to 3000 lines/mm has been tested. The results have also been found suitable for double exposure holographic interferometry.

A new photopolymer has been developed [36] which is less toxic and having sodium acrylate (from acrylic acid+sodium hydroxide) as monomer, sodium salt 5'- riboflavin monophosphate (PRF) as dye. They have proposed N,N'- (1,2-dihydroxyethylene) bisacrylamide (DHEBA) as an alternative to crosslinker used in the process. The authors have used Ar^+ laser at 514 nm wavelength, 1:1 beam ratio, 1.5 cm dia of beams, 1125 spatial frequency, and 5 mW/cm^2 power density for recording the hologram. Maximum diffraction plus transmission efficiency of about 80% has been achieved. Balan *et al* [56] have developed the process allowing in situ photochemically assisted synthesis of silver nanoparticles in a photopolmerizable acrylic formulation, and studied the photopolymerization of the formulation. An improvement has been observed in the recording characteristics of the formulation when nanoparticles precursor was present. Barichard *et al* [38] have investigated the physic-chemical role of quantum dots (QDs) in the polymerization process of acrylate based composite materials. It has been observed that the spatial distribution of QDs and the kinetics of polymerization both were responsible for the additional refractive index modulation of the recording material. There was a possibility of the above two phenomena of affecting the redistribution of the monomers inside the grating, which could additionally contribute to the increase in refractive index modulation.

Omura and Tomita [37] have investigated transmission volume holographic recording in a ZrO_2 nanoparticle-polymer composite film at 404 nm wavelength and found that the refractive index modulation was 8×10^{-3} and the material recording sensitivity was 9000 cm^2/J, at the optimum ZrO_2 nanoparticle concentration of 35 vol% and at a recording intensity of 5 mW/cm^2. Barichard *et al* [38] have investigated the physic-chemical role of quantum dots (QDs) in the polymerization process of acrylate based composite materials using 488 nm wavelength. A maximum diffraction efficiency of approximately 90% has been achieved [57] using 351 nm wavelength for recording volume holograms in pentaery-thritol tetraacrylate, isooctyl acrylate and UV photoinitiator based photopolymer (doped with TiO_2 nanoparticles).

Neipp *et al* [58] have made use of a first harmonic diffusion model to characterize a polyvinyl alcohol/acrylamide photopolymer and analyzed the effect of adding a cross-linking monomer to the acrylamide material in the temporal evolution of the transmission efficiency. Studies have been made of the effect of a depth attenuated refractive index profile in the angular response of the efficiency of higher orders in volume gratings recorded in PVA acrylamide based photopolymer [59], and the experimental results were in close agreement with theoretical results. Ortuño *et al* [60, 61] have investigated in details the effect of great thickness (up to 1 mm) for high storage density and holographic memories. Lower dye concentration was preferred with thick emulsions for information storage applications. However, lower diffraction efficiency was observed with dye concentration lower than optimum value. In order to achieve greater reproducibility the exact optimum processing conditions should be determined and the environmental condition should be perfectly controlled,

The difference between optical and physical thickness has been analyzed by applying a method based on the Rigorous Coupled Wave Theory and taking into account the attenuation in depth of the refractive index profile [62]. The holograms were recorded using Ar^+ laser at 514 nm wavelength and acrylamide based photopolymer along with yellowish eosin (YE) dye, and reported the comparison between theoretical and experimental results. Naydenova *et al* [63] have studied the patterning of acrylamide-based photopolymer surface by holographic recording using Nd:YAG (532 nm) laser. They have used EB dye to sensitize the photopolymer. They have investigated the influence of intensity, spatial frequency, photopolymer thickness, etc. on the surface patterning.

Optimization of the concentration of various constituents of the epoxy-resin based photopolymer has also been made, and enhancement in sensitivity was observed [16]. Diffraction efficiency of about 92% and an energetic sensitivity of 11.7cm^2/J at about 1940 lines/mm spatial frequency were achieved. Investigations have also been made [64] of the nanoparticle-induced refractive index modulation of organic-inorganic hybrid photopolymer (with acrylamide/poly(MMA) (PMMA) doped with silica nanoparticle and Irgacure 784 sensitizer) and found that diffraction efficiency of the photopolymer can be maximized by inducing interfacial interactions, and may be used in high-density data storage device using 532nm wavelength.

