The UV and Laser Aging for PMMA/BDK/Azo-dye Polymer Blend Cured by UV Light Beams

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Abstract. A polymeric-based solution blend composed of Azo-dye methyl red (MR) doped with polymethacrylate (PMMA) solution, in addition, to the BenzylDimethylKetal (BDK) photoinitiator was made with optimum molar ratios and deposited on glass substrate by spin coating technique. The samples were then exposed to UV light beams in order to assist the layers polymerization by the proper exposure process. The photo chemical reaction occurred during the UV light polymerization process induces photo refractive changes which were presented as a function of wavelength or photon energy. Two main strong absorption peaks were observed in the films at around 330 nm (3.75 eV) and 500 nm (2.48 eV) for different curing time periods. This phenomenon enhances the films usage for optical data storage media at these two wavelengths. Since the deposited films were then useful as based layers for Read/Write optical data storage media, they were then tested by UV or laser Read/Write beams independently. The optical properties of the films were investigated as a function of aging time in order to relate the temporary and/or permanent light-exposure effect on the films compared to their optical properties before the light exposure. The films show a low absorbance at 630 nm (1.97 eV) and high absorbance at 480 nm (2.58 eV). This fact makes it possible to record holographic gratings in the polymeric film upon light exposure. In all cases the optical properties were evaluated by using the very sensitive, non destructive surface testing spectroscopic ellipsometry technique. The films were characterized in the spectral range of 300 to 1000 nm using Lorentz oscillator model with one oscillator centred at 4.15 eV. This study has been supported by the SEM and EDAX results to investigate the effect of the UV and visible beams on their optical properties. The results of this research determined the proper conditions for depositing the proper optical materials for light sensors or Read/Write optical data storage media for the UV or the laser Read/Write heads.

1. Introduction

The PMMA/BDK/Azo-dye polymeric based composite became of a great interest recently due to its potential application in optical data storage media and fast access type memories with read-out efficiency. [1, 2] The efforts of researchers are shed on developing and the improving the storage media capacity and the data storage density for the optical disks. Furthermore, these polymeric systems allow manufacturing of reusable films yielding many thousands of write/read/erase (WRE) cycles. [3] Polymers are used in optical data storage due to their thermal stability and their capability of dissolving. [1, 2, 4-6] Polymers incorporating Azo-dyes chemically or physically have become
promising materials for photonic devices due to the reorientation of azobenzene groups through photochemical trans-cis-trans isomerization cycles under linearly and circularly polarized light. [6] Polymerization technique plays crucial role in defining the final physical and optical properties of the films. The way the polymer shrinks together to form ultimately solid film depends on the curing process used for polymerization and time of exposure. [7] The PMMA is the synthetic polymer of methylmethacrylate. This thermoplastic and hard rigid transparent plastic is commonly called acrylic glass. The chemical formula for PMMA is: \[ \text{CH}_2-\text{C (CH}_3 \text{) CO}_2\text{CH}_3 \text{n} \]. The PMMA is often used as an alternative to glass with the difference that, the PMMA is less dense than glass (less than half the density). The PMMA has also higher impact strength, softer and more easily scratched compared to glass. It transmits more light than glass, and does not filter ultraviolet (UV) light. [8] The PMMA is a versatile material and has been used in wide range of fields and applications such as, impact resistant substitute for glass, artistic uses (paints, furniture), producing laserdiscs and DVD’s, protective layer in III-V device wafer thinning application. [2, 3, 7, 8] However, the BenzylDimethylKetal (BDK) is used as a photo initiator for the polymerization (photo curing) process through seeding free radical in composite. [1] The main advantage of polymerization started by photo initiators is that; it is temperature independence and easy to be controlled. It can be conducted at very low temperatures and can be stopped simply by removing the light source. [9, 10] The BDK is characterized by its sensitivity to light (changes its colour under light-exposure and temperature). However, it is stable under recommended storage conditions (not to be exposed to light and storage temperature should not exceed 30 °C. [11] The mechanism involved in polymerization by photo-initiation is that, the BDK undergoes a fragmentation of its structure upon exposure to ultraviolet radiation which initiates the polymerization process. [12] The Azo-dye Methyl-Red (MR) has the name (Azo) comes from azote, the old name of nitrogen. In chemistry, Azo compounds generally have a molecular formula of the form R-N=N-R1, in which R and R1 can be either aromatic or aliphatic. [13] The aromatic azo compounds are usually stable and have different colours, such as red, orange or yellow. Therefore, they are used as dyes which are called azo-dyes. Some azo-dyes, such as methyl red can be used as acid-base indicators, due to their ability to function as weak acids. The colour of methyl red solution depends on the acidity (PH) value. If it is basic, the dye turns yellow. [14] The chemical formula for the methyl red is C_{15}H_{15}N_{3}O_{3}. For the past few decades, azo-dye compound attracted considerable attention due to their capability of the write/read/erase (WRE) cycles. The basic storage mechanism of azo-dye compound is that the azo-dye molecule exists in two distinct structural forms: \textit{(trans and cis)} which leads to the change in the refraction index of the polymer. The material at room temperature is initially in trans state since the \textit{trans}-isomer is thermally stable. After illuminating the material in the \textit{trans} absorption band, light induces photo isomerization transforms from \textit{trans} to \textit{cis} configuration. This change of the molecular structure can be used for memory write and read. In addition, a \textit{cis} form can be returned to a \textit{trans} form by means of thermal relaxation process or illumination. This feature can be used in memory erase. [2] This is shown in more details in figure 1.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{The complete photochemical mechanism involved in the real-time recording and erasing process.}
\end{figure}
2. Review and related work

