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INVESTIGATION OF TEMPERATURE RESPONSE OF PHOTOPOLYMER MATERIAL USED FOR HOLOGRAPHIC SENSOR

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Abstract—Recently, functionalised photopolymer has emerged as a versatile recording material in the field of optical holography due to its novel characteristics and potential use in the development of holographic based sensors, and optical elements. This work describes the temperature response of a newly developed photopolymer, containing of a monomer N-isopropylacrylamide (NIPA) which under photopolymerisation forms a temperature sensitive polymer - Poly(N-isopropylacrylamide) (PNIPA). The photonic sensor was developed by holographic recording of volume phase transmission gratings in a self-processing NIPA-based polymer with a 532 nm laser beam. A 633 nm probe beam was used to monitor real time diffraction efficiency (DE) growth curve and the temperature dependent response of DE in the temperature range 22-50 $^{\circ}$C. It was observed that the DE increased with increasing temperature at 10 $^{\circ}$C min^{-1} and started to drop by reversing the temperature at 5 $^{\circ}$C min^{-1}. It was also observed that the response depends on the rate of heating/cooling and the time spent at elevated temperature. The observed response to temperature could be used to design an indicator for packaging, showing that the content of the package has been exposed to a temperature that was above a predetermined temperature limit.

Key Words: Holographic sensor, Photopolymer, Volume phase transmission gratings

I. INTRODUCTION

In optical holography photopolymers are some of the most commonly used recording media. In recent years the research interest in photopolymers for holography has grown due to their strong potential to be used in the development of holographic sensors. Compared to other recording materials, photopolymers are considered as attractive materials for fabrication of holographic sensors due to their ability to be functionalised, large dynamic range, higher sensitivity, self-processing nature and relatively low production cost. Photopolymers have been intensively studied materials due to possible practical applications in holographic data storage, holographic optical elements, and holographic sensors. [1-7].

Among the various applications, holographic sensor is a relatively recent application of photopolymer materials. Holographic sensors are functionalised photonic structures which are developed by holographic recording [7-9]. In its simplest form the holographic sensor is a holographic diffraction grating embedded in the photopolymer material, which has all the necessary features to work as a sensor. The sensor can change its properties, such as diffraction efficiency (DE) or spectral response, upon the interaction with a target analyte. Their ability to display visual information in the presence of some stimulus (physical or chemical) is what makes holographic sensors suitable for applications ranging from medical diagnostics to environmental sensing and security. Holographic sensors have some advantages over the other sensors including feasibility for large scale production, lightweight, and possibility to be multiplexed and miniaturised [7].

N-isopropylacrylamide (NIPA)-based photopolymer has recently been developed and optimised for holographic recording both in the transmission and reflection modes [10]. The main approach used in the development of this photopolymer is the introduction of low toxicity and temperature sensitive monomer NIPA instead of acrylamide, which is often used [5-6, 11-12]. This newly developed polymer has a good recording capability and greater sensitivity to temperature. The temperature sensitivity of PNIPA is due to its phase transition that occurs at a critical temperature. PNIPA has a lower critical solution temperature (LCST) at ~32 $^{\circ}$C . The LCST can be varied by the copolymerisation with other appropriate monomers. It is expected that the copolymerisation may lead to a change in the optical response and to enhanced sensitivity of the devices.

In this work, the temperature dependent response of a newly developed photopolymer, containing a temperature sensitive monomer NIPA, has been described. This work will help to understand the temperature response of a NIPA-based optical sensor for practical applications, such as material packaging and security.

II. THEORETICAL BACKGROUND

Based on the recording geometry there are two types of holographic gratings - transmission and reflection, both can work as a sensor. Transmission grating is recorded when both the recording beams approach the photosensitive medium from the same side, while reflection grating is recorded when both the beams approach the photosensitive medium from the two opposite sides. Here, un-slanted transmission gratings are produced by placing the photosensitive medium in the region of overlapping of two coherent recording beams, such that the wave vectors of the beams are making opposite and equal angles with the surface normal of the medium. The spatial frequency of the transmission holographic grating is determined by the angle between the two recording beams and is given by:

$$2\Lambda\sin\theta = \lambda \qquad (1)$$

Where Λ is the fringe spacing and is $\Lambda = 1/F$ (here F is spatial frequency), θ is the Bragg angle and λ is the wavelength of recording beams.