Gleeson *et al* [17] have observed improvement of the spatial frequency response of the photopolymer materials by modifying polymer chain length and included a time varying change in the polymerization rate in NPDD model, and have examined the validity and generality of the model presented by them. Gleeson *et al* [65] have extended the above model more accurately to the effects of time varying primary radical production, the rate of removal of photo-sensitizer and inhibition. Here they have specifically analyzed the effects of inhibition, which occur most predominantly at the start of grating growth. Gleeson *et al* [66] have explored NPDD model, illustrating some of the useful trends (which the model predicts) and analyzed their implications on the improvement of photopolymer performance. They have suggested that utilizing a monomer with a large propagation rate constant and low bimolecular termination rate will produce a higher refractive index modulation.

Studies have been made of the molecular diffusion effects at low (between 2 lines/mm and 8 lines/mm) spatial frequencies [67]. The possibility has been shown to achieve diffraction efficiency of about 35% in first order if the in dark evolution was taken into account, and the authors have included diffraction up to 8th orders in their study. A 3-dimensional model based on direct measurements of parameters have been presented to predict the relief structures generated on the polymer with different values of monomer diffusion and discussed its importance in depth [68]. Babeva *et al* [69] have presented a theoretical two-way model for short-exposure holographic grating formed in acrylamide-based photopolymer (sensitized with EB) and shown that the suppression of short polymer diffusion improves the high-spatial frequency response. It has also been observed that fast conversion of short to long polymer chains has a positive effect on the final refractive index modulation, and low intensity was better for high spatial frequency recording. They have also studied the photoinduced surface relief modulation in photopolymers caused by illumination with a Gaussian beam of light.

Leite *et al* [18] have investigated light induced redistribution of zeolite Beta nanoparticles in an acrylamide-based photopolymer and observed that the increase in thickness of the doped layers leads to a decrease in the monomer concentration and this compensates the positive effect of the nanoparticle's redistribution and results in lower refractive index modulation. The results can be useful in fabricating holographic sensors. They have investigated optical properties of photopolymer layers consisting of an acrylamide-based photopolymer matrix, EB dye, and microporous aluminophosphate nanocrystals of AEY type. Preparation has been done of the novel nanocomposites (for sensor application) consisting of a water-soluble acrylamide-based photopolymer and colloidal zeolite nanoparticles of zeolite Beta and zeolite A, and found that the zeolite Beta nanoparticles (up to 5 wt.%) behave as a noninert additive, resulting in an effective increase in layer thickness, which causes doubling of the diffraction efficiency of the nanocomposite in comparison to that of the undoped photopolymer [70].

Studies have also been made [71] of the characteristics of holographic recording in acrylamide-based photopolymers and found that diffraction efficiency decreases above a particular thickness and absorbance due to increased scattering. They have carried out experiments to determine the threshold values of exposure and intensity for recording holograms in thick green sensitive acrylamide based photopolymer. The minimum intensity was 50μW/cm^2 with absorption less than 0.16 for EB dye for recording hologram, and minimum intensity required to achieve 1% diffraction efficiency was 90μW/cm^2 (minimum exposure required was 8mJ/

cm^2). It has also been determined that 1.5×10^{-7} mol/L was the optimum dye concentration, and no increase in sensitivity was observed above this dye concentration. Ma *et al* [39] have studied a novel photopolymer as a holographic recording material which was single dye sensitized for blue and green light recording. They have sensitized the acrylamide based polymer with Fuchin Basic (FB) dye, and achieved diffraction efficiencies of about 65% at 442 nm and 88% at 532 nm. Moothanchery *et al* [72] have characterized an acrylamide based photopolymer doped with pure silica MFI-type zeolite (silicalite-1) nanoparticles using different concentrations. They have observed high efficiency and low shrinkage.

