1.1 Photopolymers

Photopolymers are imaging compositions based on polymers/oligomers/monomers which can be selectively polymerized and/or crosslinked upon image wise exposure by electromagnetic radiation such as ultra-violet, visible or infrared. Typical photopolymer formulations contain a photoinitiator system, monomers and oligomers, a polymer or polymers to provide specific physical
and/or processing properties and a variety of additives to modify the physical properties of the light sensitive composition or the final properties of the cured photopolymer [1]. Most of these systems were originally sensitive to UV light but now, a large number of various systems allow to extend the spectral sensitivity to visible lights [2]. Since direct formation of reactive species on the monomer by light absorption is not an efficient route, the initiation step of the polymerization reaction requires the presence of a PI which, under light excitation, is capable of generating these reactive species. Among various factors which affect the efficiency of the polymerization reaction, the photoinitiator (PI) has been recognized as a key factor. Radical, cationic and anionic polymerizations can be initiated by the excitation of suitable photoinitiating systems (PISs) under light.

1.2 Basic Mechanism of Photopolymer Reactions

The basic light initiated reactions used in the diverse applications of photopolymer technology can be grouped into 5 categories based on the chemical and physical processes utilized [1].

1.2.1 Photopolymerization

The photoinitiated polymerization of monomers and oligomers to form crosslinked high molecular weight material is the basis for most of the commercial applications of photopolymer technology [1]. Photopolymerization processes present several important advantages compare to the corresponding thermal reactions. These advantages
include low energy requirement, spatial and on and off control and fulfilment of green chemistry because, polymerization processes may operate without solvent.

Photopolymerization is usually applied to all chain processes, namely free radical, cationic and anionic polymerizations, and also step-growth polycondensation [3–5]. However, most of the applications are based on the free radical mode due to the less purity demand, applicability to a wide range of formulations based on (meth) acrylates, unsaturated polyesters, and acrylated polyurethanes and the availability of photoinitiators having spectral sensitivity in a broad wavelength range [6-8]. Cation initiated crosslinking of monomeric materials with epoxy and/or vinyl ether functionality has increased practical use with the development of new high efficiency photoinitiators that generate cationic species (e.g. strong acids) upon exposure [9].

1.2.2 Photocrosslinking

The second class of photopolymer chemistry that is used in some commercial products is based on the reaction of unsaturated moieties attached to an organic polymer. This photopolymer process includes the cycloaddition of the ethylenic groups in poly (vinyl cinnamate), (PVCi) polymers and in the styryl pyridinium [10] and thiazolium [11] derivatives of poly (vinyl alcohol). The main advantage of this chemistry is that, unlike free-radical photopolymerization, they are insensitive to the presence of oxygen. This photopolymer mechanism is principally used in applications employing a washout development process (e.g. resists).
1.2.3 Photomolecular Reactions

The third basic mechanism of photopolymer chemistry relies on the light initiated reaction of small organic molecules to modify the polymer based matrix into which they are incorporated. This class of photopolymer reaction is illustrated by the rearrangement of o-quinonediazide derivatives [12] in microresist materials and by the isomerization of azobenzene derivatives in optical storage devices [13]. Other small organic materials have been used to modify the plasticization of a polymer medium to modulate tack [14] and/or adhesion and to initiate colour changes following exposure to light [15].

1.2.4 Photodegradation

The next general class of photopolymer reactions that can be used in a variety of applications is based on the light induced degradation of polymeric materials. A small number of polymers have been prepared which contain light sensitive linkages within the polymer chain. Upon exposure, these light sensitive linkages fragment leading to the degradation of the polymer into smaller polymeric units. The degradation of high molecular weight polymers to low molecular weight materials can be detected as a change in solubility [1].

1.2.5 Photo/Thermal Reactions

The fifth basic class of photopolymer chemistry that can be used in commercial applications is based more on physical changes in a polymer based matrix than on chemical reactions. A recent application of this technology is the laser ablation [16] of an organic coating on a
flat support to directly produce a printing plate. The availability of new high energy lasers will allow more applications to be based on the photo/thermal mechanism.

1.3 Applications of Photopolymer Technology

During the past three decades there has been a rapid increase in the number of commercial applications of photopolymer technology. The practical applications of this technology have been classified into 6 general categories:

- Electronic Materials
- Printing Materials
- Optical and Electro-Optical Materials
- Fabrication of Devices and Materials
- Adhesives and Sealants
- Coatings and Surface Modifications

1.3.1 Electronic Materials

Application of photopolymer technology to electronic products is probably one of the largest imaging categories in terms of sales and total number of patents and publications. A wide variety of products have been developed for the production of printed wiring boards (PWB) and the manufacture of integrated circuits (IC).

1.3.1.1 Manufacture of Printed Wiring Boards

Printed wiring boards, or printed circuit boards, are usually thin flat panels that contain one or multiple layers of thin copper patterns
that interconnect the various electronic components (e.g. integrated
circuit chips, connectors, resistors etc.) that are attached to the boards.
These panels are present in almost every consumer electronic product
and automobile sold today. The various photopolymer products used
to manufacture the printed wiring boards include film resists, liquid
resists, electrodeposited resists [17], laser exposed photoresists [18]
and polyimide interlayer insulator films [19].