Al-attar and Taqatqa [1] used a solvent composed of an Azo-dye methyl red (MR) doped polymethylmethacrylate (PMMA) polymer with benzylidimethalketal (BDK) as a photo initiator to deposit polymeric-based thin films on substrates which could be used as based layer for optical data-storage media. Upon the exposure to low power UV light (256µW/cm²) at 254 nm wavelength and using the variable angle spectroscopic ellipsometer (VASE) technique, a large change in the optical constants was found.[1] The related changes reached 90% of their maximum value in five seconds time exposure for the MR/BDK and the MR/BDK/PMMA films. These changes were seen in the refractive index (Δn = -0.47 at 570nm) and in the absorption coefficient (Δα = -1.4 x 10⁵ cm⁻¹ at 470nm) in the MR/BDK film, while the values Δn = 0.03 and Δα = -8 x 10⁴ cm⁻¹ were found in the (MR/BDK/PMMA) films. They concluded that these high changes may be attributed to the photo deportation of MR by the radicals formed by the photo decomposition of BDK by UV light. Al-Attar and Telfah [15] used the spectroscopic ellipsometry to study the optical properties for electro chemically prepared thin films of camphor sulfonic acid doped polyaniline/poly(methylmethacrylate) (PAni-CSA/PMMA) blend. The optical constants were modeled using Cauchy or Tauc-Lorentz formulas. They found that the refractive index of the blend system can be adjusted in the wavelength spectral range of (300 – 550nm) by controlling the PAni-CSA percentage contained in the system. The films were transparent and the absorption coefficients vary linearly with the concentration of PAni-CSA ratio. A study by El-Naser and Ali [16] on MR/BDK thin films showed small changes in the refractive index and extinction coefficients before and after exposed to ultraviolet irradiance of 256 µW/cm² at 254 nm. The MR/BDK/PMMA films were also analyzed and showed relatively large changes in the optical constants. In another study the changes in the optical constants (n and k) due to the effect of environmental parameters (heat and humidity) using the VASE ellipsometer. [17] They found that the optical data storage system (MR/BDK/PMMA) shows a high thermal stability in the temperature range (20 – 70°C) and the film decomposed at temperature above 110°C. The effect of humidity on BDK was less than that on MR. Increasing temperature induces reduction in the optical constants of the BDK. By blending the MR/BDK with the PMMA polymer, the humidity effect on the system was observed to be minimized sufficiently due to the insulating properties of PMMA. Yu JM. et. al. [2] studied the changes in refractive index and thickness of spin-coated polymethyl methacrylate (PMMA) thin films upon irradiation by a conventional mercury UV lamp. Significant increase in the refractive index and reduction in the thickness were observed. The thickness reduction of un irradiated PMMA film is consistent with its weight loss which is caused by the escape of the volatile molecules generated during the irradiation process. A slight increase in the refractive index was also observed in the films. Pham et. al.[3] characterized azo-dye doped PMMA samples by means of varying different parameters (thickness, concentration of PMMA and azo-dye). Gang et. al. [18] employed the technique of all-optical poling to study a system composed of azo-doped PMMA. They proposed a novel method for optical storage based on the mechanism of orientational hole-burning and photoinduced molecular reorientation of azobenzene. They found that the recorded information can be stored for a long time and also can be erased rapidly with a circularly polarized light. The effects of the temperature and the electric field on the electro-optic and photorefractive properties of the PMMA-based polymeric composite have been investigated by Zeng et. al.[19] They found that both the electro-optic coefficient and diffraction efficiency increase with increasing temperature to 60 ºC. However, the electro-optic coefficient saturates while the diffraction efficiency decreases as the temperature is further increased. Wang et. al. [20] reported a new write once optical recording medium (azo-dye in PMMA film). They studied the optical and thermal properties of the azo-dye and its films which are found to have a strong absorption band at 461 nm. The reflectivity was found to be greater than 10% in the visible region which matches well with the wavelength of the argon-ion laser. The reflectivity contrast of the films was found to be more than 30% at writing power (13.3mW) and writing pulse width (600ns) using argon-ion laser operating at 514.5nm. The films were found to have
sharp thresholds for optical recording. They concluded that the Azo-dye in the PMMA thin film has a promising potential use for short wavelength optical storage medium. In this work, we investigate the aging factor on the films cured by UV source and faced to either Laser light source or UV light source in order to investigate for how long does it take the films material to be restored or damaged the UV light source exposure. Optical properties for the films have been investigated before light application and during light application and for periods of time after light application. This approach is conducted for the first time. We did not find, up to date, any previous work related to this approach in the literature.