A new photopolymer has been presented [19] by replacing AA by diacetone acrylamide (DA) which is less toxic. They have reached refractive index modulation up to 3.3×10^{-3}. Addition of glycerol to the diacetone acrylamide (DA) based photopolymer composition [73] resulted in improved stability, faster diffusion, reduced rate of photobleaching, uniform maximum refractive index modulation, about 90% maximum diffraction efficiency at 0.5 mW/cm^2 exposure energy at 532 nm wavelength and at 100μm thickness. A new material has been described by combining a molecularly imprinted polymer (MIP) [74] for specific analyte recognition and a holographic structure for optochemical sensing. Methacrylic acid was used as functional monomer. Reflection gratings have been recorded in PVA/AA photopolymer using three different thicknesses and 532 nm wavelength, and an analytical equation for transmittance at the exit surface of the material was obtained together with an analytical expression for the field inside the material [75]. The performance of PVA/AA photopolymers (900μm thick) has been improved for holographic recording [69] by means of 4,4' azo-bis-(4-cyanopentanoic acid) (ACPA). Recently optimization has also been presented [76, 77] of the EB dye concentration as well as acrylamide concentration for high diffraction efficiency in acrylamide-based photopolymer. Higher diffraction efficiencies of 86±2% were observed for dye concentration range between 25mg and 40 mg per 100ml de-ionized water, and acrylamide concentration of approximately 2.4.g/100ml solution.

Pramitha *et al* [78] have investigated silver-doped photopolymer material for holographic recording and observed that incorporation of silver ions into a methylene blue dye-sensitized PVA/acrylamide photopolymer give better performance in comparison to other metal-ion-doped photopolymers. They have also tested the photopolymer for peristrophic multiplexing and recorded 15 gratings in 130 μm thick photopolymer film. Silver doped photopolymer has been developed [21] and the results achieved were better than other metal ion doped photopolymers. Silver doped polymers were found to have good energetic sensitivities at 633 nm, 532 nm, 488 nm wavelengths. The recorded gratings have shown good efficiency after 3 years also. Meka *et al* [79] have developed a panchromatic acrylamide-based photopolymer for multicolour reflection holography using MB, EB, and Acriflavine (ACF) dyes and recorded and characterized reflection holograms using corresponding 633nm, 532nm, and 473 nm wavelengths.

5 Holograms recorded in PMMA-based photopolymers

Suzuki *et al* [24] have recorded hologram in TiO_2 nanoparticle-dispersed methacrylate photopolymer film (with Titanocene Irgacure 784, Ciba dye) using 532 nm wavelength and found that sensitivity as well as diffraction efficiency increase with an increase of nanoparticle concentration. They have also observed suppression in volumetric shrinkage during holographic exposure by inclusion of the nanoparticles. An improvement has been demonstrated in holographic sensitivity in the green in SiO_2 nanoparticle-dispersed methacrylate photopolymers doped with pyromethane dyes. They have also observed noticeable hologram-apodization phenomena caused by the longitudinal refractive-index changes in the Bragg-angle selectivity curve. Phenanthrenequinone (PQ) – doped poly (methyl methacrylate) (PMMA) is a holographic recording photopolymer material. Steckman *et al* [25] have reported the holographic characteristics of PMMA with 1 mm thickness and demonstrated the holographic storage of binary data in PMMA. They have performed recording near the Fourier transform plane of the data mask, allowing high bit-densities to be achieved.

6 Miscellaneous investigations

A maximum diffraction efficiency of approximately 97% has been achieved [28] by recording holograms in Sol-Gel material with large enhancement of dynamic range by incorporation of high Zr-based high refractive index species and Irgacure-784 dye using 532 nm wavelength for recording the hologram at 500 lines/mm spatial frequency. Lee *et al* [80] have demonstrated that holographic photopolymers of organic/inorganic hybrid interpenetrating networks (IPNs) show both enhanced monomer diffusion and reduced volume shrinkage. It has been considered that soft organic network with low overall crosslink density results for fast monomer diffusion for photopolymerization and causes enhancement in diffraction efficiency. Further, locally dispersed inorganic networks dramatically suppresses the volume shrinkage. Blaya *et al* [81] have shown that deviation from the linear response (non-uniform grating effect) can be explained by taking into account the energetic evolution of the index modulation as well as the fringe bending in the grating. They have prepared photopolymer using HEMA monomer, PMMA binder, and PM567 dye and recorded holograms at 532 nm and 1100 lines/mm spatial frequency.

