Progress of Photopolymers Based Holographic Sensors Applications

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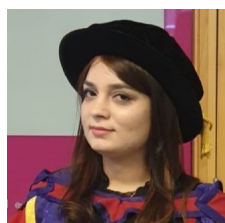
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Abstract

Photopolymer is a promising holographic recording medium due to its low cost, self-developing, highly sensitive, good optical properties, and easy fabrication process. Acrylamide and its derivatives are equally useful for recoding medium. Holographic pressure sensor, temperature sensor, gas sensor, humidity sensor and organic vapour sensor, data storage are the potential application using acrylamide monomer based photopolymer or its derivatives based photopolymer. Swelling and shrinkage are the properties of acrylamide photopolymer, which are not suitable for holographic data storage but suitable for sensor application. In this work, photopolymer based holographic recording material has been reviewed.

Introduction

Photopolymer changes its physical or chemical properties while undergoes a direct or indirect interaction with light [1, 2]. Visible spectrum absorbing photopolymers are useful for development of holographic memories, holographic optical elements or as holographic recording media [3-5]. Photopolymers are energetic-sensitive, able to record at low spatial frequency, able to record slanted gratings high efficiency, dynamic range, self-developed after formation and no need of wet processing or thermal treatment and offer long-term stability without post wet- developing process [6-8]. Photopolymer as a holographic recording material was first introduced by Close et.al. [9]. Crosslinking and polymerizable are the two types of photopolymers used in holographic application. For crosslinking type, phase change in the hologram is caused by modification of the local refractive index modulation when crosslinks between the polymers strands are broken or formed so that the molecular polarizability of these bonds is altered. Photopolymerizable type photopolymers contains polymerizable monomer, an initiator and a sensitizer. The main advantages of these materials are that they are self-developing, capable of recording 100 % diffraction efficiency gratings, and can be prepared in much greater thicknesses for volume holographic multiplexing. These materials can be sensitized to different wavelengths by using different dyes and can also be prepared with ease. Polymerizable photopolymer can be liquid type having nearly 45% diffraction efficiency [9] or solid dry photopolymers which are possible after inclusion of a binder into the liquid one [10].

Photopolymer film consists of monomer, binder or the host matrix, photosensitizing dye, electron donor, co initiator, and cross linker. Radical chain photopolymerization reactions occur in the presence of laser light having appropriate wavelength. In the film, illuminated dye molecules absorb photons from light and move to excited singlet states. Free radical photopolymerization involves five principles steps: (i) initiation, (ii) propagation, (iii) termination, (iv) inhibition, and (v) chain transfer [11]. Details of this process are described below [12-16].

Initiation

During illumination, the reaction between the photosensitiser and the electron donor (coinitiator) leads to the

production of initiator radicals ($R\bullet$) which can react with the monomers to produce chain initiators ($M\bullet$) [15]

$$I + h\mu \rightarrow R\bullet$$

$$R\bullet + M \rightarrow M \bullet$$
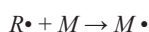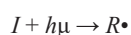
where I is the initiator, $h\mu$ indicates the energy absorbed from a photon, and M represents a monomer molecule.

### Propagation $\quad M^{\bullet} + M \rightarrow M^{\bullet}_{n+1}$

The chain initiator $M\bullet$, will attach with another monomer molecule M, by addition to the C=C bond yields a growing polymer radical [12, 17]:

$$M\bullet + M \rightarrow M\bullet$$
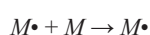
where $M\bullet$ and $M^{\bullet}_{n+1}$ are the growing macroradical chains of n and ($n+1$) repeat monomeric units ($n \geq 1$).

Termination

Termination has three ways. Two of these, disproportionation and combination, involve two growing macro radicals interacting, that is, the bimolecular termination mechanism:

$$M^{\bullet}_{n} + M^{\bullet}_{m} \rightarrow M_{n+m}$$
$$M^{\bullet}_{n} + M^{\bullet}_{m} \rightarrow M_{n} + M_{m}$$
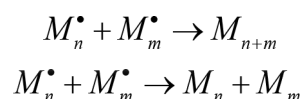
where M_{n}, M_{m} and M_{n+m} represent terminated chains which have no radical tip, that is, a dead polymer chain [15, 18]
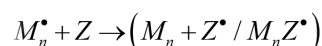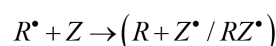
A third possible termination mechanism involves primary radical termination

$$M^{\bullet}_{n} + R^{\bullet} \rightarrow M_{n}R$$
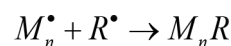
In this step, a growing macro-radical chain reacts with a primary radical (initiator radical) leading once again to the production of inactive or dead polymer chains

Inhibition

Inhibitors are chemicals, which react with the initiating and propagating radical species by rapidly removing or scavenging these radicals. Polymerization is completely halted until they are all consumed [13]. Several possible inhibitor reaction mechanisms are listed below:

$$Dye^{\bullet} + Z \rightarrow LeucoDye + Z^{\bullet}$$

$$R^{\bullet} + Z \rightarrow \left(R + Z^{\bullet} / RZ^{\bullet} \right)$$

$$M^{\bullet}_{n} + Z \rightarrow \left(M_{n} + Z^{\bullet} / M_{n}Z^{\bullet} \right)$$

Inhibition leads to a dead band at the start exposure, that is, no initial grating formation during exposure. The effects of inhibitors are especially significant when lower exposure energies are used, for example, when large areas must be exposed or short pulses must be used [13, 16, 18, 19].

Chain transfer mechanism

The chain transfer process causes a premature termination of a growing macro-radical chain and arises because of the presence of a chain transfer agent (CTA) [13,19-22]. Due to this reaction, a new radical is produced which is referred as a reinitiator. This reinitiator reacts with a monomer molecule to initiate a new growing macro-radical chain. The chain transfer reactions can be written as

$$M^{\bullet}_{n} + \left(RI - X \right) \rightarrow \left(M_{n} - X \right) + RI^{\bullet}$$
$$RI^{\bullet} + M \rightarrow \left(RI - M^{\bullet} \right)$$
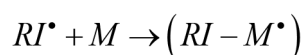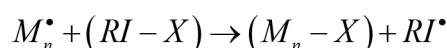
where RI-X is the chain transfer agent, -X is the atom or species transferred, and RI • is the reinitiator which has a radical tip. Due to the premature termination reaction with the chain transfer agent, RI-X, the propagating polymer chains will stop growing earlier than they would have if the CTA was not present.

Holographic recording in photopolymers involves concentration gradient driven diffusion, photopolymerization processes, and refractive index modulation of the material due to photopolymerization. Various photopolymers such as the acrylate-based, acrylamide-based, and azobenzene-based, have shown the optical storage ability.

High performance commercially available photopolymers are DuPont [23-24], OmniDex [25-26], Polaroid DMP 128 (Aprilis photopolymer) [27] and Inphase. DuPont photopolymer consists acrylate monomer an initiator system based a cellulose binder [23-24, 28]. Dupont photopolymer films (e.g., HRF-600X001), due to their large diffraction efficiency, wide spectral sensitivity, dry-processing and demonstrated stability, have gained much attention [29]. However, these photopolymers are expensive and their compositions are proprietary [24, 30]. As photopolymers are promising materials for holography, many research groups are working to improve their performance [17, 4]. Acrylamide monomer based photopolymer is gaining huge importance for holographic recording application. Holographic recording photopolymer comprise one or more monomers, a photoinitiator and an inactive component often referred as a binder. Mixture of these composition forms a viscous fluid or a solid with a low glass transition temperature, which is prepared for exposure either by coating onto a solid or flexible substrate, or by containing it between two transparent solid substrates [31]. First holographic recording using acrylamide monomer based photopolymers were done for volume hologram [9]. With this view, we focus on the various work done by using AA based photopolymer in holographic application.

1.2. Details of Holography

Holography technique is reproduction of a 3-dimensional image of an object by interference of light waves in a photosensitive recording medium. A diffraction pattern in a hologram can be formed when a light sensitive material is exposed to the pattern of interference between an object and a reference beam [32]. The beam from any laser system can be splitted (using beam splitter) into two secondary beams with an intensity ratio of 1:1 as shown in Figure1.
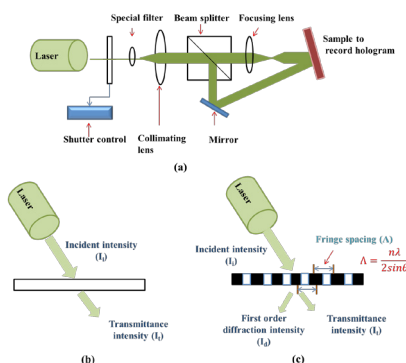
Figure 1: (a) Recording of holographic material, (b) before recoding, (c) after recording.

