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Photoinduced surface relief studies in an acrylamide-based photopolymer

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Abstract: Surface relief gratings (SRGs) have been optically recorded in a dry, self-developing acrylamide-based photopolymer. An investigation of the dependence of photoinduced surface relief amplitude and profile on recording intensity, UV post-exposure, thickness of the sample, composition of the photopolymer and temperature at constant spatial frequency was carried out using white light interferometry. Non-sinusoidal surface relief grating profiles which depend on sample thickness were observed at low spatial frequency. The surface relief effect is intended to be applied to the alignment of liquid crystals (LCs) for different applications such as voltage controllable diffraction gratings, lenses, polarizing components and switches.

1. Introduction

Photopolymers are of considerable interest for the development of holographic applications because of their unique property of self-development when exposed to light patterns. Photoinduced surface relief gratings in a photopolymer are attractive for their applications in diffractive optical elements [1, 2], optical data storage [3], recording computer generated holograms [4] and the alignment of liquid crystals [5–8]. There has been extensive growth of technological applications of liquid crystals, such as photonic components and liquid crystal displays (LCDs) in the last two decades. To fabricate these devices, uniform alignment of the liquid crystals is essential. Recently, for the alignment of liquid crystals non-rubbing techniques have been investigated to avoid the creation of static electricity and dust which are not desirable. The other promising material for the fabrication of electro-optical liquid crystal devices and their potential applications in optical communications and displays are holographic polymer dispersed liquid crystals (HPDLCs) [9–12].

When the photosensitive material is exposed to an interference pattern of light of suitable wavelength, a surface relief grating that is variation of the thickness of photosensitive material is produced. This effect is often called surface relief amplitudemodulation. Light-induced SRGs in a photopolymer have the potential to align LCs [5–8]. So, it is important to investigate the mechanism of the formation of surface relief gratings depending on recording parameters and physical parameters. These photoinduced surface relief gratings are scanned with a white light interferometer [13, 14] after recording. White light interferometry is an extremely powerful technique for surface profile measurement. This technique is based on the principle that interference fringes can only be obtained when the optical path difference is less than the coherence length of the light source. It has significant advantages in measuring surface profiles as the measurement is non-contact with very high vertical resolution. An investigation of the photoinduced

surface relief modulation in thin and thick layers of an acrylamide-based photopolymer system [15, 16], developed at the Centre for Industrial and Engineering Optics, Dublin Institute of Technology, was reported earlier [17, 18]. The resolution of the material was improved to enable reflection holograms to be recorded. Surface relief gratings can only be made at low spatial frequencies. However, it is anticipated that liquid crystal devices may be fabricated by exploiting the effect even at quite low spatial frequency (~100 lines mm−1). The main goal of this paper is to report the dependence of surface relief amplitude modulation on recording parameters such as intensity and uniform UV post-exposure, and on physical parameters. Parameters such as thickness of the layer, composition of photopolymer and the effect of heating the grating to a preset temperature were investigated.

2. Theory

The acrylamide-based photopolymer is a self-developing dry layer. The composition of the photopolymer layer generally consists of monomers, electron donor or initiator, photosensitizer and a polymer binder acting like a matrix in which to suspend the other components. Optical recording in this material is based on photopolymerization reactions caused at the areas illuminated by light. The dry photopolymer layer is illuminated with an interference pattern of monochromatic light with an appropriate wavelength. The photosensitizer absorbs a photon and reacts with an electron donor to generate a free radical. This free radical in the presence of monomer initiates the polymerization process. Due to polymerization there is a change in the density and the molecular polarizability, which in turn changes the local photopolymer refractive index, and a grating is recorded. There are different theoretical models explaining the formation of holograms in photopolymer material [19, 20] due to mass transport from dark to bright regions. From the diffusion studies of acrylamide-based photopolymer [21] it was observed that the mass transport from dark to bright regions is faster than in other photopolymer systems [22, 23].

There are two main models describing the surface relief formation in photopolymers. The first explains the relief formation by shrinkage of the photopolymer depending on the intensity of light. This model is applicable to systems where the peaks of the surface relief appear in the non-illuminated areas [24]. The second model is based on the assumption that redistribution of system components by diffusion is responsible for the relief formation, and suits systems such as ours where experimental observation shows the surface relief peaks appearing in the illuminated areas [1, 2, 15, 16].