1.3.1.2 Manufacture of Integrated Circuits

An increasingly important application of photopolymer
technology is the use of these materials for the formation of integrated
circuits (i.e. chips). Integrated circuits are multilayer microscale
electronic components (e.g. transistors) that are prepared on high purity
silicone wafers. As more and more transistors are incorporated into the
small chips for higher performance, the resolution capability of
photopolymer materials is continually being improved through the
development of novel photopolymer chemistry and manufacturing
processes [20]. Some of the photopolymer products used to
manufacture integrated circuits include Deep-UV [21-22] and electron-
beam resists [23], direct laser imaging materials plus insulating [24-25]
that are used to make conductive and resistive patterns on a scale
between the extremes of printed wiring boards and integrated circuits.

1.3.2 Printing Materials

The application of photopolymer technology to a wide variety of
imaging applications in the printing industry is quite important. Most
Introduction

printing plates and pre-press proofing products used today are based on, some element of photopolymer chemistry.

1.3.2.1 Printing Plates

Of the many technologies used to manufacture printing plates, photopolymer chemistry is used almost exclusively for the plates that print medium to high quality images. The most common photopolymer printing applications include lithographic printing plates, flexographic plates [26] and new digital laser imageable plates [27].

1.3.3 Optical and Electro-Optical Materials

Many of the newest high "value-in-use" applications of photopolymer technology are in the general area of optical and electro-optical materials. Because of the excellent spatial imaging characteristics of photopolymer materials and their ability to rigidify materials to provide aligned molecular structures, photopolymer materials are uniquely positioned to participate in these emerging "high tech" applications.

1.3.3.1 Liquid Crystal Displays (LCD)

Liquid crystal displays, once limited to small devices such as calculators, are now displacing colour cathode ray tube (CRT) displays in commercial quantities. The ability to fabricate these display devices at high quality and at low cost is partially due to the wide spread use of photopolymer-based materials. Photopolymer technology is being used for the alignment of liquid crystal (LC)
Chapter - 1

8

Department of Polymer Science and Rubber Technology, CUSAT

elements [28], the orientation of ferroelectric materials [29] and the synthesis of LC polymers [30].

1.3.3.2 Nonlinear Optical Materials

Nonlinear optical materials (NLO) rely on the ability of light to interact with specially designed inorganic and organic compounds to provide uniquely modulated light output. Photopolymer materials are being fabricated into various NLO materials and devices that are being used in applications such as optical waveguides [31], polarizing optical elements [32] and electro-optical switching devices [33].

1.3.3.3 Holographic Materials

One optical application of photopolymer technology that has been receiving a large amount of attention is the area of holographic materials and devices [1]. Polymeric materials are becoming more important for application in information processing [34-35], and one of the most challenging areas for the polymeric materials is holographic recording. Photopolymer properties, such as high diffraction efficiencies, low noise, self-developing, easy preparation, high thickness, low cost etc., make them a suitable media for holography [36]. They do not require lengthy controlled processing techniques and can be processed in situ.

1.4 Holography

Holography is a technique that makes it possible to store and reproduce three-dimensional images. It was invented by Dennis Gabor in 1947 and after the invention of laser in 1962; Leith and Upatnieks
demonstrated a new approach to holography [37]. The hologram is a record of the interference pattern created when two beams of laser light interfere on the holographic surface. When a hologram is illuminated with a coherent light wave identical to the reference wave, this wave is fixed on the hologram and acts as a sort of a diffraction grating and this diffraction reconstructs the object’s image recorded on the hologram. It has many applications in all branches of science, engineering, technology, bio-engineering, bio-medicine, art and advertising, high resolution imaging, information storage and security coding, holographic optical elements and holographic interferometry.

1.5 Types of Holograms

There are many types of holograms, like reflection hologram, transmission hologram, embossed hologram and integral hologram [38].

1.6 Hologram recording materials other than Photopolymers

When examining the suitability of a recording material, various factors to be considered [39];

- Excellent optical quality: This will lead to bright images.
- High Efficiency: The material should have maximum diffraction efficiency and minimum transmission efficiency.
- High sensitivity: The material should be sensitive to react at low exposure energies.
- High Resolution: The full characteristics of the recorded pattern should be there.
Self-processing: Without any post exposure treatment, the recorded hologram should be readable.

Long term stability of the recorded image: The recorded hologram should be stable for a long period of time.

Economic: It should be cheap and easily available.

Easiness of fabrication: The preparation method should not be complex.

In addition to photopolymers, some other materials are also used for recording hologram. They include; silver halide emulsion, dichromated gelatin material, silver halide sensitized gelatin, photoresists, photorefractive material, photochromic materials, photothermoplastics and additional materials includes chalcogenated glasses etc.