3. Materials and Methods

3.1. Substrates treatment and film preparation

The glass wares and the glass substrates were first cleaned with warm tap – water followed by rinsing with distilled water and finally dipped in acetone. The substrates were bathed for five minutes in ultrasonic path of distilled water and then dried using cold air dryer. One gram of PMMA (Aldrich Co.) with molecular weight of 150000 and 0.3gms of the BDK photoinitiator (Aldrich Co.) and a 0.3gms of Azo-dye MR with PH between 4.2–4.6 (Aldrich Co.) were dissolved separately in 30ml chlorobenzene and the three solutions with the volume fractions of 3 PMMA, 1 MR and 3 BDK values were then filtered using 0.45µm Millipore filter before spin coating on the glass substrates. All films were prepared at room temperature under atmospheric pressure. Thin films were prepared through a volume mixture ratio of 3 PMMA, 1 MR and 3 BDK by using spin coating method on glass substrates. Six to seven drops of the mixed solution were dropped using pasture pipette on top of a glass substrate. The substrate was then rotated by the spinner for 30s at a convenient speed in order to spread the fluid by centrifugal force and to produce almost similar films thickness. The polymerization process was achieved by using ultraviolet source light of 254nm wavelength and (256µW/cm²) power intensity. Ten samples were prepared, each at a time, under the same conditions and then cured by the UV source at different periods of time such as: 5, 10, 15, 20, 30, 60, 120, 180, 300 and 540s, respectively. The samples were placed 15cm away from the UV source while curing them and then left to completely polymerize under the normal room air and temperature conditions.

3.2. Ellipsometry characterization

Recent models of ellipsometers embody the use of computerized versions. The variable angle spectroscopic ellipsometer (VASE) manufactured by John A. Woollam Co. Inc. in Lincoln, Nebraska, USA has been used in our measurements and optical analysis approach. The ellipsometer does not measure the optical constants directly; instead, it measures the ellipsometric angles ψ and Δ. From these values, the optical constant were found by solving the inverse problem of ψ and Δ parameter back to the optical constants (ε1 and ε2 or n and k) through a proposed mathematical model that gives generated ψ and Δ variables similar to the measured values from the samples.

3.2.1 Measurements

One can use this instrument to measure the beam intensities of reflection and transmission and/or the polarization state (Ellipsometric ψ and Δ as functions of wavelength and angle of incident). Once getting the optical measurements, a model is constructed by which accurate prediction of optical properties can be estimated. This model should contain both known and unknown physical parameters, known parameters such as wavelength of incidence, while the unknown parameters are such as layer thickness and optical constants. Experimental data and generated data, obtained from the mathematical model, are compared to each other by a regression analysis known as fitting process. A normal fit makes similar basic shape and patterns of the experimental ellipsometric ψ and Δ data by varying the model parameters and layers thickness. The optical constants for the assumed mathematical model, are then extracted from the generated ψ and Δ curves that are equivalent to the experimental ψ and Δ curves fitting the optical constants n and k for the model at each incident wavelength. This fit is called; point by point fit which make the experimental and generated values of ψ and Δ values are equal at each point of the experiment. The fit is obtained based on the minimum
mean square error (MSE). [21] The angles were experimentally measured based on the ellipsometric equation given by:
\[
\rho = \tan \psi e^{i \Delta} = \tan \psi \cos \Delta - i \tan \psi \sin \Delta = \frac{R_p}{R_s},
\]
where \(R_p\) and \(R_s\) are the complex coefficients of reflectance for light polarized parallel (p) and perpendicular (s) to the plane of incidence, respectively, and \(\rho\) is their ratio.[22]