These two beams overlap each other on the recording plate with a predefined angle. After recording, the hologram is illuminated with laser beam and diffraction efficiency is monitored of the gratings by a power meter. In the case of holographic recording, the basic mechanism of hologram formation involves modulation of the refractive index between polymerized and non-polymerized zones, corresponding to the "bright" and "dark" zones respectively, in the diffraction grating generated due to the interference of the recording beams [33]. First holography was produced by Denis Gabor in 1948 [34-36]. Hologram contains full information about the phase and the amplitude of the object beam is created.

Diffraction efficiency of hologram can be calculated from Kogelnik's theory as equation 1[37].

$$\eta = \frac{\sin^2 \sqrt{\left(\xi^2 + v^2\right)}}{\left(1 + \frac{\xi^2}{v^2}\right)}$$

where deviation parameter

$$\xi = \frac{\Delta\theta kd}{2}$$

and modulation parameter (grating strength)

$$v = \frac{\pi n_1 d}{\lambda \cos\theta}$$

d is thickens of hologram, n_1 refractive index of modulation, $\Delta\theta$ is the deviation of Bragg angle
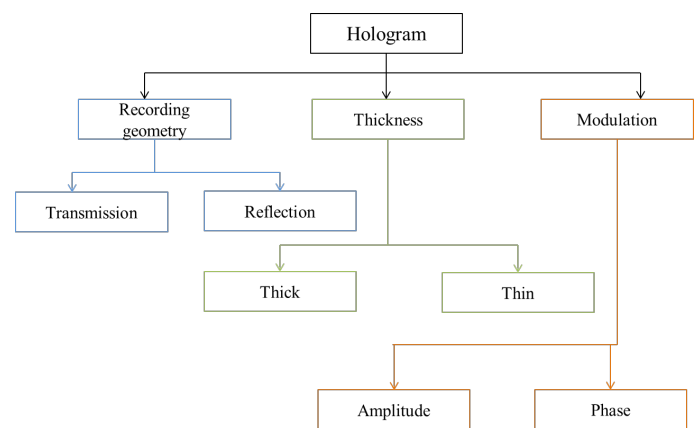
Figure 2: Taxonomy of different hologram.

Holograms are classified based on recording geometry, thickness and method of modulation of optical properties as shown in Figure 2. Finally, each of these three types of holograms may be recorded as either a phase or an amplitude hologram. Maximum achievable diffraction efficiency is listed in Table1.

Table 1: Maximum efficiencies of various types of holograms.

Achievable diffraction efficiency of hologram		
	Amplitude	Phase
Thin transmission	6.25%	33.9%
Thick transmission	3.7%	100%
Thick reflection	7.2%	100%

thin and thick holograms are possible using Q factor as equation 2 [37]. A thin hologram is one whose Q-factor is < 10. A thick hologram is one with Q > 10.

$$Q = \frac{2\pi\lambda d}{n\Lambda^2} \qquad\qquad 2$$

where, λ is the wavelength of the incident reference beam, n is the refractive index of the recording medium, Λ is fringe spacing of the holographic grating and d is the thickness of the layer on which hologram is recorded.

Based on recording geometry hologram can be transmission or reflection types. Reflection holograms offer the ability to provide visual information in the presence of a stimulus and are therefore suitable for applications where an additional readout device is not needed. In a reflection hologram, the fringes are parallel to a surface of the support medium; this causes rays to leave by the same surface at which the incident rays enter. This fringe geometry provides a hologram that may be particularly sensitive to changes in temperature [38]. Transmission hologram requires an additional readout device such as a spectrometer or an optical power meter to detect changes in the optical properties arising upon interaction with a stimulus.

Based on thickness, hologram can be thick and thin. Distinguish between

Modulation during recoding of hologram can be amplitude and phase type. In amplitude, hologram is recorded as a spatial variation of the amplitude of transmittance of the recording medium. In phase it is recorded as a variation of the refractive index or thickness of the medium then it is phase hologram.

Maximum diffraction efficiency for any holographic material depends on the thickness of the hologram. However increasing the thickness increases the selectivity, which limits the range of incident angle. Different available holographic recording material is listed in Table 2.

Table 2: Characteristics of available recording materials for holography [32]

Recordingm material	Advantages	Disadvantages	Type	Max efficiency
Dichromated gelatin	Grainless, High resolution, DE, optical quality, refractive index modulation, and, lower sensitivity (compared with SHPE), low scattering	Wet chemical processing	Phase	100
Photoresists	Low granularity, high resolution	Low sensitivities, UV sensitive, chemical processing	phase	30
Photochromics	No post processing, easy to prepare	Low sensitivity, low DE, degradation	amplitude	6
Photorefractives	No post processing, reversible, high DE, sensitivity, high thicknesses	Stability	phase	100
Photo thermo-plastics	High sensitivity, high DE, no wet chemical processing, reusable	Low spatial resolution	phase	30
Polymer composite (PDLCs)	High index modulation, unique anisotropic nature, electro optical behavior	Scattering, Complicated sample preparation		
Silver halide photographic	Usually (AgBr), High sensitivities, high	Wet chemical processing, shrinkage	Amplitude phase	6 60

emulsions (SHPE)	resolution, high diffraction efficiencies			
Photopolymers	High sensitivity, DE, resolution self-processing	Stability varies with composition of material.	phase	100

1.   Acrylamide based photopolymer for holographic recording

In case of photopolymer holographic recording, polymerization and diffusion lead to a spatially modulated change of refractive index of the material and a grating is recorded. Two way diffusion model in photopolymer was proposed from experimental results [39] and mathematically validated [40]. Monomer diffusion from dark to bright fringe areas increases the refractive index modulation while diffusion constant is $D0=1.6\times10^{-7}$ cm^2/s. During the recording, a second diffusion process also takes place due to polymer. This polymer diffusion creates short chain from bright to dark fringe areas at diffusion constant of $D0= 6.35\times10^{-10}$ cm^2/s. The ratio of the polymerisation rate to the diffusion rate is a crucial factor. When monomer diffusion rate is higher than polymerization rate, grating profile offers sinusoidal recording interference pattern and a high saturation value of the refractive index modulation. Deviation from the sinusoidal profile of the grating is observed when monomer diffusion rate is slower than the polymerization rate and thus the diffraction efficiency at saturation is lower. For fast polymerisation, the diffusion rate must be fast to facilitate the movement of the monomer molecules from dark to bright regions, so that they can be polymerised. The rate of polymerization is proportional to the recording intensity used as this controls the number of photons available to produce free radicals, which initiates the polymerization reaction. Recording continue until no more monomer is left in the unexposed region or it may be intermittent so that several recordings may be made with different spatial frequencies of illuminating light patterns [41]. However, slow diffusion is advantageous as it prevent polymer chain diffusion out of illuminated areas within a grating, which leads to reduction in grating diffraction efficiency [42]. Grating formation in photopolymer is shown in Figure 3.

(a)

(b)

(c)
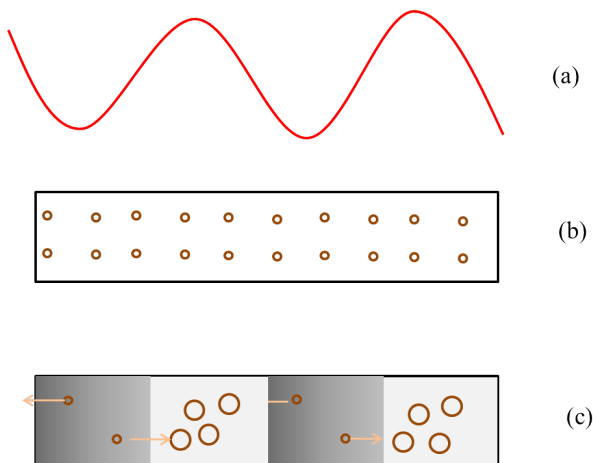
Figure 3: Grating formation in a photopolymer (a) the intensity distribution, (b) photopolymer before recording, and (c) photopolymer during recording

A photopolymer film consists of

·   monomer (acrylamide (AA), diacetone acrylamide (DA), N-isopropylacrylamide (NIPA))

·   binder or the host matrix (poly (vinyl alcohol) (PVA)

·   photosensitizing dye, (methylene blue (MB), erythrosine B (EB) and acriflavine (ACF)

·   electron donor, co initiator, (triethanolamine (TEA))

·   cross linker (silver nitrate (AgNO3), N-N methylene bisacrylamide)