1.6.1 Silver Halide Emulsion

Silver-halide recording materials for holography are interesting for many reasons. Silver halide is the first material used for recording holograms. It is also the most important material for holography for its high sensitivity and numerous applications. It can be coated on both film and glass up to very large formats. Both amplitude and phase holograms can be recorded in it. High resolving power and easily availability are its other common features. But it has some drawbacks such as high absorption characteristics, inherent noise and limited linear response, irreversible recording, wet processing requirement, printout problems in phase holograms etc.
The holographic plates are coated with an emulsion of gelatin containing suspended grains of silver halide crystals. Silver chloride and silver bromide are normally used. Silver iodide is never used alone and usually employed in a mixture along with silver bromide. These silver halide grains are sensitive to light. When a plate is exposed to light, photons from the light source pass through the emulsion. There is every possibility that a photon bumps into a silver grain. If a certain number of photons hit a grain, a small site of metallic silver is formed on that grain. The site can be considered as being a mark on a silver halide grain [40]. Silver halide emulsion is being used over hundred years as photographic plate. Initial attempt was made to use the silver halide coating as holographic recording layer and the first patent on silver halide emulsion, used for holography, is available in literature in 1972. The modifications on initial developments are attempted with newer techniques of preparation, processing and post processing. This has enabled the user to make choice from wider varieties. Most of the work has been on improving the diffraction efficiency (DE) and signal to noise ratio (SNR), particularly for reflection holograms.

1.6.2 Dichromated Gelatin (DCG) Material

Dichromated gelatin finds use in holography due to its excellent holographic properties, including low scattering and high index modulation [41]. The drawbacks of dichromated gelatin include the raw material's variability, complex wet processing, poor shelf-life, and environmental instability requiring hermetic sealing. The efficiency of
dichromated gelatin system is based on the difference in swelling
between exposed and unexposed gelatin. The recording sensitivity of
DCG has been extended to red wavelength making it possible to
record multicolour reflection holograms.

1.6.3 Silver Halide sensitized gelatin

Recent development of ultra-fine grain silver halide emulsion
has increased an interest in the silver halide sensitized gelatin (SHSG)
technique. SHSG technique is expected to provide comparable effects
with the DCG, when applied to an ultra-fine grain silver halide
emulsion. Briefly, the SHSG technique involves exposing and locally
tanning a silver halide emulsion layer. Then, silver salt or silver in the
emulsion layer diffuses out due to fixing and leaving behind only pure
gelatin. In the last step, the remaining gelatin is dehydrogenated using
organic solvent. The dried SHSG hologram includes only gelatin and
micro voids of air [42]. The gelatin has a refractive index of 1.5, and
the air filling the micro voids has a refractive index of 1.0. This
difference of refractive index can maintain excellent diffraction
grating efficiency [43].

1.6.4 Photoresists

Photoresists are suitable for producing surface relief holograms
for making masters needed for replication by embossing techniques.
This material is most sensitive to ultraviolet light only. Efforts have
recently been made to make photoresists sensitive at red wavelength. A
typical photoresists (Shipley AZ -1350) for holography has sensitivity
Introduction

of about 10 mJ/cm². It is sensitive to UV and visible upto 500 nm. The Waycoat HPR series represents another photoresists for optical imaging. Towne laboratories, Inc. manufactures coated photoresists for holography [44].

1.6.5 Photorefractive Material

The photorefractive (PR) effect is a nonlinear optical effect seen in certain crystals and other materials that respond to light by altering their refractive index. The effect can be utilized for storing temporary, erasable holograms and holographic data storage. On illumination of photorefractive material by coherent beams of light, interference between the beams results in a pattern of dark and light fringes throughout the matrix. Photorefractive crystals and photorefractive polymers include in this category. In photorefractive crystal, the refractive index (RI) of crystal changes in the regions where the field is strongest. This causes a spatially varying refractive index grating throughout the crystal and are very promising materials for real-time holography. LiNbO₃, LiTaO₃, BaTiO₃, KNbO₃, Bi₁₂TiO₂₀ are widely employed in holographic data storage. However, the difficult crystal growth and sample preparation required for inorganic photorefractive (PR) crystals has limited the widespread use of these applications [45]. Holograms recorded in this medium are erased on read out, making crystals like LiNbO₃ unsuitable for archival storage applications [46-47].
Rapid advances in the field of PR polymers and composites have lead to the development of high performance materials with RI modulations approaching 0.01 and diffraction efficiencies (DEs) close to 100%. The PR effect refers to spatial modulation of the index of refraction under non-uniform illumination via space-charge field formation and electro-optic nonlinearity. The hologram recorded in this material can be erased by uniform optical illumination. The spectral sensitivity of PR polymers can be changed by using different dopant sensitizers. PR polymers need long fabrication steps, required high bias voltage and their response time is also low.

1.6.6 Photochromic materials

Reversible colour change in a material after exposure to light is called photochromism. Photochromic materials darken after exposure to ultraviolet or blue light and either darkening or bleaching of photochromic material can be the mode of hologram recording. Since photochromism involves photochemical reactions at the molecular level, the material is grainless; hence its resolution is more than sufficient for holography and no development is required to form the hologram. The hologram recorded in this material can be erased either thermally or optically and the material is reusable. The photosensitivity of this material is at least three orders of magnitude less than that of silver halide photographic emulsion. The photosensitivity of this material decreases with increasing number of record-erase cycles and finally they become totally insensitive to light; that is the reusability of this material is limited [39].
1.6.7 Photo thermoplastics

Holograms can be recorded in a thermoplastic film by causing its structure to deform in accordance with the light intensity variations of holographic interference patterns. Thermoplastics are usually not photosensitive and must be combined with a photoconductor in a film structure which respond to light. It is highly photosensitive to all visible light and requires no lengthy wet development. Hologram recorded in this material has moderately high diffraction efficiency and is stable at room temperature until intentionally erased. The material can be reused a number of times. But the maximum resolution obtainable with this material is not much greater than 1000 cycles/mm. In addition, high quality film is difficult to prepare and the thermal development of the film is critical [48].