A. Mechanism of holographic grating formation in photopolymer

When the photopolymer layer is exposed to an interference pattern generated by recording beams having suitable wavelength, a polymerisation process is started in the illuminated areas where monomer molecules form polymer chains leading to change in molecular polarisability and density. The photopolymerisation is accompanied by diffusion processes. Due to the generated concentration gradient, monomers will diffuse from dark to bright fringe regions and short/mobile polymer chains will diffuse in opposite direction. Holographic recording in photopolymers leads to a spatial variation of the refractive index of the material due to photopolymerisation and diffusion of photopolymer components. A volume phase grating is recorded by means of a spatial variation of the refractive index and/or thickness, as shown in Fig.1.
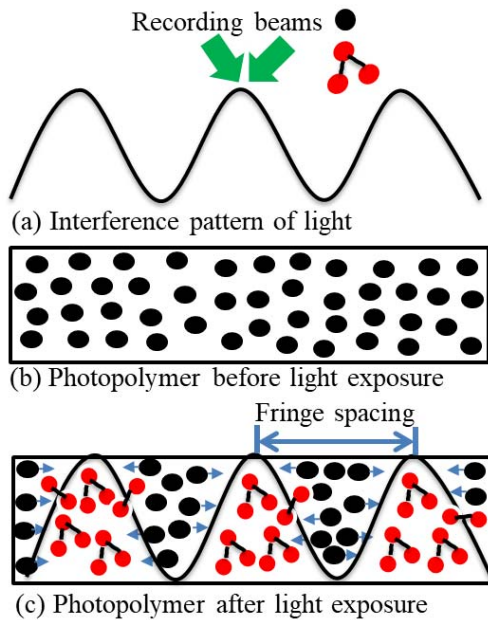

Figure 1. Schematic diagram of holographic grating recording process in photopolymer.

B. Principle of operation of a holographic sensors

The working principle of a holographic sensor is shown in Fig. 2. All holographic sensors utilise the same optical phenomena which is independent of analyte which the sensor detects. In order to use the response of hologram for the development of the sensor, it is very important to understand how the response is produced. When the analyte sensitive polymer layer (in which the grating is recorded) is exposed to the analyte, changes in the fringe spacing and the refractive index modulation of the photonic structure occur. The sensor signal is received as change in DE, Bragg angle and peak wavelength (if probed with broad spectral range source).
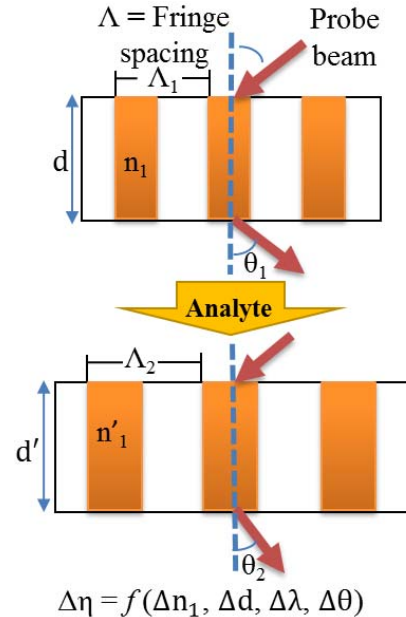

Figure 2. A diagrammatic view of the operation principle of sensor based on holographic transmission grating.

C. Characterisation of a holographic sensor

The gratings that are recorded can be either entitled as thick (volume) or thin (plain) gratings. One can easily use the value of Q-factor in order to categorise them into thick or thin. For the holographic gratings which have Q>10 are considered as thick gratings while those having Q<1 are considered as thin gratings. When 1<Q<10 the regime is intermediate and you may have one or the other depending on the refractive index modulation. For the volume phase grating regime the value of Q-factor corresponding to Q>10 is given as [13]:

$$Q = 2\pi\lambda d/n_0\Lambda^2 \qquad (2)$$

Where λ is the recording beam wavelength, d is the thickness of the polymer layer, n_0 is the average refractive index of the photosensitive medium and Λ is the fringe spacing (grating period).