1.1.   Dependency of photopolymer diffraction efficiency for different component

1.2.   Effect of exposure on diffraction efficiency (DE)

Diffraction efficiency (DE) of Photopolymer based hologram is proportional to the exposure time [43]. However, after a certain time the DE becomes saturated and further exposure decreases the DE. At the beginning, exposure energy in photopolymer is proportional to the concentration of the monomer reacted [44] and efficiency increases. Figure 4 shows the effect of exposure time on the photopolymer diffraction efficiency for AA based photopolymer. Maximum diffraction efficiency of 55% was occurred at 100 mJ/cm^2 exposure energy. After 4 s at 100 mJ/cm^2 exposure energy, due to the saturation of the index modulation no further increment of diffraction efficiency was recorded with increasing the exposure energy.
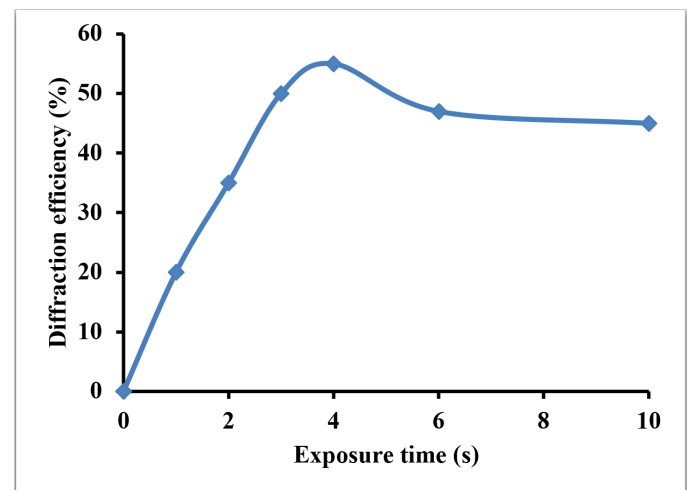
Figure 4: The relationship between exposure time and diffraction efficiency. The chemical composition of the material is AA: 0.21 M; BAA: 0.0324 M; TEA: 0.38 M; ErB: 1.13×10−4; PVA: 10%. The intensity used is 20 mW/cm^2 (Redrawn from [43])

The reason of decrement of diffraction efficiency after the saturation of exposure was proposed due to the below possible reasons [43]

·   caused by the cross-talk of holograms;

·   surface deformation of the recording material;

·   random scatter caused by the granularity of the recording material;

·   nonlinear recording of the signal wave.

1.2.1. Effect of monomer (AA, DA, NIPA, NaAO)

1.2.1.1. Acrylamide (AA) monomer based photopolymer

Acrylamide (AA) monomer based photopolymers are one of the most widely used water-soluble photopolymers for development of holographic applications. Acrylamide is a white or colourless, odourless crystalline solid [44- 52]. First AA based polymerization was performed by riboflavin sensitizer [53]. Later on using TEA initiator and Methylene Blue photosensitive dye, AA monomer based photopolymer was prepared [54]. 80 days long stability of AA based photopolymer was also reported [55]. AA based photopolymer systems having acrylamide monomer, triethanolamine as electron donor, methylene blue dye as a sensitizer and polyvinylalcohol as binder was investigated by Calixto, which offered diffraction efficiency of 10 % with exposure energy of 94 mJ/ cm^2 [46]. AA photopolymer having two photosensitive dyes, methylene blue sensitive at 633 nm and Rose bengal sensitive at 546 nm was investigated [19]. The Rose Bengal dye absorbs the photon, excites into an excited state, and reacts with the electron donor to generate free radicals. These generated free radicals react with the oxygen contained in the photopolymer layer and consumes it. Then a 633 nm red laser wavelength was used to polymerise the monomer for holographic recording. Diffraction efficiency of 40 % was achieved with exposure energy of 3 mJ/cm^2 at a spatial frequency of 1000 lines/ mm. To improve the stability and gratings of the recorded material one crosslinking monomer N,N'-methylenebisacrylamide (BA) was added using Erythrosin B as photosensitizer [8]. Mahmud et.al. [41] observed that AA photopolymer layers diffraction efficiency decrease by increasing the thickness to 250 μm or above. The diffusion coefficient estimated for this process is $1.61 \pm 0.03.10^{-7}$ cm^2/s [34]. Increase of AA concentration increases the diffraction efficiency of the photopolymer. However, concentration of AA cannot be increased indefinitely due to the compatibility and solubility of this monomer in the polymer film. Noise gratings due to high concentration of AA monomer precipitation on the surface of the film are possible. High concentration of AA also makes the film shrink greatly. A polyvinyl alcohol/acrylamide photopolymer (PVA/AA) films with thickness of 200 μm achieved 52% diffraction efficiency due to higher concentration of AA and acrylic acid (AAc) monomers. The photopolymer offered low scattering noise due to addition of AAc [56]. AA monomer form is a toxic chemical and carcinogenic to humans [57-61]. To generate environment friendly photopolymer, replace of AA is essential.

1.2.1.2. Diacetone Acrylamide (DA) monomer based photopolymer

Diacetone Acrylamide (DA) monomer is a possible replacement of AA as it is non-toxic. Investigation of non- toxicity of DA was performed using BEAS-2B and HaCaT cell line and results were compared with AA. Cellular viability was assessed using the MTT assay for three different exposure times. Two orders magnitude difference was observed in the lethal dose (LD 50) concentrations of the two monomers. DA exhibits significantly lower toxicity profile in comparison to acrylamide at all exposure times [62]. DA based photopolymer can achieve refractive index modulation up to 3.3×10^{-3}, and diffraction efficiencies >90% in 70μm thick layers [63]. DA monomer molecules diffuse at lower rate due to their large size compared to AA monomer molecules. Thus for DA monomer, lower recoding intensity is required to obtain proportional polymerization rate with diffusion rate. The optimum recording intensity for the DA photopolymer is half of the intensity required for the AA photopolymer [64]. However, this is disadvantage at low spatial frequencies of recording, where the distance over which the mass transport takes place is increased [64]. To increase monomer diffusion, glycerol plasticizer was included which is low-toxic, transparent, viscous liquid. Inclusion of glycerol can produce uniform maximum refractive index modulation for recording intensities in the range of 1-20 mW/cm^2. Glycerol's plasticizer allowed faster diffusion of un-reacted monomer within the grating during holographic recording. An optimum recording intensity of 0.5 mW/cm^2 was observed for exposure energies of 20-60 mW/cm^2. The modified photopolymer achieves a refractive index modulation of 2.2×10^{-3}, with diffraction efficiencies up to 90% in 100 μm layers. Glycerol has also shown to reduce the rate of photobleaching of the DA photopolymer as more prevalent inhibition effects caused by increased oxygenation of the photopolymer layers. Addition of glycerol also improved the stability of photopolymer sample [64].

1.2.1.3. N-isopropylacrylamide (NIPA) monomer based photopolymer

Thermo sensitive hydrogel N-isopropylacrylamide (NIPA) is another nontoxic monomer, for photopolymer holographic material. Thermo-sensitive hydrogels have positive or negative temperature sensitivity. A positive temperature-sensitive hydrogel has an upper critical solution temperature (UCST) which contract upon cooling below the UCST. Negative temperature-sensitive hydrogels have a lower critical solution temperature (LCST).

These hydrogels contract upon heating above the LCST, and are known as thermo reversible hydrogels as the contraction is totally reversible upon cooling [65-66]. Poly NIPA (PNIPA) has lower LCST at about 32 °C [67]

i.e. it shrinks with increasing temperature. PNIPA forms swollen hydrogels of crosslinked species due to the presence of both hydrophilic amide groups and hydrophobic isopropyl groups in its side chains. PNIPA hydrogel in an aqueous solution exhibits a rapid and reversible hydration–dehydration change in response to small temperature changes around its LCST. The refractive index before and after polymerization was obtained and it was found that a bigger differences exists in the case of NIPA photopolymer when compared to acrylamide based

photopolymer besides a lower toxicity as shown in Figure 5.
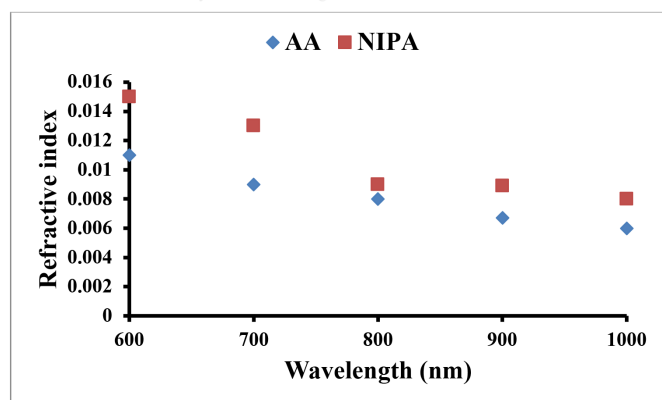
Figure 5: Difference in the refractive index between NIPA and AA monomer based photopolymer.