3.2.2. Structural Model used in ellipsometry characterization

Optical constants of a film vary with both depth and wavelength (optical profile and optical dispersion, respectively). In order to get reliable optical characteristics, an accurate description to the thin film microstructure is required. Our structural model representing the samples is made of glass substrate mathematically modelled with Cauchy dispersions' formula and the film representing the PMMA + BDK + Azo-dye solid cured composite represented by Lorentz oscillator mathematical formula. [21, 23, 24] An interface layer between the substrate and the film is represented by Bruggeman effective medium approximation (BEMA) mathematical formula containing glass and the film material by certain percentages. [21, 23, 24] The roughness layer was also represented by BEMA formula containing the film material and a percentage of void fractions. The structural model built in the VASE system equipped with the powerful windows based software (WVASE32 ®) is shown if figure 2.

\[
\text{Bruggeman EMA} = (\text{PMMA} + \text{BDK} + \text{Azo-dye}) + \text{void \%} \quad \text{(Roughness layer)}
\]

\[
\text{Film} = \text{PMMA} + \text{BDK} + \text{Azo-dye} \quad \text{(By Lorentz)}
\]

\[
\text{Bruggeman EMA} = (\text{PMMA} + \text{BDK} + \text{Azo-dye}) + \text{glass \%} \quad \text{(Interface layer)}
\]

Cauchy dispersion
Glass substrate modelled

Figure 2. Structural model represented by glass substrate modelled by Cauchy dispersion, interface layer modelled by BEMA which contains glass% and the composite material of the film and the film material represented by and Lorentz oscillator formula.

The complex refractive index is decomposed into real \(n\) and imaginary \(k\) parts and is related to complex dielectric function \(\varepsilon = \varepsilon_1 + i\varepsilon_2 = \varepsilon_0 (n + ik)^2\) where \(\varepsilon_0\) is the real part of complex dielectric function and \(\varepsilon_2\) is the imaginary part and \(N\) is the complex index of refraction. [21, 23, 24] The index of refraction \(n\) and extinction coefficient \(k\) for glass substrate was represented by Cauchy model through a slowly varying functions of wavelength \(\lambda\), such as: [21, 23, 24]
\[
n(\lambda) = A + B/\lambda^2 + C/\lambda^4
\]
\[
k(\lambda) = \alpha \exp[\beta \{ 1240[(1/\lambda) - (1/\gamma)] \}]
\]
where \(A, B\) and \(C\) are constants, \(\alpha\) is the coefficient amplitude, \(\beta\) is the exponent factor, \(\gamma\) is the band edge and all are fitting parameters for \(n\) and \(k\), respectively. [7] The interface thin layer is then modelled in terms of Bruggeman effective medium approximation (BEMA) which contains a mixture of glass and the (PMMA/BDK/Azo-dye) film material. [7] The PMMA/BDK/Azo-dye is modelled by Lorentz oscillator model. In dielectric materials, such the PMMA/BDK/Azo-dye, electrons bonded with nucleus by a force that can be considered as a mass attached to a spring oscillator. [25] The Lorentz oscillator model formulated in the WVASE32 ® software is a multi-oscillator dispersion representing the film layer is described by: [25]
\[
\varepsilon(E) = \varepsilon_1(\infty) + A[(E_o)^2 - (h\nu)^2 - iB \cdot h\nu)]
\]
Where $\varepsilon (E)$ is the dimensionless complex dielectric function that depends on photon energy $E=\hbar \nu$, $\varepsilon_1(E)$ is the value of the real part of the dielectric function at very large photon energies. The oscillator is described by three parameters, the amplitude of the oscillator $A$ having the units of $(\text{eV})^2$, $B$ the broadening of the oscillator which has units of (eV) and $E_o$ is the energy location centre of the oscillator measured in units of (eV).