1.6.8 Additional Materials

Chalcogenide glasses, ferroelectric photoconductors, liquid crystals, magneto-optic films, metal and organic dye-ablative films, transparent electrographic films and light harvesting protein (bacteriorhodopsin) [44] are other materials used for recording hologram.

1.7 Photopolymers in holography

According to holographic point of view, photopolymers can classified into two large groups; one which able to produce high diffraction efficiency or generates phase holograms (formation of grating by modulation in refractive index) such as acrylamides, acrylates, methyl
methacrylates or those which are photocrosslinkable systems like poly (vinyl carbazole) (PVK), dichromated poly (vinyl alcohol) (DCPVA), poly (acrylic acid) (PAA) and other with low diffraction efficiency or generate amplitude holograms (grating formation as a result of modulation in absorption) such as doped polymers (photochromic compounds, bacteriorhodopsin). Photopolymerizable systems include within the first group. The photopolymerizable system can be further divided into two large categories; liquid compositions and dry films. The latter can be sub divided into acrylates, methylmethacrylates, acrylamides etc depending on the type of monomer used [39].

1.8 Photopolymers as hologram recording media- A brief review

Since about 1970, a number of photopolymer based refractive index imaging systems have been discussed [48]. Their versatility, ease of use and self processing ability give them many advantages over more traditional materials such as silver halide and DCG. [49-50]. Photopolymers have been considered for use as holographic recording media for several decades [51]. The ability to change sample shape, and the inherent tunability of the physical properties for most polymer systems by changing component content and ratios are additional advantages [46].

Photopolymers were first used as a holographic recording material by Close et al. in 1969. They mentioned the use of a polymeric solution formed with acrylates and methylene blue (MB). For this, the exposure needed was 1- 30 mJ/cm² for a working wavelength of 694 nm with
diffraction efficiency of 45 %. This material had a short shelf life. Fixing process was also done using UV irradiation [52].

*Jenney* was the first to report the use of an acrylamide (AAm) system as a holographic recording material in 1970 and the system was a solution of acrylamide initiated by methylene blue and p-toluene sulfonic acid. This photopolymerizable solution was sandwiched between two glasses and producing an energy sensitivity around 0.6 mJ/cm² and diffraction efficiencies of nearly 20% was obtained when irradiated at 633 nm. Here also fixing process was used [53].

The property of this mixture was improved by *Van Renesse* in 1972 by adding N, N’- methylene-bis-acrylamide (BMA) to speed up polymerization reaction to this system. Sensitivity of the material was 5 mJ/cm² but the recorded hologram could be stored only for one week [54]. *Sugawara* et al. reported the use of acrylmide and methylene-bis-acrylamide with acetyl acetone or triethanolamine (TEA) as photo reductant and they got a diffraction efficiency of ~ 65% for exposure of 50 mJ/cm² [55]. *Sutherland* et al. demonstrated by using liquid crystals in an acrylate system and DE reaches 100% for holograms registered at 488 and 514 nm [56].

*Fimia* et al. continued the work of Sugawara et al and used two aqueous solutions, one containing polymerizable system with acrylamide, zinc acrylate and N,N’-methylene- bis- acrylamide and photo initiator system with MB and rose bengal (RB). Here pre-exposure was given and a DE of 50% was obtained with energetic sensitivity lower than 10mJ/cm² [57].
**D J Lognot et al.** reported a self processing formulation based on β-hydroxy ethyloxazolidone acrylate and hologram recorded using Ar\(^+\) and reconstructed using He-Ne laser. They developed a formulation named as PHG-530N having a maximum DE of 80% with exposure energy less than 150mJ/cm\(^2\) [58].

**Bartkiewicz and Miniewicz** developed methylene blue sensitized poly (methyl methacrylate). Phase and/or amplitude holograms could be written in the methylene blue sensitized films of poly (methyl methacrylate) (PMMA) with He-Ne laser operating at 632.8 nm. Diffraction efficiencies of 60% were found for thick holograms [59].

**Zhao** used gelatin as binder along with acrylamide and acrylic monomers, methylene blue, p-toluenesulphonic acid and triethanolamine as initiators and a maximum DE above 80 % was obtained with exposure energy of 2 mJ/cm\(^2\) [60].

**Fimia et al.** reported a new aqueous photopolymer containing the monomer acrylamide, BMA and zinc acrylate. The initiators used were 4,5,di iodo succinylfluorescein (2ISF) and MB and co-initiator sodium p-toluenesulphinate and DE of 15-20% obtained with 15-60 mJ/cm\(^2\) [61]. **Diamond et al.** used Epotek-21 resin as a polymer binder, dipentaerythriol pentacrylate (monomer) and a DE of 3.5% was obtained [62].

**Pavel Cheben** introduced a modified silica glass containing titanocene photoinitiator and ethyleneglycol phenyl ether acrylate.
Hologram was recorded using Ar⁺ laser and He-Ne laser was used as read-out laser. A DE of 98% obtained with exposure of 0.23 J/cm² [63].