The dependence of surface relief gratings on spatial frequency of recording and exposure was previously investigated in thin (2–7 μm) and thick (50–250 μm) photopolymer layers [9, 10]. It was observed that as the spatial frequency increases the surface relief amplitude modulation decreases at constant exposure conditions. From these experiments, it was found that when the design of electro-optical devices is considered it is best to work at 100 lines mm−1, as at higher spatial frequency the surface relief amplitude modulation is very low.

From the dependence of surface relief amplitude modulation on exposure, it was observed that there is an optimum exposure to obtain maximum surface relief amplitude modulation at constant intensity. One possible explanation of this observation is that it could be due to gelification in the polymerization region which decreases the diffusion of monomer.

3. Experimental

3.1. Sample preparation

The material used here is a self-developing acrylamide-based water-soluble photopolymer. The general composition of this material is acrylamide, *N*,*N*_-methylene-bisacrylamide monomers, triethanolamine initiator, polyvinyl alcohol binderand Erythrosin B sensitizing dye [9, 10]. The above components were mixed well by using a magnetic stirrer andthe dye was added finally. Good optical quality layers were prepared by the gravity-settling method. For gravity-settled samples, the photopolymer solution was diluted with deionized water and then spread on a 5×5 cm2 glass plate. The thickness of the sample depended on the amount of the solution spread on the glass plate. The samples were allowed to dry for 18–24 h. By making a cut on the samples, their thickness was measured using the white light interferometer.

3.2. Experimental method

Surface relief gratings were optically recorded in dry, self-developing acrylamide-based photopolymer at different spatial frequencies. Two different optical recording systems were used to record surface relief gratings of spatial frequencies of 10 and 100 lines mm^{-1}.

The optical set-up used to record surface relief transmission diffraction gratings at 10 lines mm^{-1} is a Michelson interferometer. The spatial frequency is adjusted by rotating one of the mirrors shown in figure 1.

A two-arm holographic optical set-up which is shown in figure 2 was used to record surface relief gratings at 100 lines mm^{-1} spatial frequency. A laser with λ = 532 nm was used to record the transmission diffraction gratings.

The spatial frequency was calculated by using the Bragg equation

$$2\Lambda \sin\theta = \lambda$$

where Λ– fringe spacing, 2θ = inter-beam angle and λ = probe beam wavelength.

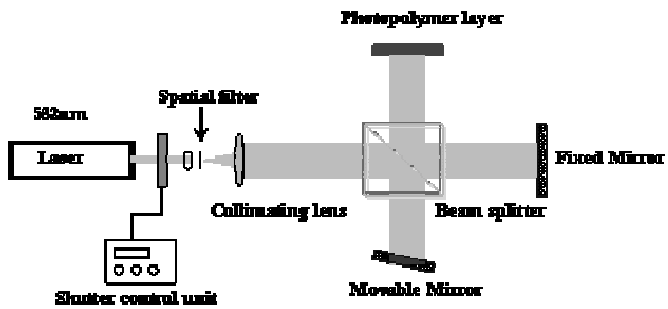

Figure 1 Experimental set up to record low spatial frequency patterns

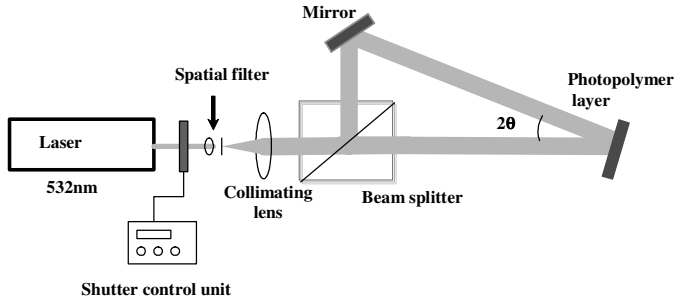

Figure 2 Experimental set up to record high spatial frequency patterns

The surface relief gratings were recorded on photopolymer samples of different thickness at different recording intensities and spatial frequencies. These samples were scanned typically an hour after recording using a white light interferometer **MicroXAM S/N 8038**. This has a vertical resolution of 1 nm and vertical scanning range of 100 μm.

4. Results and discussion

4.1. Effect of recording parameters on surface relief modulation

4.1.1. Dependence on intensity and exposure.

The dependence of the amplitude modulation of the surface relief gratings on the intensity of recording is shown in figure 3. Layers of thickness 17 μm were illuminated by different intensities at a spatial frequency of 100 lines mm−1. At this spatial frequency, the effect observed in layers with such thickness was different from those seen in very thin (below 7 μm) and thick photopolymer layers (above 50 μm) [6, 7]. In layers of 2.5 μm thickness it was observed that with increase in the recording intensity, the surface relief amplitude modulation increased. In thick layers of above 50 μm, it was observed that there is no dependence of surface relief amplitude modulation on the recording intensity.