4. Results and Discussion

4.1. Spectroscopic analysis

The VASE software (WVASE32 ®) is enabled to generate ellipsometric $\psi$ and $\Delta$ data based on the structural model (figure 2) including the mathematical representation of each layer, sub layer and the substrate. Detailed description for the method of extracting the optical constants for the samples are shown in previous works. [21, 23, 24] All measurements were performed in air at room temperature for three angles of incidence ($55^\circ$, $65^\circ$, $75^\circ$) and in the wavelength range of (300 – 1000nm) in steps of 5nm.

4.2. Analysis methodology

The results of this work are presented according to the method they have been performed experimentally and then in the sequence of analysis. First; the set of samples have been prepared and categorized according to the 254 nm wavelength UV curing time periods including the reference sample which was treated with normal air drying (zero time). Second; another set of samples have been analyzed where the aging factor (time response) was the intended to be the varying factor. One sample is selected and exposed to UV light source ($\lambda = 336$ nm) another has been exposed to laser light source ($\lambda = 632$ nm) for a fixed period of time (during measurement of $\psi$ and $\Delta$ around 15min). An experimental data has been performed before light exposure, during light exposure and then a sequence of spectroscopic scans has been performed in order to investigate the effect of the light exposure on the films after the light is turned off. The optical constants are then evaluated as a function of aging time after light exposure is turned off. This aging process is helpful to investigate for how long does it take the film while it still affected by the light exposure.

4.3. Results and analysis

4.3.1 Samples cured with 254nm wavelength UV light source.

All the samples have been exposed to a UV light source of 254 nm wave length for a period of time. Based on the comparison between the experimental and generated $\psi$ and $\Delta$ values a regression analysis fit has been carried out to solve for the best film thickness as well as the optical constants (index of refraction and extinction coefficient) at each experimental photon energy or wavelength. All the samples cured with UV source light have been analyzed and the results of the films thickness, interfaces, glass fraction in the interface (EMA) and the surface roughness are presented in table 1 below. The final normal fitting values for Lorentz parameters (equation 4) which gives the best normal fitting results for all the samples are given by: $\varepsilon_1(\infty) = 2.25$, $A = 0.1(\text{eV})^2$, $B = 0.04\text{eV}$ and $E_o = 4.15\text{eV}$. 

**Table 1.** Structural model thickness for the composite film (Lorentz oscillator) and interface (BEMA) as related to the UV curing time.