Using 2-hydroxyethyl methacrylate in PMMA containing dye 1,3,5,7,8 pentamethyl-2,6-diethylpyrromethane difluoroborate as a photo initiator, Blaya et al. got a DE of 60% in 500µm film with exposure energy of 1J/cm² [64]. Ushamani et al. used complexed methylene blue sensitized poly (vinyl chloride) (PVC) for holography and a DE of 4.46% obtained for 193 lines/mm [65].

Carretero reported acrylamide, BMA, triethanolamine and yellowish eosin in silica glass and a DE higher than 80% obtained with 10mJ/cm² having the film thickness of 113µm [66]. Park and Kim prepared sol gel-organic-inorganic composites with thickness greater than 200µm on the basis of aromatic methacrylates and DE>95% was obtained with 532 nm laser light [67].

Shelkovnikov et al. introduced a hybrid organic-inorganic matrix prepared by the synthesis of N-vinylpyrrolidone and triethoxyvinylsilane copolymer followed by hydrolytic condensation of the copolymer with a tetraethoxy silane presol. Here acrylamide and acrylomorpholine (monomers), bis-acryloyl piperazine (crosslinking monomer), triethanolamine and mercaptomethyltriazole (initiators), MB (photosensitizer) were used. For a thickness of 0.46 mm, holograms with DE of 80% were recorded at exposure of 300 mJ/cm² [68].

Kim proposed a new phase stable acrylamide based photopolymer with PMMA as binder, TEA as co-initiator and MB as photosensitizer.
Here methacrylic acid was introduced into the system for phase stability and DE higher than 90% was obtained using He-Ne laser [69].

*B.M John et al.* developed a new reusable photopolymer medium containing MB as sensitizer, PVA as binder and vinyl acetate (VAc) as monomer. For optimized ratio of PVA-VAc, a DE of 6.3% was obtained with 750 mJ/cm² at a dye concentration of 9.3 x 10^{-4} M [70].

*Dae –Won Chung et al.* could record gratings with DE of 48-50% in poly dimethyl siloxanes having four epoxide functionalities [71]. *B.M. John et al.* reported MBPVC film with enhanced DE and storage life by the incorporation of pyridine as electron donor. Without electron donor, the DE was 0.2% with exposure energy 2000mJ/cm² and storage life was just 24 hrs. For a particular concentration of pyridine, DE improved to 0.46% and could be stored for 2-3 days [72].

*Jeong et al.* used photopolymer system based on epoxy resin. Here yellowish eosin was used as the sensitizer, acrylamide as monomer and TEA as co-initiator. DE of 9% obtained with exposure 11.7 x10^{-3} J/cm² [73].

*Ortuno et al.* reported riboflavin sensitized PVA/sodium acrylate, TEA and (DHEBA) and they got a DE of 77% in this system [74].

*Yasushi Takamastu et al.* developed a holographic photopolymer based on SU-8 epoxy resin as the binder. Here trimethylolpropane ethoxylate triacrylate (TET) (monomer) with an iodonium salt
(photoinitiator) were used. A diffraction efficiency of 93% was obtained from a 16µm thick sample with write beam intensities of 50mW/cm² at a wavelength of 514.5 nm, at an exposure time of 60 s, and a post baking at 65°C for 1 h [75].

In addition to the above photopolymer system, PVA/acrylamide systems are widely used as hologram recording material.

1.8.1 PVA/acrylamide photopolymer

In 1975, Jeudy and Robillard were the first to use acrylamide in a poly (vinyl alcohol) film, and a diffraction efficiency of ~ 80% obtained for energy density of 100 mJ/cm² but it should be used within 4-5 days after preparation [76].

Calixto in 1987 reported a DE of 10 % with energetic sensitivity of 94 mJ/cm² using acrylamide as monomer, methylene blue as sensitizer, tri ethanol amine as electron donor and poly (vinyl alcohol) as binder [77]. A method was used by Fimia et al. to raise the sensitivity of acrylamide photopolymers by dropping the inhibition time caused by oxygen. The system comprised of two photosensitizers, MB (sensitive at 633 nm) and RB (sensitive at 546 nm) and a DE of 40 % with exposure energy of 3 mJ/cm² was obtained [78,79].

Calixto’s photopolymer was optimised for recording in the 514 nm region by the addition of xanthenes dye and a DE greater than 80% was obtained with exposure energy of 80 mJ/cm² having spatial frequency 2750 lines/mm [80].
Wiess et al. improved the sensitivity of Close material at 514 nm by adding diphenyl iodonium chloride (DPI) as sensitizer and triethanolamine as electron donor. Here glutaraldehyde was used as the second crosslinker and DE of higher than 90% was achievable with exposure of 12 mJ/cm² [81].

When bisacrylamide was added to PVA/acrylamide system with erythrosine B (ErB) as sensitizer, Martin et al. got a DE of 40% at exposure energy of 300mJ/cm² [82].

Blaya et al. in 1998 reported poly (vinyl alcohol)/ acrylamide photopolymer film with 80% DE with energetic exposure of 40 mJ/cm². The thickness of the film was 35 µm and a spatial frequency of 1000 lines/mm was obtained [83]. In another approach, Blaya et al. prepared acrylamide and BMA in PVA system with a DE of 80% with an exposure of 12 mJ/cm² having a spatial frequency of 1000 lines/mm. Here the molecular weight of PVA used was 25,000 and the thickness was 75µm [84]. Blaya et al. [85] reported acrylamide photopolymer by adding N, N-dihydroethylenebisacrylamide (DHEBA) as crosslinker and a DE of 70% obtained with 5 mJ/cm².