Gallego *et al* [23] have proposed different composition of new competitive photopolymers (PVA+NaAO) with high environmental compatibility and analyzed the limit of zero frequency response. They have compared the results produced by new (biophotopol) photopolymer with known acrylate and acrylamide based photopolymers and observed that the new photopolymer is less toxic. Gallego *et al* [82] have compared and characterized four different photopolymers on the basis of their suitability for holographic data storage using a spatial zero frequency analysis and very low spatial frequency recording. Hata and Tomita [83] have investigated the impact of stoichiometric thiol-ene ratio on the photopolymerization properties (such as refractive index modulation) in case of volume holographic recording in their nanoparticle-polymer-composites system. They have prepared the material using a secondary dithiol monomer, 1,4-bis(3-mercaptobutyryloxy) butane (dithiol, Showa Denko, K K) and a triene monomer, triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TATATO, Aldrich).

Tomlinson *et al* [84] have shown that one can obtain large refractive index modulations with multi-component photopolymer (cyclohexyl methacrylate as the high-reactivity monomer and vinylcarbazole as the low-reactivity monomer) systems where two-way diffusion model is used. They have considered that more reactive monomer is polymerized during the image forming exposure and the less reactive species are excluded from the irradiated region. A theoretical model has been proposed [85] for hologram recording in photoformers. Photoformers means a polymer having two or more monomers with different characteristics and predicted 90% diffraction efficiency. They have recorded holograms at 488 nm wavelength in photopolymer (mixture of acrylic oligomers as monomers and system based on α-diketone as initiator).

7 Experimental procedure

Experimental arrangement has been shown for recording and reconstruction of hologram in Fig 2 [(a) recording of hologram using two parallel beams and (b) reconstruction of holograms]. As shown in the experimental arrangement, the half wave plates were used to change the beam ratio as well as to match the polarization of the two beams. The complete set up was arranged on a vibration isolation table. The exposure was given from one to multiple seconds using shutter. The photopolymer coating was made on the glass slides of the size of approx. (75 mm × 25mm × 1.35 mm) using the following method: 13g PVA was first dissolved in 100ml of de-ionized water using a heater cum magnetic stirrer apparatus at about 40 degree centigrade temperature. The solution was allowed to cool at room temperature and 8ml triethanolamine was added. 2.4g acrylamide and 0.8g bisacrylamide were also added to the solution and dissolved completely. The solution was allowed to settle for overnight so that most of the bubbles get out of it. Various samples of the above compositions were prepared. 16ml of dye solutions with different concentration of Erythrosine-B (from 17mg to 80mg/100ml de-ionized water) were added to different samples in dark room for making photopolymer solutions.