| Curing time (s) | 0  | 5  | 10 | 15 | 20 | 30 | 60 | 120 | 180 | 300 | 540 |
|----------------|----|----|----|----|----|----|----|-----|-----|-----|-----|
| Interface (nm) | 20 | 7  | 17 | 18 | 3  | 18 | 3  | 19  | 7   | 8   | 0   |
| Film (nm)      | 159| 169| 165| 163| 178| 163| 180| 165 | 169 | 170 | 180 |
| $\Delta n \times 10^{-2}$ | 0 | -3 | -2 | -1 | +3 | -7 | +11| -9  | +5  | -3  | +5  |
In order to discuss the optical constants for the films, the samples were divided into three groups based on the curing time: low periods, medium periods and long periods, respectively. The index of refraction (n) is shown in figure 3 with low periods (figure 3 a), medium periods (figure 3 b) and long periods (figure 3 c). It is worth noting that the index of refraction is almost constant in the visible range while deviates in the UV and short visible range due to light-material interactions. A peak shift (towards the UV) in the index of refraction at low UV light exposure (5 seconds) is observed as seen in the figure (3 a). More time of exposure (10 to 15s) restores the index of refraction almost to its original peak. The sample with 20 seconds curing time exhibits a peak shift and an increase toward the visible range rather than figure (3 b). More time exposure (30 seconds) produces dramatic UV peak shifting and peak height too. Sixty seconds of time exposure exhibits the highest peak shift and an increase toward the UV range. 540s of time exposure (figure 3 c) makes almost similar effect as the 20s time exposure. It makes a visible shifting and peak enlargement. The sample cured for 120s time exposure restores the index of refraction with rather smaller peak. The sample with 180s of curing time shows almost similar effect as the sixty seconds period of time exposure. It makes a UV peak shifting but with smaller peak value. The change in the peak value of the index of refraction (Δn) as a function of UV curing time is shown in table 1. Our results are in consistence with the results obtained by Al-attar and Taqatqa [1] where Δn was found to be 0.03 at 5s curing time. However, the maximum change found in our experiment is + 0.11 at 3 hours of UV light exposure. Similar discussion on the extinction coefficient applies to the absorption coefficient due to their defined relation. The absorption coefficient (α) is shown in figure 4 and calculated form the extinction coefficient (k) based on the formula; α(λ) = 4πk(λ)/λ and represented in terms of photon energy rather than wavelength. They are divide similarly into low periods (figure 4 a), medium periods (figure 4 b) and long periods (figure 4 c) of curing time, respectively. Since our composite material behaves like semiconductors, the absorption coefficient curves indicates of at what photon energy the absorption takes place dramatically and hence, indicates the value of the band gap. A strong absorption band of the film is located in the range of 2.4-3.8 eV as seen in figure 4 a. The film of 5s UV light curing shows an absorption peak at 3.75 eV (330 nm) and at 2.48 eV (500 nm), this indicates that the polymeric material is highly influenced by the light of such photon energy (wavelength) for READ/WRITE memory response. However, the UV curing process for various periods of time causes a blue shift to the absorption (extension coefficient) peaks. The film processed with 540s UV curing time gives the highest absorption peak at similar energy as the 5s UV curing time (See figure 4 a). This means that the material memory has been restored and even enhanced at 540s curing time period (See figure 4 c). However, the 2.48eV absorption peak obtained with 5s UV curing time has been restored without peak value enhancement with 60s UV curing time as seen in figure 4 b. The change in absorption coefficient (Δα) at 5s curing time is -2.0 x 10^4 cm^{-1} which is less than what was found by Al-attar and Taqatqa [1] where Δα = - 8.0 x 10^4 cm^{-1}. However, the change in α is +7.4 x 10^4 cm^{-1} for the sample cured at 540s. This result has no comparison in the literature.

4.3.2 Optical band gap transmission

The absorption coefficient dependence on the incident photon energy is described by the well-known Tauc plot relation (αhν)^2 = B(hν - E_g), where B is a constant represents the slope of linear part above the band gap (E_g) for the relation.[21, 23, 24] Drawing the relationship between (αhν)^2 vs. (hν) gives a linear relation above the band edge. The optical band gap energy (E_g) is extracted by extrapolating the linear part of the curve to the incident photon energy. This approach has been applied for all the samples and the relationship between E_g and the UV curing time is shown in figure 5. Increasing the UV time of exposure to the films causes a sharp increase in the band gap as long as the exposure time is up to two hours (120min). However, a further increase in the UV curing time decreases the band gap but with slower trend.
Figure 3. Index of Refraction for samples cured by UV with (a) short periods, (b) medium periods and (c) long periods of time.

The room temperature Optical transmissions for the films have been taken using the ellipsometer at normal angle of incidence. Figures 6 shows the transmission with respect to incident photon energy for the samples cured at short periods of time and compared with that for glass. The transmission for the samples cured for medium and long periods of time (not shown) were performed and showed almost similar trends as those for the short period of exposure (figure 6). All the films have transmittance over 85%. The dip part of the transmission spectrum is due to the absorption occurs which is not seen for glass curve. The steepness of the transmission at the dip feature is maximum for 5s time exposure while it decreases for higher time exposure which is consistent with the results for $E_g$ obtained from Tauc plot.

Figure 4. The absorption coefficients ($\alpha$) for samples cured by UV with (a) short periods, (b) medium periods and (c) long periods of time.
4.3.3. Film Morphology and structural changes due to aging by laser and UV sources