Lawrence et al. prepared PVA/acrylamide photopolymer containing BMA as crosslinker and ErB as sensitizer and holograms were recorded using Ar⁺ laser and reconstructed by He-Ne laser. A DE of 80% obtained with 1000 lines/mm and 30% DE at 2750 lines/mm [50].

Mallavia et al. used an ion pair (RB and MB) in PVA/ acrylamide system. Irradiation using He-Ne and Ar⁺ laser, DE of 60%
and 38% was obtained with sensitivity of 30 and 125 mJ/cm² with spatial frequency of 1000 lines/mm [86].

Pascual et al. reported PVA/acrylamide photopolymer with yellowish eosin as sensitizer and TEA as photoinitiator. When gratings were recorded on the film with thickness 70± 5µm using Ar⁺ laser and reconstructed with He-Ne laser, a DE of 75% was obtained [39]. Pascual et al. could improve the DE of the above system to 80% by increasing the film thickness to 110± 5µm with energetic sensitivity of 200mJ/cm² [39].

Yao et al. developed PVA/acrylamide photopolymer system with BMA with a DE of 55% for an exposure of 60 mJ/cm² with thickness 150µm and a spatial frequency of 2750 lines/mm using Ar⁺ laser [87].

Garcia et al. prepared PVA/acrylamide photopolymer films with yellow eosin as sensitizer and triethanolamine as initiator. They used frequency doubled Nd:YAG (532 nm) Q-switched laser for recording and a DE of 62 % was obtained [88].

Blaya et al. developed PVA based photopolymers (PPMs) by the co-polymerization of acrylamide with 2-hydroxyethyl methacrylate (HEMA) and a DE of 70% was obtained with exposure energy of 65 mJ/cm² when recorded using He-Ne laser and reconstructed with He-Cd laser [89].

Huang et al. prepared 150 µm layers containing PVA, ErB, TEA, AAm and BMA. At optimum concentration, hologram with
DE ~55% was recorded at an exposure energy of 60 mJ/cm² with 2750 lines/mm [90].

*Neipp et al.* prepared photopolymer film using acrylamide and BMA as monomers, TEA as initiator, yellowish eosin as sensitizer and poly (vinyl alcohol) as binder. A DE of 80% obtained with spatial frequency of 545 lines/mm and 60% DE obtained with 1125 lines/mm [91].

*Gallego et al.* used dimethylacrylamide (DMAA) in PVA/acrylamide system containing yellowish eosin as sensitizer and triethanolamine as initiator. A DE of 98% was obtained for a film thickness of 75±2 µm using Ar⁺ laser and He-Ne laser for recording and reconstruction [92].

*Blaya et al.* have developed PVA/acrylamide system with methylene blue as sensitizer and triethanolamine as co-initiator and hologram was recorded using He-Ne laser. A DE of 80% was obtained at exposure energy of 35 mJ/cm² with spatial frequency of 1000 lines/mm. Here BK 7 glass plates were used and films were prepared using thin layer coater (TLC) coater and a thickness of 65µm was obtained [93].

*Gallego et al.* reported PVA/acrylamide system containing N,N’-methylene-bis-acrylamide having a DE higher than 90% when heated to 80°C. Here yellowish eosin was used as the sensitizer. Ar⁺ laser was used for recording and He-Ne laser was used for reconstruction [94].
Kim et al. reported photopolymer system with acrylamide and N,N'-methylene- bis- acrylamide as monomers, triethanolamine as initiator, methylene blue as sensitizer and poly (vinyl alcohol) replaced by poly (methyl methacrylate) as binder. Here a methacrylic acid unit was inserted to enhance the phase stability and a DE close to 90 % was obtained [95].

Gong et al. used N-Phenyl glycine (NPG) as co-initiator in PVA/acrylamide system containing BMA and ErB. In a 150µm film, DE of 50% obtained with 60mJ/cm². When Diphenyl iodonium salt was introduced into the mixture, sensitivity increased to 24mJ/cm² with DE of 40% with spatial frequency 2751 lines/mm [96].

Ortuno et al. reported a DE of 70% in PVA/acrylamide system with yellowish eosin as sensitizer and BMA as crosslinker with exposure energy of 35mJ/cm² having the film thickness of 110µm [97].

Gong Qiao-Xia et al. developed a new photopolymerizable holographic recording material based on acrylamide and N-hydroxy methyl acrylamide (HMA). Here ErB was used as photosensitizer and TEA as co-initiator. Ar⁺ laser was used to record hologram and He-Ne laser used to readout the diffraction pattern. A DE of 50% obtained with exposure energy of 80 mJ/cm² having a spatial frequency of 2275 lines/mm [98].

Jallapuram et al. could record transmission gratings with DE of 50% with spatial frequency of 3000 lines/mm in PVA/acrylamide photopolymer system [99].
B.M. John et al. developed copper doped PVA/AAm system containing methylene blue as photo sensitizer and triethanolamine as co-initiator. For optimized film, a DE of 24% was obtained and remained as such for more than three months [100]. Okhawa and Sekine reported PVA/acrylamide–triethanol system with methyl violet as sensitizer with a DE of 40% obtained [101].