1.2.1.4. *Sodium acrylate (NaAO) monomer based photopolymer*

Sodium acrylate (NaAO) is another type of non-toxic monomer can be used in photopolymer for holographic recording. The toxicity of NaAO is lower than that of AA [68]. 900μm thick photopolymer material made by NaAO achieved maximum diffraction efficiency of 77% under the exposure 197 mJ/cm² intensity [69]. The NaAO diffusion inside the photopolymer is 10 times smaller than PVA/AA photopolymer and suitable for slow diffusion rate application. The molecular weight is similar for both substances (71.08 u AA, 94.04 NaAO). Diffusion rate varies between 1.4×10^{-9} cm² s^{-1}- 2.9×10^{-9} cm² s^{-1} [70].

Effect of Binder (PVA) on DE

In Photopolymer, binder helps to achieve dry photopolymer. PVA as a binder in AA based photopolymer was proposed by Sadlej and Smolinska [71] and PVA also improved the self-life of photopolymer. PVA as polymer binder has strong moisture absorption capacity. Therefore water or other vapour molecule, such as acetone molecule, can osmoses into the binder matrix and bounds with the polar molecules [72]. PVA binder comes with percentage hydrolysis. It can be 80% to 90% hydrolysis. Percentage hydrolysis decrease, increase the diffraction efficiency. Lower hydrolysis contains two types of polymers. 80% hydrolysis binder contains 80% polyvinyl alcohol and remains 20% polyvinyl acetate. Poly vinyl acetate is hydrophobic and closely packed clusters, which restrict the diffusion of free radical or terminated the short polymer chain during the grating formation [73]. Higher molecular weight of PVA binder increases the DE.

Effect of dye on DE

Effect on photopolymer DE due to dye molecule (in this case Erythrosine B) concentration is shown in Figure 6. Higher dye molecules concentration in photopolymer enhances the photons absorption by dye molecule, which make easier for initiator to be excited. Thus, the overall polymerization rate becomes quicker. However, sensitivity analysis also shows that dye sensitivity decrease after a certain concentration. High concentrations of the dye [54] form dimeric dye. This involves in

a polymerization termination reaction, which results decrease in the overall rate of polymerization. After those dye molecules participating in the polymerization have been consumed, the dimeric molecules of the dye will decompose; the monomers in the material will polymerize perfectly as long as the exposure time is long enough. The decomposition process of the dimeric dye influences the polymerization rate, leading to the decrease in the sensitivity of material. However, the diffraction efficiency changes were significantly low [43]. From sensitivity curve it is clear that the material decreases with increasing concentration of Erythrosine B when it is greater than 0.05×10^{-3} M.
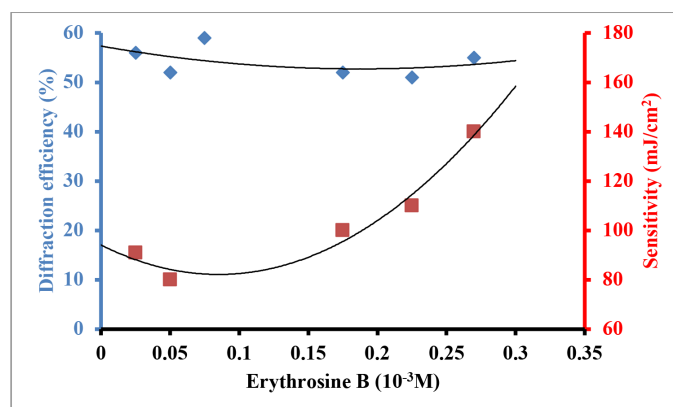
Figure 6: Effect of the concentration of Erythrosine B on the holographic parameters in a holographic material. The chemical composition of the material is AA: 0.21 M; BAA: 0.0324 M; TEA: 0.38 M; PVA: 10%. The intensity used is 20 mW/cm² (Redrawn from [43]).

Effect of Initiator (TEA)

Triethanolamine (TEA) and NPG are the two types of initiator have been used so far for AA and its derivatives based photopolymer. TEA as an initiator was first investigated by Chen 1965 for photo sensitive mythelene blue dye to initiate polymerisation in an aqueous AA based solution [54]. It can generate a radical in a redox reaction under excitation by light [74]. A photo polymer material under the exposure of monochromatic light and similar absorption band of dye, starts photopolymerization. Dye molecules become excited under light and become radicals, which react with TEA quickly. TEA becomes radical cation, then reacts with the monomer molecules, and makes them polymerize. Excited dye molecules after reaction with TEA become bleached, thus photopolymer become transparent after illumination [75]. High concentration of TEA is advantageous due to plasticizer nature which improve the quality of the material, reduce the precipitation of the monomer on the surface of the film, and consequently, reduce the noise of the gratings as well. However, above the threshold limit for a particular material, higher amount of TEA makes the film shrink greatly. For AA based photopolymer, concentration above 0.6 M, shrinkage of the film is greater than 10%.

However, NIPA based photopolymer is humidity sensitive which can be improved by using N-phenylglycine (NPG) photo initiator. NPG as a photo initiator offers better diffraction efficiency compared to TEA under humid conditions [76-77]. Humidity response of transmission gratings recorded in an acrylamide-based photopolymer containing NPG as a photoinitiator is studied at RH = 20 – 90 %. It was observed that

the hologram was completely insensitive to humidity at RH below 70 % and its diffraction efficiency remains constant. RH between 80-90%, DE of holographic material is fully reversible. This work concluded that NPG photopolymer offers excellent resistance to humidity [78].

4,4′ azo-bis- or 4-cyanopentanoic acid (ACPA), is a water soluble radical initiator also used for AA based photopolymer. The molecule produces two radicals and one nitrogen molecule when it reacts with the excited dye in the initiation and the radicals generated react with the monomer in the propagation step. A holographic recording material that contains ACPA and pyrromethene dye in a PVA matrix was investigated [69]. ACPA is an interesting initiator for this kind of dyes, as this dye cannot react with TEA in a redox reaction.

Effect of cross linker

Cross-linker binds the polymer chains, which reduce the mobility of the polymer chains, and ensures the stability of the grating formed during the recording process. Absence of cross-linker will allow the polymer chains to diffuse out of the bright regions of the recorded fringe pattern, resulting in a decay of the grating refractive index modulation with time. Van Renesse 1972 [79] improved this acrylamide based photopolymer by adding N N'methylene-bis-acrylamide which served as a cross-linker to the main polymer network.

Addition of acrylamides and N,N9-methylenebisacrylamide speed up the polymerization reaction [80]. BAA can speed-up the polymerization reaction of AA in the photopolymer, so the materials with high concentration of BAA have high diffraction efficiency and sensitivity at the same time, but higher concentration of BAA will also lead to high shrinkage of the material [43].

Effect of chain transfer

Chain transfer agent (CTA) limits or control of polymerization by stopping the chain growth or molecular weight by its presence in the polymerizing system. Chain transfer agents are compounds that can react with growing chains to interrupt the growth of a particular molecule. Chain transfer agents (CTAs) have long been used to control the molecular weight and viscosity of acrylamide (AA)-based polymers in an attempt to improve their spatial resolution [81-83]. Available CTA, which was used with AA photopolymer, is sodium formate (HCOONa) [84], 4,4′-azobis(4-cyanopentanoic acid) or ACPA, citric acid [85].

Addition of CTA in holographic photopolymer was first investigated by Cole et.al. [86]. At higher spatial frequencies CTA promote short chain growth [84]. It was also found from experimental result that an increase in diffraction efficiency from 12.6 to 18.07% at a spatial frequency of 4286 l/mm due to the incorporation of the CTA sodium formate (HCOONa) [84].

ACPA as a chain transfer agent (CTA) was also used due to its capacity to generate two identical radicals. TEA/YE is the redox system with TEA as initiator. The improvement is enhanced in the case of compositions that include the crosslinker BMA because their noise level is higher. We obtained a diffraction efficiency DEmax > 85% using ACPA [67].

Fernández et al. report on the use of two different CTAs, namely, 4,

4′-azobis(4-cyanopentanoic acid) (ACPA)58,59 and HCOONa,60 for reflection mode recording with an AA-based photopolymer. Although the inclusion of ACPA was shown to reduce the amount of polymerization induced shrinkage occurring in the layers, only small increases in diffraction efficiency were observed (maximum of 8.3% at a spatial frequency of 4553 l/mm), and no improvement in diffraction efficiency was observed with HCOONa. A method for improvement of the diffraction efficiency in reflection mode by control of the permeability of the binder matrix and thus achieving restriction of the diffusion of short polymer chains

Challenges

Photopolymer material in holographic application mainly suffers from shrinkage. Individual monomer molecules during polymerization become tightly packed in chain formation. Thus, overall volume of the material shrinks which distort the formed grating and diffraction efficiency is deteriorated [88-90]. In particular, holographic data storage application (HDS) suffers from this shrinkage. HDS works at higher angular selectivity during the process of holograms and requires thick photopolymer layers (500 μm or more) [91-95]. Shrinkage of material changes the fringe spacing and therefore the reconstruction angle, resulting in no light being diffracted at the expected reconstruction angle and the stored data page cannot be recovered. Common monomers such as methacrylates, acrylamides, and styrene undergo large polymerization shrinkages of 14–23% [96]. DuPont photopolymer having thickness of thickness 20 μm achieved 5.25% shrinkage after holographic gratings were recorded using an Argon Ion laser 514.6 nm [97].