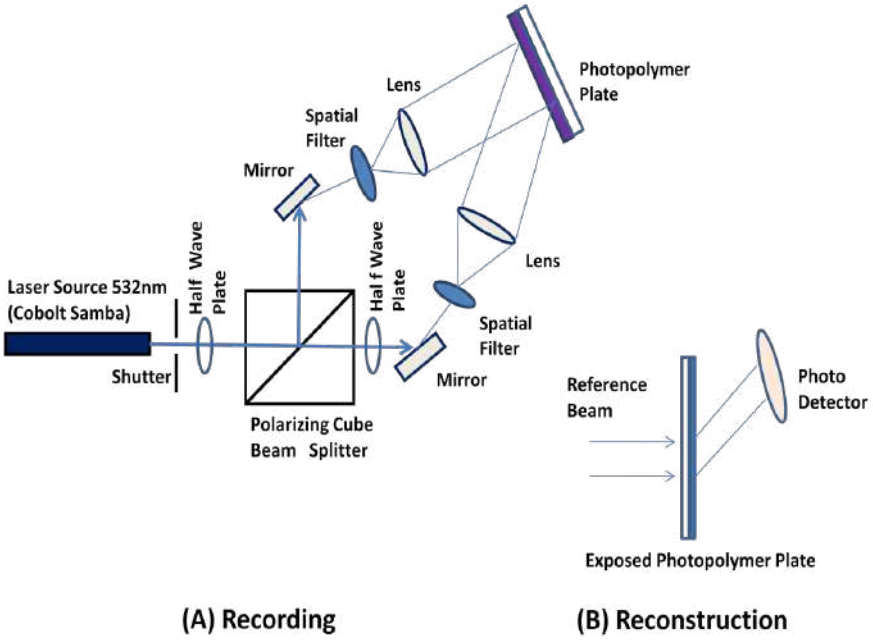

Fig 2. Schematic Diagram of (A) Recording and (B) Reconstruction

Each photopolymer solution was coated on a number of glass slides by gravity settling method. The coated plates were kept in light proof cardboard boxes for getting them dried, and the complete process took two days at approximately 60% relative humidity and about 28 degree centigrade room temperature in summer season. Further, the photopolymer coating was also made on the similar glass slides using the following compositions: 13g PVA/100ml de-ionized water, 8ml triethanolamine, different quantity of acrylamide (1.4g, 2.1g, 2.4g, 3.5g, and 4.1g were used for making the photopolymer.), 0.8g bis-acrylamide, and 16 ml of dye solution with 30 mg Erythrosine-B per 100 ml de-ionized water.

The recording room was kept free of air currents and temperature gradients. Holographic diffraction gratings were recorded with two collimated beams (cross-section diameter approximately 15mm) making 20° angle and of equal intensity illuminating the glass slides from the same side. Cobolt Samba^{TM} 1000 532nm laser was used to get the two parallel beams. The exposure was varied from 200 mJ/cm^2 to 5200 mJ/cm^2 . The photopolymer plates were post exposed to a flood of uniform white light from 100 Watt spot bulb (at a distance of 15 inch) for 30 minutes for the purpose of fixing the gratings.

Each glass slide was illuminated by the readout beam which was incident perpendicularly on the photopolymer plate from opposite side of the emulsion and was arranged to satisfy the Bragg condition. The central area of the hologram was used to reconstruct the hologram and to measure the diffraction efficiency of each hologram. Approximately 190μm average thickness of the photopolymer layer on the glass slides was measured. Incident and diffracted intensities were measured by using Gentec Maestro power meter. The diffraction efficiency η is defined here by the relation $\eta = I_d / I_i$, where I_d is the power in the first diffracted order at Bragg angle and I_i is the incident power minus the losses due to reflection at the two glass surfaces and the absorption of the glass of the plate, that is the power incident on the grating emulsion.

8 Results and discussion

All the diffraction gratings were reconstructed using 532 nm wavelength at which they were recorded and diffracted light intensity of each hologram was measured at Bragg angle. Figure 3 shows the variation

in diffraction efficiency as a function of exposure for different acrylamide concentrations. It is understood that higher monomer concentration will lead to higher polymerization, but to sustain the polymerization, higher dye concentration would be required. However, at higher dye concentration, absorption of light is higher and there is little contribution towards initiation of polymerization due to lower penetration [37]. Hence, at optimum acrylamide concentration, there should be optimum dye molecules to sustain the reaction to get desired refractive index modulation.