Intensities of 5, 10 and 20 mW cm−2 were used. It is seen from figure 3 that at constant intensity with increase in exposure time, the surface relief amplitude modulation increases. It is observed that there is not much difference in surface relief amplitude modulation for intensities 5 and 10 mW cm−2 with increase in exposure time. When the intensity was increased to 20 mW cm−2, the observed surface relief modulation was smaller. So it is concluded that 10 mW cm−2 is the maximum useful intensity. The reason for higher surface relief amplitude modulations at lower intensities could be that fewer photons per unit time are absorbed by the photopolymer layer and so the polymerization process is slower in the illuminated regions. The monomer molecules which diffuse into bright regions have more time to diffuse, which increases the surface relief amplitude modulation. Therefore one would observe higher surface relief amplitude modulation at low intensity. As the intensity increases the number of photons absorbed by the photosensitive layer will be higher and so the polymerization process will be faster. When polymerization is fast, the rate of consumption of diffused monomer is higher, which should increase the surface relief amplitude modulation. However, at

higher intensities it is likely that shorter polymer chains are formed. These could diffuse out of the illuminated regions more easily, resulting in a decrease in the surface relief amplitude modulation. Diffusion of short polymer chains at high intensities of recording from bright regions to dark region was also observed in volume gratings recorded in the same material [25].

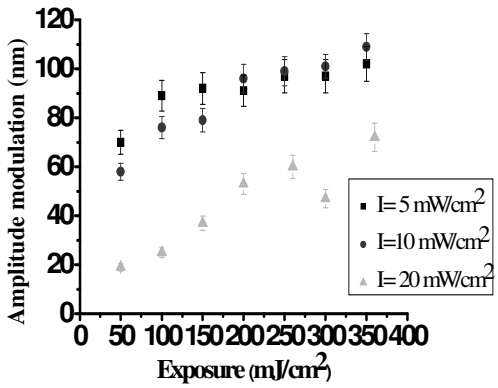

Figure3 Dependence of surface relief amplitude on the intensity of recording in the samples of thickness 17µm at spatial frequency 100 lines/mm.

4.1.2. Dependence on uniform UV post-exposure. The influence of uniform UV post-exposure is shown in figure 4. Similar dependence was observed in thicker layers (50 µm) and thin layers (2.5 µm). After recording a surface relief grating on the photopolymer layer of thickness 17 µm at intensity 10 mW cm−2 and spatial frequency 100 lines mm−1, the sample was exposed to uniform UV intensity of 16 W for 45 min and then the amplitude modulation was measured after a further 30 min. It was observed that after post-exposure with UV light there was an average 30% increase in the amplitude modulation. It was previously observed that the surface relief peaks appear in the bright regions of the interference pattern. This was experimentally observed by using a Dektak profilometer [9, 10]. When exposed to uniform UV light intensity, there will be no effect in the bright region as the monomer is already polymerized, but the unconsumed monomer in dark regions polymerizes. Monomer absorbs in the UV region so polymerization proceeds even if it does not contain dye for photopolymerization. The photosensitizer, erythrosin B, also absorbs in the UV region and so polymerization is possible with dye presence as well. The increase in surface relief amplitude modulation with uniform UV post-exposure could be due to shrinkage upon photopolymerization in dark regions.

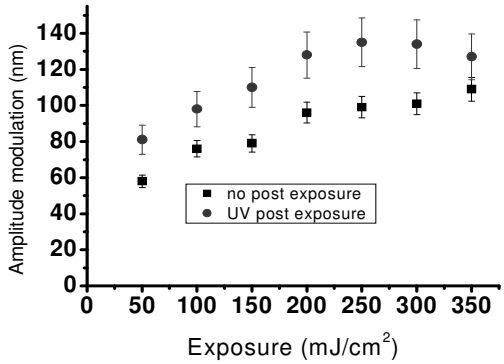

Figure. 4 Dependence of surface relief amplitude on uniform UV post exposure in the layers of thickness 17μm at spatial frequency 100 lines/mm.