Katherine Pacheco et al. have reported acridine orange sensitized acrylamide. In which, N,N’-dimethylacrylamide (DMAA) and N,N’-methylene- bis- acrylamide (BMA) were used as the crosslinking agents. With DMAA, DE of ~ 10% was obtained at spatial frequency 1000 lines/mm and with DMAA combined with BMA, a DE of 40% was obtained with a spatial frequency of 2000 lines/mm [102].

Katherine B Pacheco used PVA/acrylamide system containing BMA as crosslinker and a DE of 40% was obtained with a spatial frequency of 1767 lines/mm using He-Ne laser [80].

Lu Hai et al. used different photo-initiators in PVA/acrylamide system containing MB as sensitizer and BMA as crosslinking agent. Maximum DE of 59% was obtained for TEA with sensitivity of 1.72 x 10⁻³ mJ/cm². Here film had a thickness of 270-300 µm [103].

1.8.2 Commercially available photopolymers

E.I. Dupont de Nemours made a dry form of the photosensitive system, which consists of liquid acrylic monomer, cellulosic binder and photoinitiating system, and a plasticizer [77,104-109]. Diffraction
efficiencies of up to 90% could be obtained with an optimum exposure of 30 mJ/cm² and the material has a resolution of 3000 lines/mm. But it has very poor spatial frequency response. Because of the limited resolution this material could not be used for reflection holograms. To rectify this, DuPont developed the Omnidex photopolymer system [110-113]. This material has a resolution of about 6000 lines/mm with efficiency of 99%. These results could be achieved with exposure energies of 50–100 mJ/cm². The material is a dry layer consisting of an acrylic monomer, a photosensitising dye, an initiator, a chain transfer agent, a plasticizer and a polymer binder coated on to polyethyleneterephtalate film substrate.

In another case, poly (methyl methacrylate) was used [77,114-117] with p-benzoquinone as sensitizer. Diffraction efficiency of ~70% could be obtained with exposure 1-8 J/cm², but problems with irreproducibility of results have been found. Mixtures of photopolymer containing PMMA were studied [118-120] and a refractive index of ~ 10⁻² was obtained.

Another approach in the fabrication of photopolymers was done at RCA laboratories [121-122]. They used alfa diketones and matrices used were acrylics, poly (esters) and epoxies. In this case, a DE of ~ 70% was obtained with high exposure of ~ 240 J/cm².

The recording media of the HRF series (HRF-150, HRF-800) designed by DuPont containing aromatic or aliphatic acrylate monomers in cellulose acetate butyrate with DE -100% was obtained at exposure of 3 mJ/cm² in 100µm thick layer [123].
A commercial material, DMP-128, was developed by Ingwall et al. of the Polaroid Corporation. It consists of a mixture of methylenebisacrylamide and lithium acrylate as the monomer and a poly (N-vinylpyrrolidone) as binder. The dry material must be incubated in a 50% humidity environment before use. Post recording treatment was needed to increase the efficiency from 0.1% to 80%. The material can be used to record transmission and reflection holograms with exposure energies between 5 and 30 mJ/cm². Although it is more sensitive than the Du- Pont material the need for wet chemical processing is a significant disadvantage [124].

1.8.3 Nano Photopolymers

During polymerization in photopolymer system, there occurs considerable volume shrinkage due to loss of covalent bond and formation of Vander Waals attraction and this leads to reduction in effective thickness and this will affect the stored grating period.

Inorganic materials possess a wide variety of refractive indices (RIs) that give us the opportunity of obtaining much higher index modulation as compared with conventional photopolymers. The inclusion of nanoparticles also contributes to rapid build up of fixed holograms and noticeable suppression of polymerization shrinkage, thus giving high recording sensitivity and dimensional stability. In pure polymer system, it is difficult to achieve large RI modulation, therefore; Bunning et al. pioneered the idea to use inorganic nanoparticles (NP), having substantially higher or lower RI, in holographic mixtures as a movable non-reactive component [125].
Later this idea has been further developed by three different groups; particularly successful was the application of TiO$_2$ nanoparticles. The values of RI modulation ranging from 0.005 to 0.015 have been achieved [126-130]. SiO$_2$ dispersed in methacrylate photopolymer got a DE close to 100% in 90 μm thickness film [133].

*Suzuki and Tomita* reported ZrO$_2$ nanoparticles in acrylate photopolymer system and RI modulation of $5.3 \times 10^{-3}$ obtained [132].

*Sakhno et al.* in 2007 developed surface modified ZrO$_2$ and TiO$_2$ nanoparticles in acrylate polymer system with high RI modulation and the ZrO$_2$ incorporated polymer composite showed much photo stability than TiO$_2$ incorporated polymer matrix [133].

*Leite et al.* reported aluminophosphate nano crystals incorporated PVA/acrylamide system and a DE of 70% obtained and can be applied in optical sensors [134].

1.9 Mechanism of Hologram Formation in PVA/ acrylamide photopolymer system

The hologram formation in the photopolymer film has been discussed by several researchers [135-136]. Lawrence et al. [49] has studied the mechanism in acrylamide photopolymer, in which gratings were recorded by photopolymerization of acrylamide.