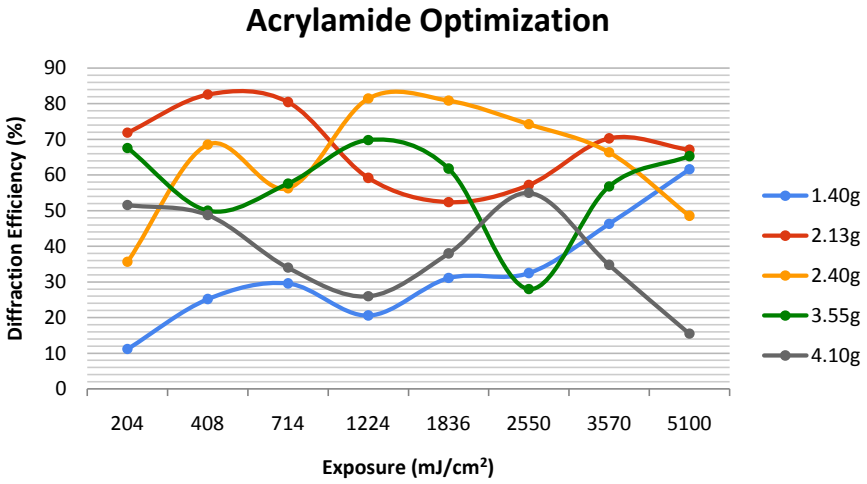

Fig 3. Diffraction Efficiency vs Exposure curves for acrylamide concentrations of 1.40g, 2.13g, 2.40g, 3.55g, and 4.10g/100ml PVA solution

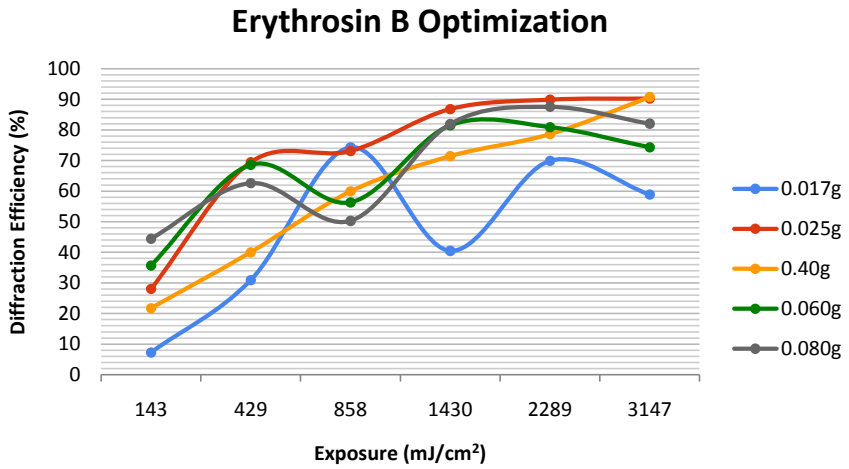

Fig 4. Diffraction Efficiency vs Exposure curves for different dye (EB) Concentrations between 0.017g to 0.080g/100ml de-ionized water.

It has been observed that as we increase the exposure the diffraction efficiency increases first, then decreases and again increases before showing the continuously decreasing trend [46]. Maximum diffraction efficiency of about 88% has been achieved at acrylamide concentration of 2.4g/100ml solution for wide range of exposures. We have observed the consistency in the results within the accuracy of ±2.5% in diffraction efficiency. We have observed that the emulsion peels off the base of the glass plate after keeping in the shelf for few months. It has also been observed that the thickness varies from one place to the other for the

photopolymer coated with gravity settling method. However, the drying time for this type of photopolymer is only few days for more than 150 micrometer thickness of emulsion. Figure 4 shows the variation in diffraction efficiency as a function of exposure for dye concentrations of 17mg, 25mg, 40mg, 60mg, and 80mg per 100ml de-ionized water.

Further, after observing the higher diffraction efficiency for the dye concentrations of 25mg and 40 mg per 100ml de-ionized water, it was decided to minutely study the effect of dye concentration between 20mg and 40mg/100ml de-ionized water. Figure 5 shows the diffraction efficiency vs exposure curves for the dye concentrations of 20mg, 25mg, 30mg, and 35mg per 100ml de-ionized water. The holograms recorded on photopolymer with higher dye concentration tend to slightly regain the dye colour back after storage [14] and some light exposure is needed to make the holograms transparent again. The holograms recorded on the photopolymer with lower dye concentration show negligible regain of its dye colour. It has been experienced that lower dye concentration range is preferable for getting maximum diffraction efficiency.