4.2. Effect of physical characteristics of the photopolymer layer on surface relief

4.2.1. Dependence on the thickness of sample. Figure 5 shows the surface relief over a range of different thicknesses.

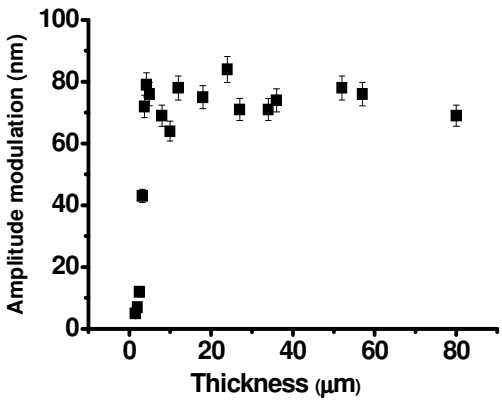

Figure 5 Dependence of surface relief amplitude on the thickness of the layers at spatial frequency 100 lines/mm and constant exposure.

These samples were exposed at 5 mW cm−2 intensity for 40 s. As has already been shown in figure 3, at 10 mWcm−2, the surface relief amplitude modulation is not much different than the one at 5 mW cm−2. The spatial frequency of recording was 100 lines mm−1. Above 15 μm thicknesses there is not much change in the amplitude modulation. The observed thickness dependence could be explained as follows. When the sample is exposed to a light pattern, polymerization starts in bright regions. As monomer diffuses into the polymerization region from dark regions, this increases the surface relief amplitude modulation. One possible reason for the existence of a strong thickness dependence below 15 μm could be the existence of interaction forces acting between the substrate and the photopolymer layer [2, 9] to oppose the diffusion of the monomer, and this effect would be more pronounced when the layers are thinner. When the sample is

thick enough the diffusion-assisted surface relief formation which takes place closer to the photopolymer surface would not be influenced by the substrate and would proceed normally.

Another possible explanation of the thickness dependence of the photoinduced surface relief could be that the polymerized area extends through the depth of the layer. In thicker layers the amount of diffusing material would be higher and a simple proportionality between the amplitude modulation and the layer thickness could be expected. Indeed thicker layers produce a greater surface relief amplitude modulation. Above a certain thickness of the sample there is not much additional increase in the surface relief amplitude modulation, possibly due to the inability of the surface to deform further due to increased surface tension upon polymerization. As the influence of the surface tension increases with the increase in the spatial frequency, one should observe that the surface relief amplitude modulation reaches saturation at smaller thickness of the layers when recording at high spatial frequency than the thickness at which the surface relief amplitude modulation reaches saturation at low spatial frequencies. Such dependence of the thickness of the layer at which the saturation occurs on the spatial frequency of recording was observed earlier [9].

The existence of a plateau in the surface relief modulation could also be explained as follows. When the thickness of the layer increases, there will be more monomer to diffuse into the bright region contributing to an increase in the surface relief amplitude modulation as shown in figure 6, but polymerization in bright regions causes the material to become more viscous, inhibiting diffusion of the monomer.

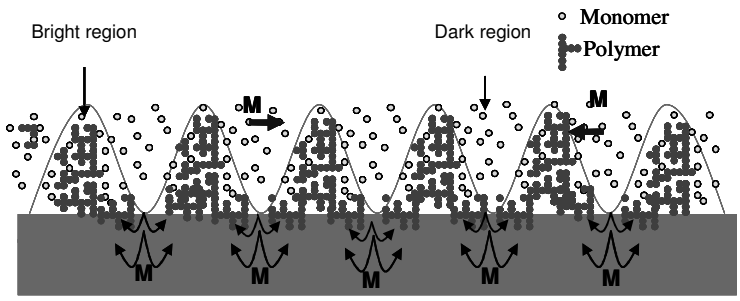

Figure 6 Recording mechanism

An increase of the surface relief amplitude modulation with layer thickness up to a maximum was also observed at 10 lines mm−1. However, unusual surface relief profiles (splitting of the peak into two) were observed at 10 lines mm−1 but not at 100 lines mm−1. Experiments were carried out to study this surface relief effect at low spatial frequencies. Samples of different thickness were prepared and exposed to an interference pattern of intensity 10 mW cm−2. Figure 7 shows experimentally observed surface relief grating profiles, recorded at 10 lines mm−1. It is observed that splitting is pronounced in layers of thickness 17 μm as if there is a change in the spatial frequency of recording. It is observed that the surface relief amplitude modulation also decreased along with splitting.

It is also observed that the splitting depends on the thickness and exposure time. The splitting effect is observed after 5 s of exposure in layers of thickness 4.5 and 17 μm.

This could be due to generation of higher-order diffracted beams. In 17 μm thick layers the splitting is greater and the intensity of the second-order beams is higher. These are preliminary experimental observations and more detailed investigations will be carried out.