In the present research work the value of Q-factor was calculated for the recorded transmission gratings with a spatial frequency of 830 lines/mm and the thickness of the polymer layer used 80 ± 5 μm. Hence, the value of Q-factor obtained is in the range of 115 to 130, which clearly justifies the application of coupled wave theory [14] for the calculation of DE which is given by:

$$\eta = \sin^2(\pi n_1 d/\lambda\cos\theta) \qquad (3)$$

Here η is the DE, n_1 is refractive index modulation, d is the thickness of the grating, λ is the probe (reconstructing) beam wavelength, θ is the Bragg angle inside the polymer layer.

When the transmission grating is exposed to an analyte, this will change the DE ($\Delta\eta$) caused by the effect of different parameters which is obtained by differentiation of equation (3) and is given by [7]:

Proceedings of 2018 15th International Bhurban Conference on Applied Sciences & Technology (IBCAST)
Islamabad, Pakistan, 9th – 13th January, 2018

23

$$\Delta\eta/\eta = \left|2\pi n_1 d/\tan(\pi n_1 d/\lambda\cos\theta)\lambda\cos\theta\right|(\Delta n_1/n_1 + \Delta d/d - \Delta\lambda/\lambda + \tan\theta \, \Delta\theta) \qquad (4)$$

Where Δn_1 represents the refractive index modulation change, Δd is the change in thickness of the layer, $\Delta\lambda$ is the variation in wavelength of probe beam and $\Delta\theta$ is the shift in Bragg angle. In the present work, the probe wavelength and the probe beam angle are kept constant, thus only the first two parameters – refractive index modulation and thickness influence the DE change.

III. METHODS AND MATERIALS

A. Photopolymer solution preparation

Photopolymer composition previously [10] optimised for holographic recording was used in this study. The chemical components are given in Table I. The chemicals were purchased from Fisher Scientific and Sigma Aldrich and used without any further purification.

TABLE I. THE AMOUNT OF CHEMICAL COMPONENTS USED IN PREPARATION OF PHOTOPOLYMER SOLUTION

Components	Molar Concentration in polymer solution
(N-Isopropylacrylamide), NIPA	0.097 M
(N,N'Methylenebisacrylamide), BA	0.053 M
(Polyvinyl alcohol 10 %w/v), PVA	8.79 %w/v
(N-Phenylglycine), NPG	0.0145 M
(Erythrosine B dye 0.11 %w/v), Er B	1.37×10^{-4} M
Glycerol	0.15 M

To obtain a 10 %w/v PVA stock solution, 10 g of polyvinyl alcohol (molecular weight 9,000-10,000, 80 % hydrolysed) was dissolved in 100 ml deionised water using a magnetic stirring and heated in open ambient laboratory conditions at 75 °C. Similarly, 0.11 g of Erythrosine B was dissolved in 100 ml deionised water at room temperature by magnetic stirring to obtain a dye solution of the desired concentration (0.11 % w/v).

For the preparation of photopolymer solution the optimised amount of all the components as given in [10], were mixed thoroughly with magnetic stirrer for 2 hours at ambient laboratory conditions (temperature 24±0.5 °C and relative humidity (RH) 38 %).

B. Photopolymer layer preparation

Photopolymer layers for holographic recording were prepared using 1.5 ml of the solution which was evenly spread over on the microscopic glass slide of dimensions 7.6 cm x 2.6 cm. The slides with the polymer layer were placed on a levelled surface and allowed to dry in the dark room for 18 hours at the 38% RH and 24±0.5 °C.