It consists of photo-physical and photo-chemical processes.

**Photo-physical process**

When the dye molecule D, is exposed to laser, it absorbs a photon and is promoted into a singlet excited state $^1D^e$
The singlet excited state dye can return to the ground state by fluorescence

\[ {^1D^*} \rightarrow \text{D} + \text{h} \nu \] ................................................ (1.2)

or by radiation less transfer to another molecule and here it is the electron donor (ED).

\[ {^1D^*} + \text{ED} \rightarrow \text{D} + \text{ED}^* \] ................................................. (1.3)

The singlet state can also undergo inter-system crossing into more stable and longer lived triplet state

\[ {^1D^*} \rightarrow {^3D^*} \] ................................................................. (1.4)

Here the excited dye molecule can undergo a reaction with the electron donor by abstracting two hydrogens to form leuco form of the dye. Here the electron donor is triethanolamine and it donates an electron to the excited triplet state of the dye, leaving the dye with one unpaired electron and an overall negative charge

\[ {^3D^*} + (\text{OHCH}_2\text{CH}_2)_3\text{N}^- \rightarrow \text{D}^- + (\text{OHCH}_2\text{CH}_2)_2\text{N}^+ \] ..... (1.5)

The radical cation of the electron donor loses a proton and becomes a free radical.

\[ (\text{OHCH}_2\text{CH}_2)_2\text{N}^+ \rightarrow (\text{OHCH}_2\text{CH}_2)_2\text{NC}^-\text{HCH}_2\text{OH} + \text{H}^+ \] (1.6)
Introduction

The radical anion of the dye molecule abstracts hydrogen from the free radical of the electron donor.

\[(\text{OHCH}_2\text{CH}_2)_{n}\text{NCHCH}_2\text{OH} + \text{H}^+ + \text{D}^\cdot \rightarrow (\text{OHCH}_2\text{CH}_2)_{n}\text{NCH=CHOH} + \text{H}_2\text{D}\] (1.7)

Photo-chemical process

The photo-chemical process involves free radical polymerization [49]. It consists of three steps, initiation, propagation and termination.

Initiation

Initiation takes place when the free radical initiator attaches to the monomer by addition across the C-C double bond.

While bond formation, in order to attach itself to the monomer, the free radical uses its own unpaired electron and a π electron from C-C bond. This leaves one of the carbons with an unpaired electron therefore the monomer becomes free radical (scheme.1.1).

![Scheme 1.1. Initiation](image)

Propagation

Propagation occurs when the new radical attaches itself to another monomer by addition across the double bond by the same method as above. The second monomer now becomes a radical and in this way a polymer grows (scheme.1.2).
After initiation and propagation, the newly formed chain will continue to grow until it is stopped by a termination reaction. This process can arise by two reactions known as disproponation or combination [49]. Dispropanation takes place when hydrogen is abstracted from one propagating chain by another. The hydrogen reacts with the free radical and the original double bond is reformed. This process results in two separate chains (scheme 1.3).

The second method of termination is combination, this consists when the radicals at the ends of two propagating react forming one long chain (scheme 1.4).
On polymerization, each carbon double bond is converted into a carbon single bond, lowering the molar refractivity. This lowers the refractive index of the material and this is usually accompanied by an increase in density which leads to an increase in refractive index. The combination of these two processes results in a higher refractive index in polymerised regions compared to unpolymerized regions so that a refractive index modulation exists between exposed and unexposed areas. It is also thought that during exposure, monomer diffuses into bright region as a result of the concentration gradient induced by the depletion of these components. This causes a further difference in density (and so refractive index) between bright and dark regions. As a result of modulation in refractive index, phase hologram is recorded [49].
Monomer, dye and co-initiator are uniformly distributed in the polymer matrix

On laser exposure, dye get excited and polymerization starts

Monomer diffusion from dark region to bright region

Formation of grating as a result of modulation in refractive index

Fig. 1.1. Mechanism of grating formation

1.10 Objectives of the work

Photopolymers are write-once, read-many times (WORM) materials and therefore, storage life has great importance [94]. Methylene blue sensitized poly (vinyl alcohol)/acrylamide films were developed in our lab with 70% diffraction efficiency at 120 mJ/cm². But a decrease in DE was observed on storage (decreased to 10% within 6 days after recording). The reason for decrease in DE is due to the diffusion of monomers from destructive interference region to constructive interference region and instability of the leuco state of the dye [137]. So for stabilizing the gratings, the concentration of the dye was reduced. For stabilizing grating, incorporation of crosslinkers are reported [102] as one of the method and therefore, crosslinkers were
tried. In another approach to stabilize the grating, UV exposure was employed. When the photopolymer film was used for application, it must be protected from external contaminants and therefore, sealants must be used and the sealants used will not affect the properties of the film. Experiments were done for optimizing the sealant used. The molecular weight of the polymer binder has influence on the diffraction efficiency [138] of the photopolymer film and therefore, the effect of molecular weight of poly (vinyl alcohol) on the diffraction efficiency was also studied.

1.11 Conclusions

An introduction to photopolymers and different mechanisms used in the applications are discussed. The application of the photopolymer technology in various fields especially in the field of holography was presented. A brief description about different types of hologram recording materials was given and a brief review of photopolymers as hologram recording media was also presented.

References


Introduction


Introduction