4.2.2. Dependence on the chemical composition of photopolymer layer. In order to increase the surface relief amplitude modulation the effect of the chemical composition was studied. In the composition of photopolymer, triethanolamine (TEA) is an electron donor (coinitiator), which plays an important role in the generation of the free radicals. It also acts as a plasticizer, which favours the solution and stability of other components in the matrix, which in turn influences the performance of the material. High concentration of TEA produces stable layers without precipitation of monomer on the surface. Experiments were carried out to study the dependence of the surface relief amplitude modulation on the chemical composition of the photopolymer material by changing the concentration of TEA. Three different stock solutions (TEA1, TEA2 and TEA3) of photopolymer were prepared containing 1.5, 2 and 2.5 ml TEA respectively, and used in the normal photopolymer composition [17]. The typical thickness of TEA1 was 15 ± 3 μm, TEA2 was 17 ± 3 μm and TEA3 was 19 ± 3 μm. The thickness and optical quality of the layer were repeatable. These samples, after drying, were exposed to an interference pattern of intensity 10 mW cm−2 for 35 s at 100 lines mm−1 spatial frequency.

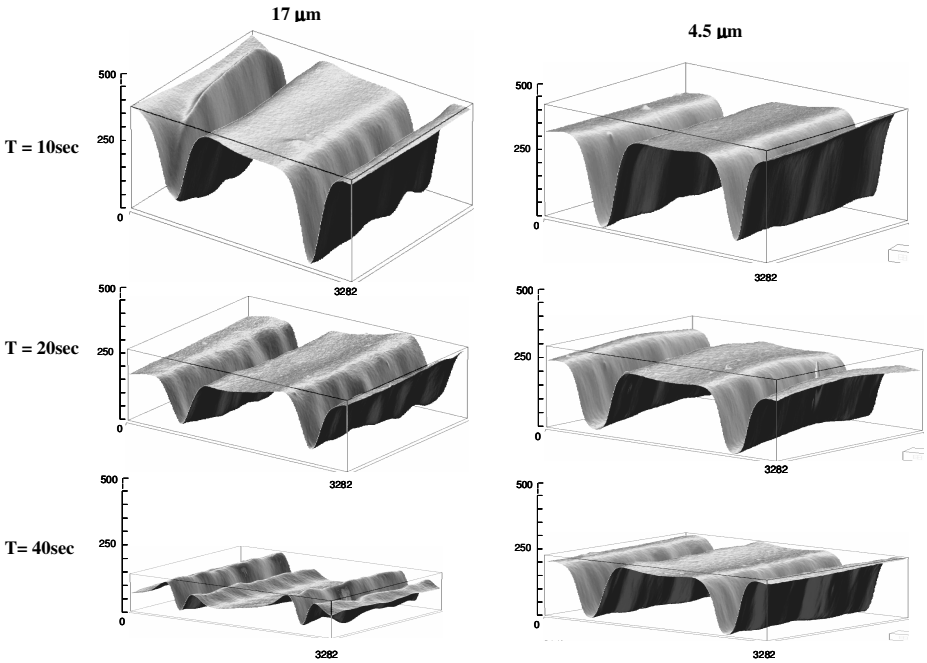

Figure 7: Surface relief gratings at 10 lines/mm in layers of different thickness.

From figure 8 it is observed that an increase in TEA concentration decreases the surface relief amplitude modulation. Even at the lowest TEA concentration there are enough TEA molecules for the given concentration of dye molecules (2.6 mM) to generate free radicals. A 2.6 mM concentration of dye molecules contains 6.16×10^{18} dye molecules, and the sample with the smallest concentration of TEA (1.5 ml) contains 7.4 × 1021 TEA molecules. That is for each dye molecule there are 1000 TEA molecules available even at this lowest TEA concentration. So, the decrease in amplitude modulation could be related to the role of TEA as plasticizer rather than its role as co-initiator of the photopolymerization reaction. Another possible explanation could be that with the increase in TEA concentration (TEA3), the monomer concentration is decreased to 23% of the initial monomer concentration (TEA1). This decrease in the monomer concentration decreases the number of monomer molecules that diffuse and contribute to the final surface relief amplitude modulation. But when compared to the total mass of the layer, the difference of the monomer concentration between TEA1 and TEA3 is only 4%. This 4% difference in monomer concentration can hardly be responsible for the more than four times decrease in the surface relief amplitude modulation seen in figure 8. Also it should be noted that with the increase of the TEA concentration the thickness of the layers slightly increases. According to the previously observed dependence of the surface relief amplitude on the thickness of the photopolymer layers (figure 5) this would imply that the effect of the TEA concentration is even greater as, instead of an increase in the surface relief amplitude modulation, a decrease is observed. The most probable reason for the strong dependence of the surface relief modulation on the TEA concentration is TEA's plasticizing role. With the increase of the number of TEA molecules the layers become less viscous and there could be a possibility of diffusion of short polymer chains into dark regions [16] which in turn decreases the amplitude modulation.