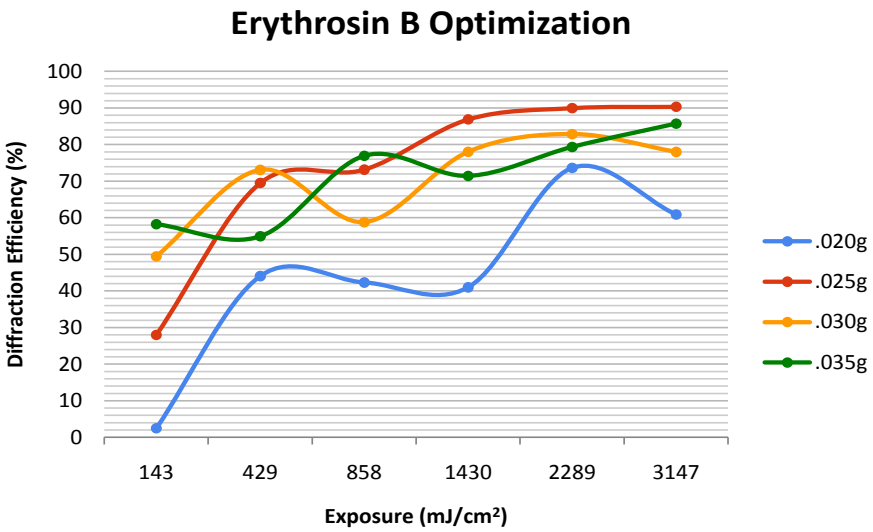

Fig 5. Diffraction Efficiency vs Exposure curves for dye (EB) concentrations of 0.020g. 0.025g, 0.030g, and 0.035g/100ml de-ionized water.

After comparing the results it has been concluded that we can choose any dye concentration between 25mg and 40mg per 100ml de-ionized water. The maximum diffraction efficiency of approx. 88% has been achieved for this range of dye concentration. After a time of approx. 6 months it has been observed that some minor droplets type humidity was adhered to the surface of the recorded photopolymer plate. Further, we have tried to record hologram on the unexposed plates made approximately six months back and no successful recording was made on them.

9 Applications of holograms recorded in photopolymers

On the basis of the literature survey it may be noted that holograms in photopolymers have various applications including non destructive testing, information storage, integrated optics, optical interconnects, double exposure holographic interferometry, holographic data storage, hybrid optoelectronics, holographic sensors, display holography, diffractive optical elements, solar concentrators, self-traping of light, etc. Steckman *et al* [25] have demonstrated the holographic storage of binary data in PMMA. They have performed recording near the Fourier transform plane of the data mask, allowing high bit-densities to be achieved. Fernández *et al* [86] have demonstrated the capability of PVA/acrylamide- based photopolymer (with YE

dye and 532 nm wavelength) for data storage using a combination of angular and peristrophic holographic multiplexing, and recorded 60 holograms with approximately uniform (>1.6%) diffraction efficiency. The holograms were recorded at 1125 lines/mm spatial frequency. Investigations have been made [87] of the the application of acrylamide-based photopolymer sensitized with EB dye for bit-format microholographic data storage and recorded reflection holograms of 5640 lines/mm spatial frequency and 0.2% diffraction efficiency of each, using 532 nm wavelength. Cheben and Calvo [88] have demonstrated a photopolymerizable glass (using modified silica glass) with diffraction efficiency near 100% for holographic data storage. They have prepared the glass by dispersing a titanocene photoinitiator and a high refractive index acrylic monomer in a porous silica matrix and shown the possibility of high sensitivity to green light, and several mm thickness of photopolymer. Kim *et al* [64] have investigated nanoparticle-induced refractive index modulation of organic-inorganic hybrid photopolymer suggested that the results may be used in high-density data storage device.