A widely used method to find out shrinkage is shown in equation 3 and 4. Fraction change of thickness of the sample is calculated from shift of initial and final slant angle.
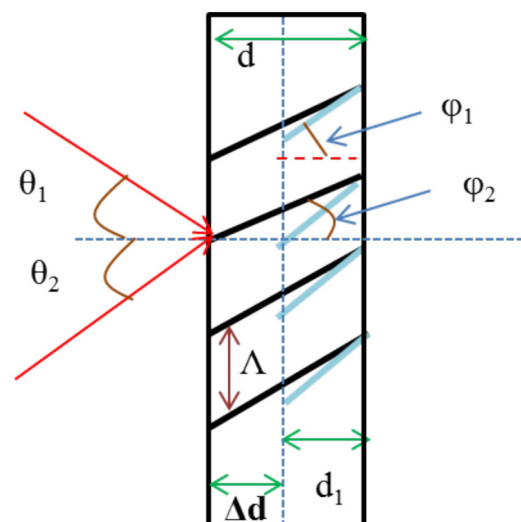
Figure 7: Schematic diagram showing of fringe re-orientation in a transmission grating due to shrinkage.

When two collimated beams interfere in a holographic medium grating is form and period Λ and slant angle φ

$$\Lambda = \frac{\dfrac{\lambda}{n}}{2\sin\left(\dfrac{\theta_1 + \theta_2}{2}\right)} \qquad (3)$$

$$\varphi = \frac{\pi - \left(\theta_1 - \theta_2\right)}{2} \qquad (4)$$

θ_1 and θ_2 are the angles of incidence of signal and reference beams, λ is the recording wavelength, n is the average refractive index of the material.

The material shrinks from its original thickness d to thickness d1. Due to the change in thickness of the recording material the orientation of the fringes will change in volume transmission grating as shown in Figure 7.

$$d_1 = \left(1 - \tau\right)d \qquad (5)$$

τ is the coefficient of shrinkage (2% shrinkage corresponds to 0.02). Fractional change of grating can be found from the below equation.

$$\frac{\Delta d}{d} = \frac{\tan\varphi_1}{\tan\varphi_2} - 1$$

Where

ϕ_1, ϕ_2 are the final and initial slant angles.

Shrinkage in photopolymer layers can be determined by measuring the shift in the angular position of the Bragg peak. The disadvantage of the Bragg curve measurement is that the shrinkage can be measured only after recording the grating. Holographic interferometry is a dynamic method by which deformations, including photo induced dimensional changes, in a material can be monitored throughout the entire experiment.
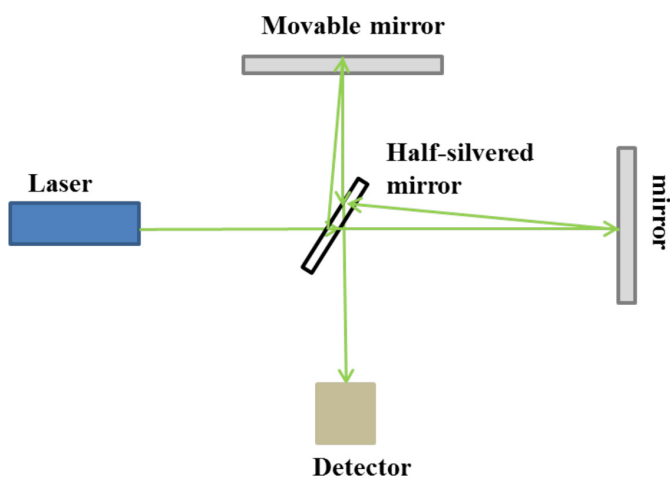

Figure 8: Michelson interferometer set up.

Real time holographic interferometry has been used to characterise the process of shrinkage in acrylamide based photopolymer during holographic recording as shown in Figure 8. Initial tests were carried out in order to confirm that the observed interference fringes are the result of the shrinkage during the holographic recording. The absolute shrinkage in the layer is proportional to the layer thickness. Comparison is made with data previously obtained using the Bragg shift method.

Gallego et al [98] reported different values of shrinkages or swelling in photopolymer layer using a reflection interferometer. Their results suggested that at higher spatial frequencies, monomer diffusion from the dark zones to the bright ones, together with surface tension effects, could considerably affect the material volume changes. In particular, molecular migration (mass transport) reduced shrinkage. Shrinkage of around 2% (without crosslinker) and 3% (with crosslinker) were obtained. The reduction in shrinkage was observed to increase with the spatial frequency and with the monomer diffusion velocity.

However, shrinkage property is advantageous in holographic photopolymer sensor application. This polymerization-induced shrinkage can be reduced by diluting the monomer content with an inert matrix or partially prepolymerizing the monomers. In holographic applications, both these options reduce RI contrast and dynamic range. Addition of nano particle improves this shrinkage issue of photopolymers.

Solution

Addition of nano particle in photopolymer is attractive as it improves the mechanical, thermal [99] stability, and suppress polymerization shrinkage, increase the saturated refractive index modulation, and optical properties of polymers and giving high dimensional stability [100]. Details of nanocomposition in photopolymer are shown in Figure 9. Nanoparticles are non-reactive components known for having low scattering, stability in water suspensions and are available with a broad range of refractive index. Nanoparticles with a refractive index significantly different to that of the host photopolymer material, offer a low refractive index of the composite. Large refractive index modulation (Δn) can be achieved due to spatial redistribution of the nanoparticles during holographic recording. The idea of incorporating inorganic nanoparticles into holographic photopolymers was first introduced in 1996 by Oliveira et al [101].
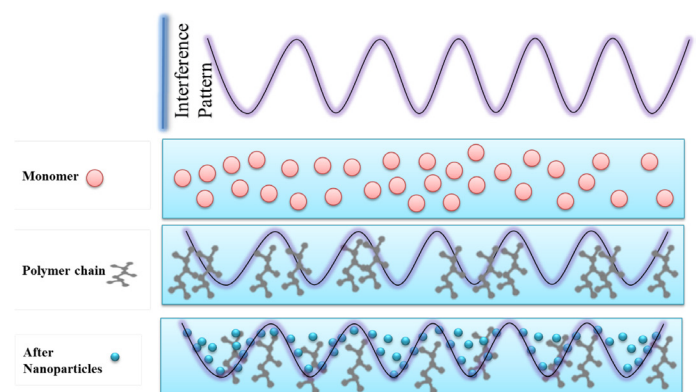

Figure 9: Details of nanocomposition in photopolymer during holographic recording.

Nanocomposite photopolymer for shrinkage and refractive index enhancement

Zeolites are a class of microporous inorganic aluminosilicate ($Al_x Si_{2-x} O_4 . nH_2 O$; n the water content and $0 < x < 1$) or aluminophosphates ($[(AlO_2)_x (PO_2) . yH_2 O]$) crystals material, which contain molecular sized voids (pores) within their three-dimensional crystal structures [102]. Because of their unique size and shape of the zeolite pores and their large specific surface areas, zeolites can discriminate between molecules based on size and shape selectivity. Pure silica MFI-type zeolitesnanoparticles with sizes of 50 nm and 100 nm (samples MFI-50 and MFI-100) under suspended conditions and their toxicological effects on human lung alveolar (A549) cells under in vitro conditions [103] were investigated to find out the toxic effect of zeolite. As a sensing layer, zeolites are very favourable due to their extremely high thermal stability and chemical resistance. Natural zeolites also have applications in areas such as agriculture [104], gas separation [105], and animal husbandry [106]. Zeolite lowers the shrinkage in acrylamide-based photopolymers. Zeolites are negatively surface charged it is expected to be an appropriate dopant for photopolymers [107]. The advantages of using zeolite nanoparticles in colloidal form are their stability in water suspension, the same pH as the photopolymer and can be synthesized with different shape, size and chemical composition. Varying porosity and structure zeolite can be [108-112]

· Silicalite-1 has MFI-structure and diameter of 30 nm, hydrophobic [113]

· AlPO-18 has AEI-structure and diameter of 180 nm, hydrophilic [114]

· Beta which has BEA-structure with diameter of 40 nm

· Zeolite A which has LTA structure small pore than Beta

· Zeolite L which has LTL structure

An acrylamide based photopolymer doped with pure silica MFI type zeolite (silicalite-1) nanoparticles has been characterized for holographic recording purposes. Due to the hydrophobic nature, the MFI zeolites ensures its pores remain empty when incorporated in the host photopolymer. It decreased the refractive index and reduce the shrinkage from 1.32% to 0.57% [115] resulted in an increase of the diffraction efficiency by up to 40% which is just above the commercial limit of shrinkage for data storage applications. The best results were obtained in layers doped with 5 wt. % silicalite-1 nanoparticles. In an another work, behaviour of diffraction gratings recorded in thick (1-mm) acrylamide-based photopolymer layers doped with Si-MFI Zeolite nanoparticles (1.9% w/V) was studied. The gratings were recorded at a spatial frequency of 1000 lines/mm at three different values of absorbance (0.10, 0.18 and 0.37). A modified method was developed for the preparation of l-mm thick layers with uniform layer thickness and at lower surface roughness. By measuring the diffraction efficiency growth and studying the diffraction pattern, the influence of nanoparticles (Si-MFI) doped thick volume holographic gratings was analyzed. For all above absorbances, Si-MFI nanocomposite doped 1-mm thick layers showed higher diffraction efficiency (DE) than the undoped thick layers. High-contrast image and DE was observed for the absorbance of 0.18 in 1-mm thick Si-MFI nanocomposite layers (Mahmud et.al. 2013.