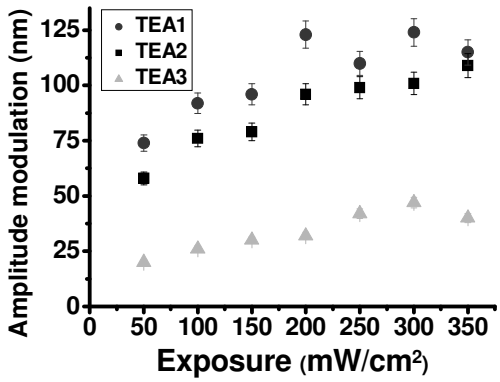

Figure 8 Dependence of surface relief amplitude modulation on chemical composition of the photopolymer layer at 100 lines/mm

4.2.3. Dependence on the temperature. The main goal of this work is to fabricate liquid-crystal devices by filling the surface relief grooves with liquid crystals. During the fabrication process, after filling the surface relief gratings with liquid crystals the cells will be heated to the clear point of the liquid crystals, for example 58 ◦C for E7 LCs. Experiments were carried out to study the influence of temperature on the surface relief amplitude modulation. Samples of thickness 5 to 5.4 μm were exposed to intensity 10

mW cm−2 for 35 s and spatial frequency 100 lines mm−1. To study the temperature dependence, after recording, the SRG was heated for 1 min at a particular temperature and cooled to room temperature. Then they were scanned with the white light interferometer to measure the surface relief amplitude modulation. Figure 9 shows the surface relief amplitude modulation increasing to a maximum and then decreasing. This shows that there is an optimum temperature for maximum surface relief amplitude modulation. When the temperature increases, non-polymerized monomer diffuses more easily from dark to bright regions and consequently the surface relief amplitude modulation is greater [2]. Polymerization of the monomer in dark regions could also occur due to heating, thus increasing the surface relief amplitude modulation. The decrease in the amplitude modulation above a certain temperature could be as a result of short polymer chains diffusing into dark regions.

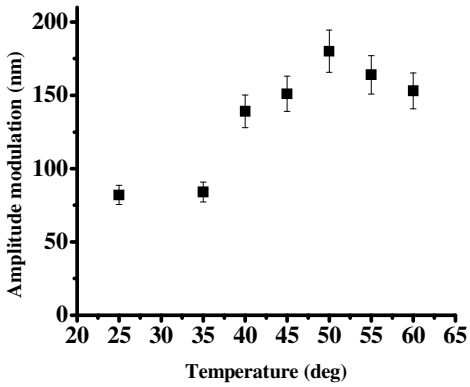

Figure 9: Dependence of surface relief amplitude modulation on temperature

5. Conclusions

Photoinduced surface relief gratings in acrylamide-based photopolymer were investigated. The outstanding advantage of this material is the absence of any chemical post-treatment. From the studies of the dependence of surface relief on intensity, thickness and composition it is concluded that diffusion of monomer from dark to bright regions is the main mechanism which governs the formation of surface relief gratings. As the intensity increases, the amplitude modulation decreases in layers of thickness 17 μm, which is different from the behaviour of thin (2.5 μm) and thick (above 50 μm) layers. Post-exposure of the exposed gratings to uniform UV light leads to a more than 30% increase in the surface relief amplitude. As the TEA content increases the surface relief amplitude modulation decreases. It was observed that when the thickness of the photopolymer layer increases, the modulation depth increases up to certain point, and after that there is not much change at constant exposure, at given spatial frequency. With increase in temperature there is an optimum temperature at which to obtain maximum surface relief amplitude modulation. At low spatial frequency nonsinusoidal profiles are observed which depend on the thickness and exposure time, which shows that shrinkage is also involved in the formation of SRGs. So it can be concluded that by changing the recording parameters and physical characteristics, the surface relief amplitude modulation and shape can be controlled. The outlook of this work is to fill surface relief gratings with LCs and to fabricate optoelectronic LC devices.

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