C. Holographic recording

As shown in Fig. 3, a photonic structure was created by holographic recording of an un-slanted volume phase transmission gratings with spatial frequency of 830 lines/mm in the NIPA based photopolymer. The two recording beams were obtained by splitting the laser light from a 532 nm Nd:YVO$_4$ laser by a polarising beam splitter. The polarisation of the transmitted beam was rotated with the help of a half-wave-plate in order to ensure that the two recording beams were s-polarised, thus providing conditions for maximum visibility of the recorded interference fringes. The sample was mounted on a computer controlled rotational stage (Newport ESP300) and recorded for 100 s with total recording intensity 3.8 mW/cm^2. The optimum intensity was previously determined by studying the intensity dependence of the DE [10]. A 633 nm He-Ne laser was used as a probe beam to monitor a real time growth curve of the DE given in Fig. 4(a). The Bragg selectivity curve measurement was performed by monitoring the diffracted beam intensity with an optical power meter (Newport Model 840) while the sample was rotated. After recording, the gratings were bleached with ultraviolet (UV) light for 100 s using a UV exposure intensity 60 mW/cm^2 provided by Dymax UV-curing system (model ECE-200) to polymerise remaining monomers. In this experiment, DE was calculated as the ratio of the diffracted beam intensity (I_d) and the incident beam intensity (I_i). Fig. 4(b) shows Bragg selectivity curves of the diffracted beam acquired through LabVIEW software before and after the UV-curing. Only a small decrease of the DE was observed after UV post-recording curing. This indicates that the recorded grating is mainly due to density changes caused by concentration gradient driven monomer diffusion which occurs during the holographic recording process.
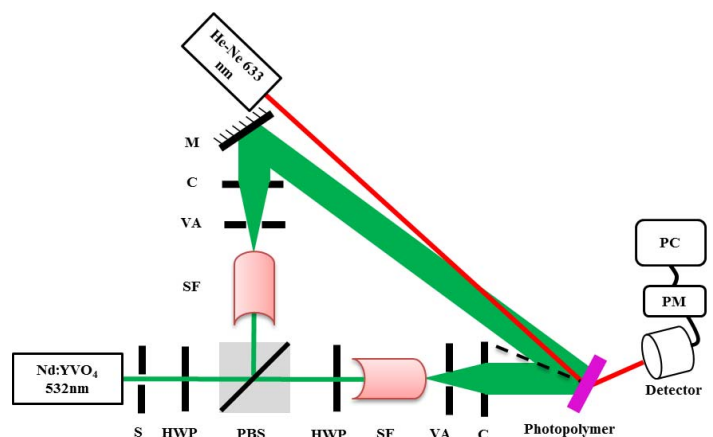

Figure 3. Experimental setup used for the recording of transmission holographic gratings. S-electronic shutter, HWP-half wave plate, PBS-polarising beam splitter, SF-spatial filter, VA-variable aperture, C-collimator, M-mirror, PM-power meter, PC-computer.
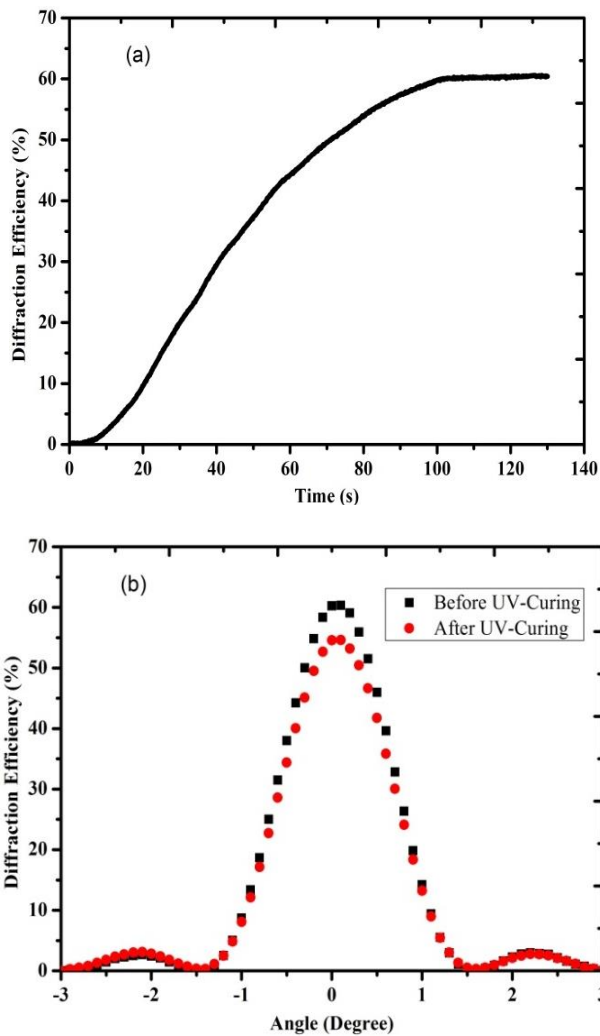
Proceedings of 2018 15th International Bhurban Conference on Applied Sciences & Technology (IBCAST)
Islamabad, Pakistan, 9th – 13th January, 2018