Sakai *et al* [89] have fabricated holographic diffuser using 532 nm wavelength and Azobenzene polymer film which needs no post treatment, and was erasable by light or heat. Li *et al* [90] have reported the theoretical analysis and experimental results for a novel interaplane and interplane V-shaped 1-to-many optical interconnect using 2D multiplexed waveguide hologram array and substrate guided waves. Experimental results of 1-to-2 interaplane and of 1-to-32 interplane V-shaped fanouts have been delineated. They have also confirmed theoretically as well as experimentally the coupling efficiencies of 48% for surface normal and 45% for near surface normal interplane fanout beams. Zhou *et al* [91] have recorded the volume hologram using 514 nm wavelength using DuPont HRF-600 Photopolymer. The formation of a surface-normal wavelength selective non-blocking crossbar is reported using the above hologram in conjugation with graded index (GRIN) lenses. It is important to use crossbar for the realization of computer to computer interconnect. The employment of GRIN lenses has reduced nine wavelengths to three wavelengths.

Leite *et al* [18, 70] have investigated light induced redistribution of zeolite Beta nanoparticles in an acrylamide-based photopolymer and observed that the increase in thickness of the doped layers leads to a decrease in the monomer concentration and this compensates the positive effect of the nanoparticle's redistribution and results in lower refractive index modulation. The results can be useful in fabricating holographic sensors. Leite *et al* [92] have designed and fabricated an irreversible humidity sensor based on a transmission holographic grating using the optical properties of the photopolymer layers combined with the redistribution of the AEI nanoparticles. Fuchs *et al* [74] have described a new material combining a molecularly imprinted polymer (MIP) for specific analyte recognition and a holographic structure for optochemical sensing. Methacrylic acid was used as functional monomer. Mihaylova *et al* [93] have presented a good review on the recent developments in holographic sensors technology. Blanche *et al* [94] have used holographic stereographic technique and a photorefractive polymer as a recording material to demonstrate a holographic display that can refresh images every two seconds. They have recorded multicoloured holographic 3D images using angular multiplexing. They have demonstrated 3D telepresence by taking multiple images from one location and transmitting the image bia Ethernet to another location where the hologram is printed with the quasi-real-time dynamic 3D display.

Márquez *et al* [95] have investigated the results dealing with the calibration of recording set up and photopolymer, and analyzed the performance of phase-only diffractive lenses using liquid crystal display. They have introduced a real-time setup allowing for recording of diffractive lenses, while monitoring its performance. Saglimbeni *et al* [96] have demonstrated that Digital Holographic Microscopy (DHM) allows the characterization of individual microbubbles in terms of radius, shell thickness and shell refractive index, all in a fraction of a second and in a nondestructive way. They have easily spoted and characterized hundreds of individual microbubbles by fitting recorded digital holograms to the exact electromagnetic solution of a coated sphere. These microbubbles enable the gas release in about two hours, a time span suitable for clot treatment. Naydenova *et al* [22] have reviewed the work relating to holographic optical elements for solar

concentrators including multiplexed holograms. They have considered various types of holographic optical elements. Smith *et al* [97] have reviewed the fundamental characteristics and parameters of holographic polymerization (HP), exemplified the versatility of the nanofabrication technique by presenting a diverse selection of HP patterned soft materials and discussed some unique applications of such HP structures.

10 Conclusions

Initially a brief review of the work reported on the subject is given. It has been noticed that the holograms recorded in photopolymer have a considerable number of applications including non destructive testing, information storage, optical interconnects, double exposure holographic interferometry, integrated optics, holographic data storage, hybrid optoelectronics, holographic sensors, diffractive optical elements, solar concentrators, self-traping of light, etc. Further, optimization has been made of the diffraction efficiency as a function of exposure of the holograms recorded in photopolymer sensitized with Erythrosin B dye having different acrylamide concentrations. Maximum diffraction efficiency of about 88% has been observed for the acrylamide concentration of 2.4g /100 ml solution. Optimization has also been made of the diffraction efficiency as a function of exposure of the holograms recorded in PVA/acrylamide based photopolymer using different dye (Erythrosine B) concentrations. Maximum diffraction efficiency has been observed for the dye concentration between 25mg and 40mg/100ml solution. The consistency in the results has been observed for this range of dye concentration within the accuracy of ± 2.5% in diffraction efficiency. The results achieved can be useful in light coupling devices and holographic solar concentrators where the requirement of high diffraction efficiency of the hologram is a must.

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