Depending on the chemical composition and types of the structure, the zeolites will exhibit variable refractive index. Among the different types of zeolite nanoparticles used for doping of photopolymers, the pure silica MFI (Si-MFI) has shown the best results [116]. AA monomer based photopolymer and zeolite nanocomposites showed a maximum improvement of the light induced refractive index modulation of the grating of 16% for a small addition of 1%wt. Low refractive index improvement happened due to high hydrophilicity and small pores of zeolite A which offered low interaction between nanoparticles and photopolymer component [117].

Zeolite beta nano particle to the AA photopolymer has no refractive index modulation improvement with photopolymer and it has no effect on self-aging of photopolymer. Small size of AA monomer (approximate size of 5 × 4 Å) could be the reason of low refractive index difference as due to small size monomer molecules redistributed in to the zeolite pores. Doping of the DA photopolymer (approximate size of 10 × 4 Å) with BEA zeolites results in an 11% decrease of the average refractive index of the nanocomposite layer [118].

Nanoparticles for refractive index

Metal NP chromium (Cr), ferric (Fe), copper (Cu), silver (Ag), gold (Au) exhibit unique optical properties in the visible spectral range due to the collective excitation of conducting electrons known as surface plasmons [119]. Au nanoparticle into a PVA/AA photopolymer offered maximum diffraction efficiency improvement from 71% to 90%, the maximum refractive index modulation increased from 1.82×10^{-3} to 2.27×10^{-3} [120]. Nanoparticles of Fe3O4 was modified by sodium citrate (SC) using the chemical co-precipitation and doped into AA photopolymer. Different quantum dot nanoparticles such as CdSe [121] and ZnO [122] have been incorporated into photopolymer formulations due to their high fluorescence at certain wavelengths. This property is particularly interesting for holographic applications such as sensing and product authentication. Table 3 listed refractive index of different nanoparticle and nanoparticle with photopolymer composition.

Problems with these nanocomposites can arise due to incompatibility of the nanoparticles with the photopolymer material, as well as increased optical losses due to scattering, if the difference between the refractive index of the nanoparticles and host material is too great [123]

Table 3: Refractive index of nanoparticle and nanocomposition with photopolymer.

nanoparticle	size	Refractive index	Refractive index of composite	Ref
ZrO2		2.1	1.5×10^{-2}	[101]
TiO2	15 nm	2.55	5.1×10^{-3}	[124]
TiO2	4 nm		15.5×10^{-3}	[125]
SiO2	13 nm	1.46	8×10^{-3}	[126]
Au	1.7 nm		7.3×10^{-3}	[127]
Ag	5 nm		7.5×10^{-3}	[128]

Au	12		2.27×10^{-3}	[120]
Fe3O4	15 nm		2.083×10^{-3}	[129]
Zeolite (BEA)			$6.1 \times 10^{-4} \pm 8 \times 10^{-5}$	
Zeolite (AEI)			$1.3 \times 10^{-4} \pm 1 \times 10^{-5}$	
Zeolite (MFI)			$1 \times 10^{-3} \pm 1 \times 10^{-4}$	[130]

Nanostructured polymers possess highly branched main chains such as dendrimers8 and hyperbranched polymers (HBP). HBPs are preferable due to easy preparation, uniform dispersion in a monomer without any substantive aggregation and unwanted chemical reaction/ geometrical entanglement with monomer molecules. HBPs can be employed as another candidate for size and refractive-index controllable nanoparticles [131]. HBPs nanoparticles dispersed in methacrylate photopolymers were investigated [132]. Two types of reduced HBPs, hyperbranched poly (ethyl methacrylate) (HPEMA) and hyperbranched polystyrene (HPS), having average size of 10 nm were synthesized. HBP nano particles were able to suppress shrinkage in photopolymer material using thiol-ene step-growth polymerisation mechanism. Due to the effect of crosslinked thiol-ene, polymerisation proceeded very rapidly. Low shrinkage of as 0.3% was observed for HBP nanoparticle concentration of 35 vol. % [133]. Reduction of shrinkage in photopolymer by introducing epoxy-cured silsesquioxane (hyper-branched POSS molecules) in PVC matrix was investigated. Addition of 15 % POSS hyper-branched, 62% reduction of shrinkage was possible as hyper-branched POSS enhanced the dimensional stability of the material [134].

Other possibilities to improve the shrinkage of photopolymer

Short glass fibers of size 1.6 mm length and 15.8 μm diameter into a urethane acrylic based photo-polymer, was able to lower the shrinkage of the material. Addition of fibers has displaced some of the volume originally

occupied by partially cured and uncured polymer within the structure. Shrinkages in longitudinal and transverse directions decreased [135]. Shrinkage was also reduced by using cyclic allylic sulphides (LS-CASs) ring-opening monomers in a free radical polymerisation holographic recording medium. The percentage volume shrinkage measured was 0.02%, a fivefold decrease in volume shrinkage compared to 4-bromostyrene monomer system [135].

Chen et.al [136] reported an organic-inorganic hybrid matrix with low shrinkage. The matrix is triethoxysilylpropyl polyethyleneglycol carbamate (TSPEG) homogeneously bonded with tetraethyl orthosilicate (TEOS) prepared by the solgel method. Diallyl phthalate pre-polymer (DAPP, 10 wt% of the matrix) was used as monomer and 9,10-Phenanthrenequinone (PQ, 2 wt% of the monomer) as photoinitiator. Optical data recording was performed with a blue laser source (405 nm) having intensity 2 mW/cm². Shrinkage investigation of a 0.6 mm thick photopolymer was performed by measuring the Bragg detuning was

0.145 %. Presence of the silica inorganic component was liable for low shrinkage as it has good mechanical properties to resist the deformation caused by shrinkage during photopolymerisation of DAPP monomer.

Trentler et al [137] reported photopolymer systems with epoxy resins as a matrix. The crosslink density of epoxy resins plays a crucial role in the holographic performance with regards to diffraction efficiency and volume shrinkage. Shrinkage was determined by measuring the Bragg detuning of the holograms. Epoxy resins with high crosslink density lead to low volume shrinkage, due to their high dimensional stability. It also results in reduced diffraction efficiency due to restricted monomer diffusion for photopolymerisation. Whereas epoxy resin with a low crosslink density makes monomer diffusion more efficient and high diffraction efficiency can be obtained. The relation between dimensional stability and diffraction efficiency is a challenging factor for high performance in a crosslinked polymeric matrix. Diffraction efficiency near 92% and volume shrinkage of 0.67% was also obtained by the addition of epoxy resin to the matrix. It was found that the epoxy-resin based photopolymer with low cross-linking density could significantly enhance the energetic sensitivity without reducing both the diffraction efficiency and dimensional stability.

Lee et.al [138] reported a photopolymer material using organic/inorganic hybrid interpenetrating networks (IPNs) as matrix, which exhibits both high monomer diffusion and low volume shrinkage. Slanted gratings (slant angle 5°) were recorded in the material in order to determine shrinkage. It was shown that the hybrid IPNs enable the enhancement of dimensional stability (reduced volume shrinkage) without sacrificing monomer diffusion or diffraction efficiency in crosslinked matrix photopolymer system. The estimated volume shrinkage coefficients were 0.101–0.151 %.

A blue laser-sensitized photopolymers were prepared using benzylmethacrylate, (monomer), irgacure 819 (initiator), propylene glycol diglycidylether (PPGDGE), and pentaethylenehexamine (PHA) without any solvent. PHA is a multi-crosslinkable hardener, and enhances the mechanical strength of the matrix and therefore effectively suppresses volume shrinkage [139].