24

Figure 4. Characterisation of the holographic diffraction grating. (a) Real time growth curve of DE; (b) Bragg selectivity curve of DE for the photopolymer

D. Temperature response

The temperature response study of the developed photonic structure was carried out by exposing the structure to temperature in the range of 22 ^{o}C to 50 ^{o}C, and by monitoring the DE. The experimental setup used for measurement is shown in Fig. 5. The sample was placed on the temperature controlled stage (Linkam Model THMS600) and the lid of the cell was tightly closed. The temperature was controlled in the required range using a temperature controller (Linkam Model TMS 93). Initially, temperature of the stage was increased from 22 ^{o}C to 50 ^{o}C. Then cool air was pumped into the stage with a cooling pump (Linkam Model LNP) to decrease the temperature back to 22 ^{o}C to study reversibility of the structure. A dewar flask filled with ice was used to produce the cool air which was needed to decrease the stage temperature to 22 ^{o}C. During the temperature exposure, the changes in the intensity of the first order diffracted beam (I_1) and intensity of the transmitted beam (I_0) were monitored simultaneously by two optical power meters (Newport Model 840). The DE in this experiment was defined by $I_1/(I_1+ I_0)$.
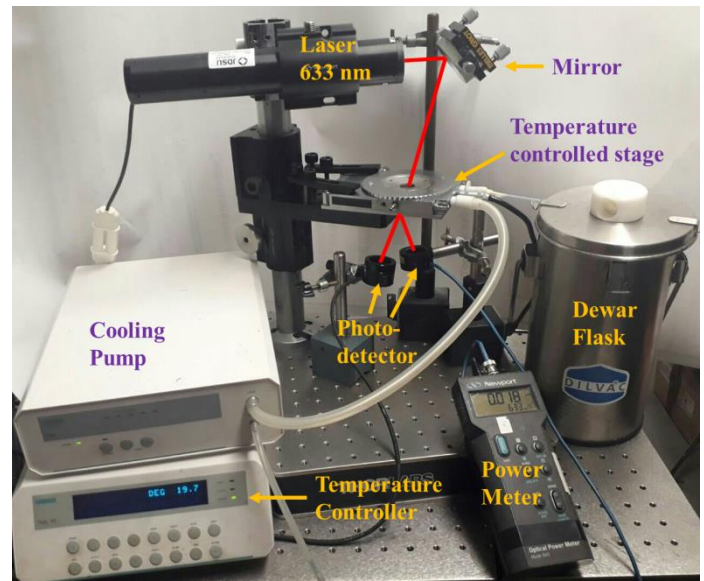

Figure 5. Experimental setup used for checking temperature response of recorded gratings.