Holographic polymer-dispersed liquid crystal devices (H-PDLCs) combine the advantages of photopolymer media with that of photonic crystals. Holographic patterning of these materials produces switchable devices, an effect which has interesting application for holographic optical elements [140]. H-PDLC materials are reported to achieve diffraction efficiencies greater than 90% and Δn values of up to 1.8×10^{-2} in 23 μm layers [141].

Holographic application using AA based photopolymer

Photopolymer for sensor application

Holographic sensor is advantageous than other available sensor technology due to its low operational time, no need to electrical supply and not so bulky device [142]. Holographic sensors are used for glucose sensing [143, 144], sensor for spore-specific calcium dipicolinate [145], sensor for volatile organic compounds (VOCs) and hydrocarbon gases [146]. Due to some external influences pressure, gas, humidity, and temperature holographic material changes its dimension (shrink

or swell). These shrinkage or swelling changes the fringe spacing of recorded grating in hologram which results in a change in the angular position of the Bragg peak for transmission hologram or a change in the spectral position of the Bragg peak in the reflection hologram.

In a holographic sensor, volume change of the material alters the fringe spacing. This causes a change in the wavelength of the reflected light according to the Bragg equation

$$\Lambda = \lambda / 2n \sin \theta \qquad (6)$$

(6) Where Λ is spatial period of the grating, n is the average refractive index of the recording medium, λ is the

recording wavelength and θ is the half of the angle between the two recording beams. When the grating is illuminated with white light, the diffracted light in a specific direction will be of wavelength λ given by equation 6 and a single colour will be observed. The principle of operation of such sensor can be given by differentiation of equation 7.

$$\Delta \lambda = 2 \sin \theta \left(n \Delta \Lambda + \Lambda \Delta n \right) + 2n \Lambda \cos \theta \, \Delta \theta \qquad (7)$$

A change of the wavelength of the diffracted light could be caused by change of the average refractive index, change in the grating period or when observing at different angle.
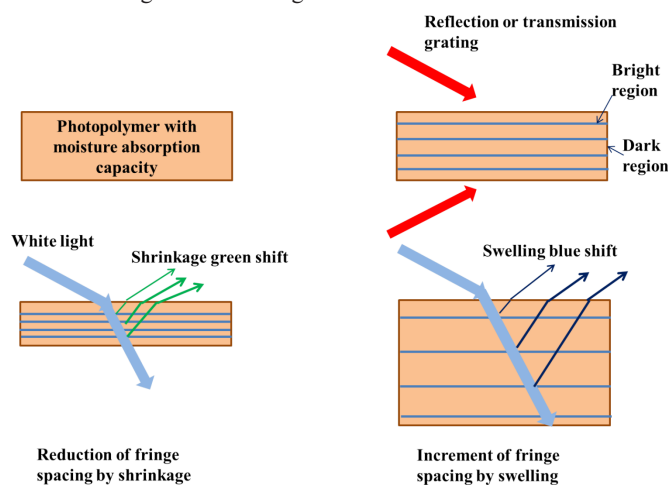

Figure 10: Schematic description of holographic sensing process

The schematic principle of holographic sensing is shown in Figure 10. Swelling of sensitive medium thickness as a significant parameter is the focus of holographic sensing process. When water or other vapour molecules osmoses into the matrix of polymer, polar hydrophilic group can bonded with water molecules in the form of hydrogen bonds. Subsequently, the molecular distances are enhanced significantly. Generally, the swelling process is only characterized by swelling ratio. However, the explorations on swelling mechanism and corresponding theoretical model are still absent for describing the holographic sensing process.

Photopolymer for humidity sensor

Humidity sensor based on acrylamide monomer photopolymer was investigated for reflection [147] and transmission [148] hologram. Swell and shrinkage properties of photopolymer make it a potential candidate for humidity sensor application. An acrylamide photopolymer reflection hologram as a humidity sensor was examined using controlled environment chamber with humidity control system at a set point in the range of 5%–100% RH with accuracy better than ±1% (Electro-Tech systems model 503-20 having RH). The hologram changed its colour under exposure to varying humidity and found to be fully reversible. A 30 μm thick reflection hologram's spectral responses increased by 130 nm due to relative humidity changes from 5% to 80% at 23^0C [147]. The response time of this reversible sensor was thickness dependent. Under high humidity exposition, hologram absorbs water and swells, resulting in a red shift in the diffracted light wavelength. When the hologram is exposed to low humidity the water is released, the hologram shrinks and a blue shift in the diffracted light wavelength is observed [149]. Effect of high humidity on volume phase transmission gratings recorded in PVA/AA materials was also investigated. Under 80 % and 90 % relative humidity exposure, hologram's properties was reversible 8^0C ambient temperature and irreversible at 16^0C ambient temperature [148].

Photopolymer for pressure sensor

An AA monomer based pressure sensor was first investigated by Lowe et.al. [38]. AA co-polymer with a 2:1 ratio of acrylamidezmethacrylamide and 5% of the cross-linker MBA was prepared. This monomer solution was polymerised onto a glass and holographic recording was done using Nd:YAG laser. Pressure given by G clamps which resulted in a contraction in the volume of the hologram, thus causing the diffraction signal to blue-shift by a total of 3 nm [38].

A DA monomer based photopolymer and reflection mode recording was performed to achieve holographic pressure sensor by Cody et.al. [118]. Photo polymer material is elastic and can be compressed. Photopolymer solution was deposited on a microscopic glass slide and after drying for 24 hrs it was laminated with 50 μm thick melinex polyester film to protect the grating during pressure. Details of holographic pressure sensor is shown in **Figure 11**.
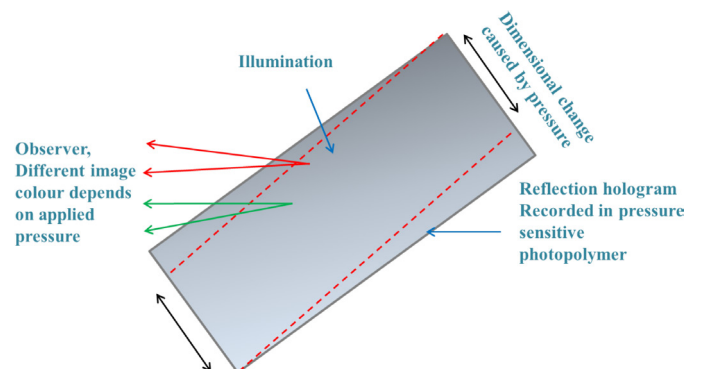

Figure 11: Operating principle of holographic pressure sensor
Pressure sensors could be used for food quality monitoring where a vacuum or a pressurised atmosphere is used to seal a product and keep

it fresh. Loss of the vacuum or pressured atmosphere would change the hologram. Also, this could be an authenticity feature where pressure from touch changes the colour or image to show that the hologram is genuine.

Photopolymer for gas sensor

Gas sensors are useful to detect potentially hazardous or toxic gases in the workplace and/ or the volatile organic compounds or hydrocarbons, which are hazarders to human health and environment [150]. This type of sensorcan also detect the level of toxic fumes from waste products to minimize contamination to the environment. Due to easy detection, holographic gas sensors are suitable. Zeolite BEA-doped AA photopolymer can be used as a holographic gas sensor for toluene, due to changes in the grating's optical properties on exposure to the gas [151]. However, gas sensing photonic structures are limited to operation based on light absorption properties of gas molecules in near infrared [152-153]. The use of hydrogel holographic sensors is limited to aqueous environments. Fabrication of holograms in hydrophobic materials enables their use in non-aqueous environments or without interference from water. This is paramount for gas sensing since water moisture is present in the atmosphere and would affect the holographic sensor performance.

Acrylamide monomer based photopolymer sensor to detect alcohol organic vapour has been evaluated by Mao et.al [154]. Y nanozeolites were dispersed in to the photopolymer to enhance the absorption and sensitivity of the holographic sensor.

Photopolymer for temperature sensor

Holographic temperature sensors are based on thermal expansion/ contraction of the polymer matrix. The rigid polymer structure collapses due to rise of temperature. Thus, produce a significant shift in the wavelength of reflection [38]. Temperature changes the reflectivity/transmittance of the holographic grating or the wavelength of the refracted light. Acrylamide-based photopolymers have low glass transition temperatures ($< 80^0C$). Under temperature exposure, refractive index and dimensions of these materials changes [88]. Thus, the ability of photopolymers to expand under temperature can be implemented for the development of holographic temperature sensors. Hologram made by NIPA monomer has also high temperature sensitivity [38]. NIPA has water-swollen polymer networks. Around 35-40^{0}C this polymer collapses into a denser, more compact structure due to a switch in the balance of solvation and hydrophobic forces. Due to its temperature sensitive properties, it is suitable for temperature sensor [155].

AA Photopolymer for holographic data storage

Binary data is usually encoded on the surface for optical disc. In read only memory (ROM) type discs, bits are encoded as pits and lands in a reflective surface (e.g., aluminium). In compact discs (CDs), disc capacity is increased using multilayers or making it double sided. In writable discs (CD-R and CD-RW), information can be registered by locally modifying the optical properties of a photosensitive material film by using a focused laser. In both ROM and CD-RW systems, information can be retrieved by illuminating the data path with a laser and analyzing the reflected light with an optical detection system. Available types of optical storage systems suffer from absorbance of materials and optics in this spectral region. These two-dimensional optical discs are limited by light diffraction [156]. Holographic data storage has wide potential as a promising data storage technology due to its exceptional features like high capacities, high storage density, and high data transfer rates [157-160]. Holographic volume gratings are Bragg selective, i.e. both wavelength and angularly selective which allow multiple holograms to be stored in the same volume of a recording medium [161].

Holographic data storage can be bit orientated or page orientated. In bit-orientated hologram, bits of data are stored by recording microholograms in the focus of two counter propagating beams [163-163]. Large capacities are possible with these bit-oriented systems [164]. In page-orientated hologram, data pages are imprinted on an

image beam that is subsequently recorded by holography in the volume of the recording material by interfering it with a reference beam [165-166]. In contrast to page-oriented holographic storage and also bit-oriented holographic data storage has been suggested and where single bits of information are stored as microscopic gratings. Holographic recording in 3D allows using the whole volume of a photosensitive medium. In page- oriented holographic memories, an entire page of digital data can be stored at once as an interference pattern of two intersecting laser beams within a thick photosensitive optical material.

Photopolymers offer high photosensitivity, format flexibility good light sensitivity, real-time image development, large dynamic range, good image stability and relatively low cost compared to the previously used inorganic photorefractive crystals [167-168]. The self-processing dye sensitized acrylamide-based photopolymer systems have attracted great deal of attention because of their high diffraction efficiency (DE) and low cost.

When a photopolymer is used in holographic data storage, the stability of the recorded data is a major challenge, and the media should be free from fixing processes. Silver doped photopolymer recording material is a promising candidate for holographic applications [169]. Gratings recorded in these films could be stored for years with good diffraction efficiency. The panchromaticity of the silver doped photopolymer and its suitability to record multiple gratings in a 100 μm thick film was also successfully demonstrated [169-170].

AA Photopolymer for holographic solar concentrator

Holographic optical element (HOE) can be used as static solar concentrator [171-173]. Angular and wavelength selectivity, the diffraction efficiency and the stability of exposure to the sun are the four optical characteristics of a holographic solar concentrator for solar applications. Ludman in 1982 first proposed the use of holographic solar concentrator for PV power generation. Research work has been carried out for designing and analysis of concentrated photovoltaic (CPV) technology using holographic optical element [174-176]. Available holographic recording material was used as concentrator are silver halide [177-179], dichromated gelatin [180-181], phenanthrenequinone doped poly methyl methacrylate [182] and photopolymer [183-184]. Transmission hologram recorded in silver halide coupled with dye-sensitized solar cells achieved 32.9% energy enhancement. However, tracking would be required in a usable device as the enhancement is just at one angle

and it is challenging to mass-produce silver halide [185]. Theoretically, maximum optical efficiency of 40% was achieved for dichromated gelatin hologram [186].
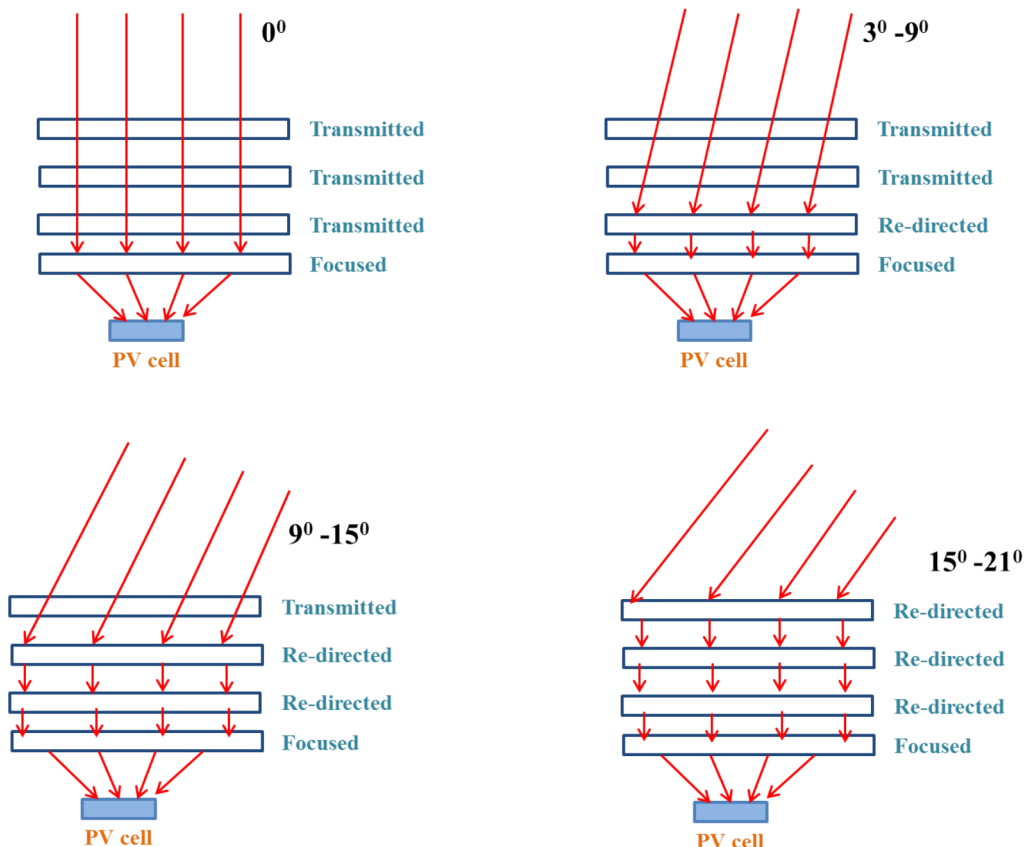
Photopolymer holographic material as a diffractive solar concentrator is attractive due to its low cost which is suitable for mass production. Volume gratings and photopolymers are particularly suitable to collect diurnal solar radiation at a single point. Higher diffraction efficiency from HOE is possible from thicker hologram, which increases the angular selectivity but restricts the angle of incidence. For static solar concentrator broad range of incident angle is required. Higher incident angle is possible by multiplexing or stacking a number of holograms as shown in Figure 12. Selectivity also depends on the spatial frequency of the grating. At a given thickness, a grating with a lower spatial frequency will have a much greater angular working range. To obtain diffractive solar concentrator, combination of several low spatial frequency photopolymer gratings laminated or stacked together so that light is collected from a broad range of angles. Theoretically and experimental validation of AA monomer photopolymer based solar concentrator has been examined [183-184].

Theoretically, it was found that at low spatial frequency, minimum of 25-50 microns grating thickness is required to produce good diffraction efficiency. It was also reported that reduction of spatial frequency rather than thickness gives better experimental results. The results from modelling confirmed that lower spatial frequencies of 300 l/mm are more suitable for capturing light over a wide range of angles. To maintain minimum number of grating in multiplexing few hundred lines per millimetre spatial frequency is suitable for solar collector low. A range of cylindrical/spherical HOEs was recorded using 532 nm lasers at spatial frequency of 300 l/mm with the total exposure energy of 60 mJ/cm^2. The thicknesses of the recorded HOEs were about 50 ± 5 μm. However, outdoor characterisation is required to valid the theoretical

Figure 12: Schematic of the combined diffractive device showing the path of light incident from a range of angles (Redrawn from [183]

work.

Conclusions:

Photopolymer material for holographic application has been reviewed in this work. Acrylamide is the widely used monomer for photopolymer material for three decades. Acrylamide based holographic material can achieve nearly 70-80% diffraction efficiency. Acrylamide monomer based photopolymer has moisture absorption capacity, which enhances its applicability as humidity sensor. Pressure sensor, gas sensor and temperature sensor are also investigated using this type of material. Nano composition of photopolymer material is also attractive for such application where humidity can create an issue. However, acrylamide in its monomer form has toxic nature. Thus, acrylamide can be replaced by its different derivatives such as diacetone acrylamide, sodium acrylate, N- isopropylacrylamide. Acrylamide photopolymer was also investigated for solar application. Further investigation is required to use this as solar concentrator. It can be concluded that for three decades acrylamide based

photopolymer showed an impressive improvement as a holographic

recording material and its applicability in varieties of different field.

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