IV.   RESULTS AND DISCUSSION

A.   Investigation of the dependence of temperature response on the rate of temperature change

1.   Slow rate of temperature change

Fig. 6 shows the temperature dependent response of the developed NIPA based photonics structure in the temperature range of 22 ^{o}C to 50 ^{o}C, with increasing temperature at rate of 5 ^{o}C min^{-1} in the forward direction and at a decreasing rate of 1 ^{o}C min^{-1} in the reversed direction. Clearly, the DE increases at temperatures below 35 ^{o}C and decreases above 35 ^{o}C. This behavior of the DE with the increasing temperature can be explained by the switching from hydrophilic to hydrophobic character of the photopolymer layer when the temperature changes from below LCST to above LCST. The LCST of pure PNIPA is at 32 ^{o}C, and the change was observed close to this temperature. Below 32 ^{o}C photopolymer layer has a hydrophilic character and as the temperature increases the layer absorbs water molecules from air and this causes a swelling of the layer. Increase of the refractive index modulation due to different absorption of the water in the bright and dark fringe areas is also possible. At temperature above 35 ^{o}C a decrease in the DE is observed and this must be related to the hydrophobic character of PNIPA above LCST. Water molecules are expelled from the PNIPA rich areas and this causes shrinkage and decreases the refractive index modulation which leads to a decrease in the DE [10]. In this experiment the temperature of the stage was decreased immediately after reaching 50 ^{o}C.

With decrease in temperature in the reversed direction the DE is still decreasing until reaching 35 ^{o}C. After that the DE remains almost unchanged. The normalised DE was defined as the ratio of the DE at the current temperature and the DE at the start of the experiment at 22 ^{o}C.
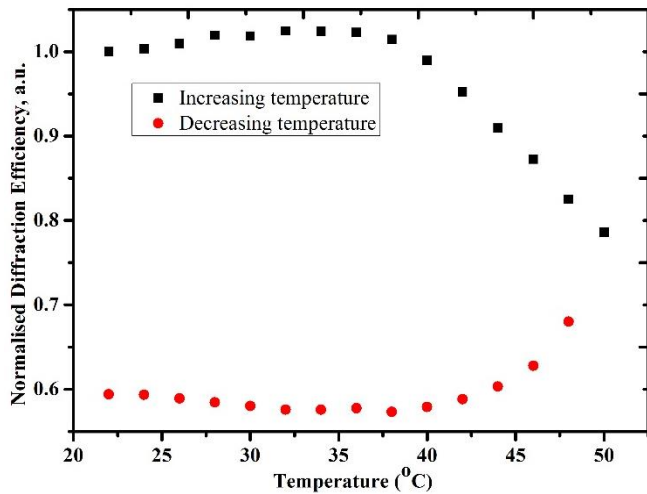
Proceedings of 2018 15th International Bhurban Conference on Applied Sciences & Technology (IBCAST)
Islamabad, Pakistan, 9th – 13th January, 2018

25

Figure 6. Normalised DE Vs Temp, temperature increased at rate 5 ^{o}C min^{-1} and decreased at rate of 1 ^{o}C min^{-1}.

Fig 8. Normalised DE Vs Temp, temperature increased at rate 10 ^{o}C min^{-1} and decreased at rate of 5 ^{o}C min^{-1}. Temperature of the stage was kept at 50 ^{o}C for 10min.

2. Fast rate of temperature change

The temperature response was also monitored at a faster rate of 10 ^{o}C min^{-1} in the forward half cycle followed by the next half cycle in the reversed direction with a decreasing temperature rate of 5 ^{o}C min^{-1}. The DE response is displayed in Fig. 7. In this case it is expected that the polymer is only in the hydrophilic state as it does not achieve the LCST of PNIPA quickly enough until it reaches to a temperature above 45 ^{o}C. At these temperatures DE continuously increases probably due to water molecules absorbed by the polymer. Above 45 ^{o}C, the polymer achieves LCST and DE reaches saturation. The temperature of the stage was decreased immediately after reaching 50 ^{o}C. During the reversed half cycle from 50-22 ^{o}C, DE is still decreasing. DE is decreasing possibly due to the fact that the actual polymer temperature is still above LCST of the PNIPA, due to which it continues to expel water molecules. In order to check this hypothesis the layer was left at 50 ^{o}C for longer amount of time. Fig. 8 shows the measured DE when the layer was left for 10 min at 50 ^{o}C.

B. Effect of exposure time at elevated temperature

The effect of elevated temperature on the DE of gratings for different exposure time was studied by exposing the photonic structure to 50 ^{o}C. The dependence of normalised DE on exposure time at 50 ^{o}C is shown in Fig. 9. The temperature controller was used to keep the samples temperature constant while varying the exposure time in the range of 1-10min. Clearly, for a constant exposure temperature 50 ^{o}C, the rate of decrease of DE is different and seems approaching to saturation for a longer exposure time of 10 min. As shown in Fig. 10, it was also observed that the irreversibility of the temperature induced changes depend on duration of the time spent at temperature above the LCST of the PNIPA. The irreversible changes in the DE were observed by exposing the structure to elevated temperature for the duration 1-10 min.

Figure 7. Normalised DE Vs Temp, temperature increased at rate 10 ^{o}C min^{-1} and decreased at rate of 5 ^{o}C min^{-1}. Temperature of the stage was decreased immediately after reaching 50 ^{o}C.
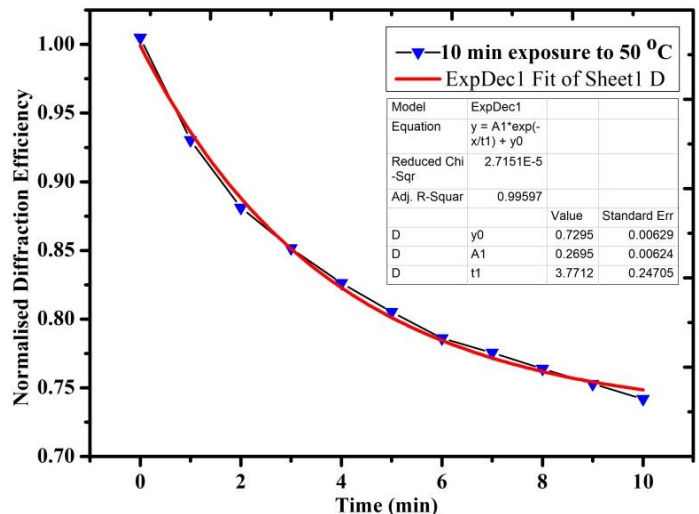

Figure 9. Normalised DE Vs exposure time at 50 ^{o}C.

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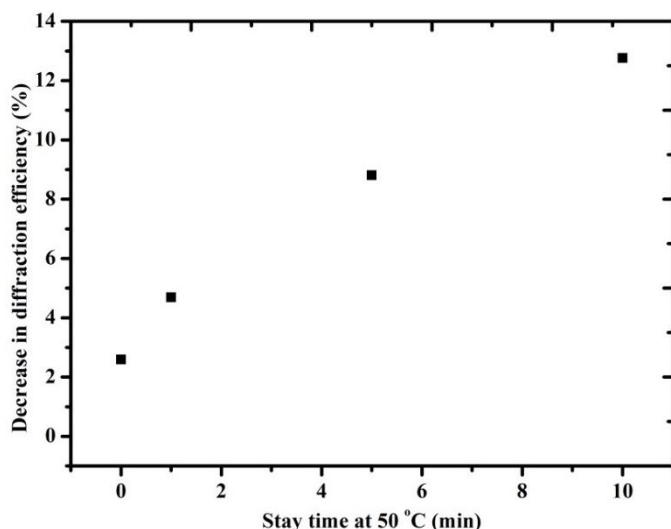Islamabad, Pakistan, 9th – 13th January, 2018

26

Figure 10. Irreversible decrease in DE (measured at 22 °C before and after exposure to 50 °C) Vs time spent at 50 °C

V. CONCLUSION

The temperature sensitivity of the un-slanted transmission phase holographic gratings recorded in NIPA-based photopolymer was studied. The DE of the holographic gratings are highly temperature dependent. The variation in DE depends upon the rate of temperature variation and the time spent at temperature above the LCST. The temperature response of the holographic transmission gratings can be used for the development of holographic temperature sensors operating in the temperature range from 22 °C to 50 °C.

VI. ACKNOWLEDGMENT

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Proceedings of 2018 15th International Bhurban Conference on Applied Sciences & Technology (IBCAST)
Islamabad, Pakistan, 9th – 13th January, 2018

27