The microstructural changes are presented and discussed using the Scanning electron microscopy (SEM) images while the chemical changes are presented in Electron dispersive analysis of X-rays (EDAX) analysis. Figure 7 shows the SEM images for the samples as deposited (figure 7 a), cured for 5s (figure 7 b), cured for 20s (figure 7 c) and cured for 540s (9min) (figure 7d), respectively. Small nanoparticle features are shown in figure 7 a, when the film is air dried normally at room temperature. These are expected due to the room light which initiate few defrag mentions in the BDK photo initiator throughout the PMMA/BDK/Azo-dye(BDK) composite in the film. However, as the film is cured for 5s, more nanoparticle sites are observed showing an enhancement of UV light-material interactions with particle size is increased. When the film is cured by UV light for 20s, more particle sites are observed with even larger sizes (see figure 7 c). Long period of UV light curing diffuses the particles features and smoothen the surface of the film. The EDAX analysis shown in figure 8 represents the elemental ratios between carbon and oxygen as a function of curing time. Figure 8 b shows the C/O ratio to be 6.52/1 for the as-deposited film (i.e. air normal air dry curing) with low composite arrangements as seen by the area under the curve. This indicates that the BDK photo initiator is in cis form under room temperature and no light initiation. However, when the film is subjected to the UV light for 5s, the C/O ratio decreases to 5.37/1 which indicates that carbon is released for the oxygen bond under light action. However, the area under the curve is enlarged highly indicating that huge number of BDK defragmentations is taking place in the microstructure. This indicates that the material memory has been transformed form cis-state to tran- state as illustrated in figure 1. This phenomenon is also shown in figure 8 c, where the C/O ratio is decreased to 5.23/1 while cured for 20s with UV light. The memory transition from cis-state to trans- state represents the WRITE/READ action in the film. When the curing time is increased to 540s (9min), the ratio of C/O is returned back almost to original ratio ( 6.4/1 ) seen for the film treated with normal air dry curing. Also one can see that the area under the curve of the cumulative composites decrease dramatically to almost vanishes. This phenomenon implies that the memory of the material under goes (returned back) to its cis-state from the trans-state produced with short curing period of time (5s and 20s). This returned memory implies that the memory is ERASED under the action of thermal heat or light.
Figure 7. SEM images for samples: as deposited (a), cured for 5s (b), cured for 20 s (c) and cured for 540 s (9min) (d).

Figure 8. The EDAX analysis for the composites of the PMMA/BDK/Azo-dye solid cured films (a) with air dry, (b) 5s UV, (c) 20s UV and (d) 540s or 9min UV curing periods.
4.4. Analysis for the sample aging by UV and laser

Similar procedure conducted for obtaining the optical properties for the samples cured by UV light is repeated in finding the optical properties for the sample under the aging study by using either laser or UV lights. Our focus is shed towards the effect of light exposure on the absorption coefficient of the sample before, during and after exposure. In this technique, a laser beam of light (He–Ne, 632nm wavelength) with 30mW/cm² power intensity is applied one-meter distance from the sample perpendicular to the sample surface. The \( \psi \) and \( \Delta \) values were taken before, during and after laser exposure for periods of time (20, 40, 60 and 90min), respectively. Similar measurements and analysis have performed before, during applying 336nm wavelength UV source and after UV light exposure by one or 160min, respectively. The absorption coefficient curves found for the laser treated sample is shown in figure 9, while those obtained by the UV treated sample are shown in figure 10, respectively. The absorption coefficient (\( \alpha \)) for the as deposited sample is shown in figure 9 (solid red colour). The absorption coefficient for the film while it is exposed the laser beam is shown in Open Square. It looks that \( \alpha \) did not change over all the spectral range, except in the UV region (>3.3eV) where an increase in the absorption is observed. After turning off the laser beam by 20min, the absorption coefficient is restored completely over the whole spectrum, except the peak is slightly increased. However, after 40mn, huge change in the absorption spectrum is observed all over the spectral range. The peak decreases in favour of forming a small glitch of absorption at about 1.4eV while increases sharply above 3.7eV which observed after 40min from switching the laser source off. However, 90min later, the sharp increment in the absorption coefficient vanishes and its value is restored to the value of the as deposited sample (4.1eV). The absorption coefficient for the as deposited film (before exposure) is also seen in solid red colour in figure 10. The absorption coefficient for the sample while it is under UV light exposure as seen in solid line with open squares in figure 10 shows dramatic decrease all over the spectrum, but formed a considerable absorption peak at around 3.85eV which is expected to be due to the defragmentation of the seeds of the photo initiator (BDK) in the solid composite of the film. One minute after the UV source is switched off, the curve for \( \alpha \) is decreased further with even the photo initiated peak at 3.85eV (330nm) dies sharply. After 160min, \( \alpha \) decreases all over and the photo induced peak vanishes completely in favour of inducing sharp absorption peak at around 1.4eV (886nm). We conclude from this that although the film has not been affected by the laser beam during exposure, UV beam did make a dramatic change in the UV range centred at 3.75eV (330nm).
5. Conclusion

The optical properties (refractive index, extinction coefficient, absorption coefficient, energy band gap, and transmission) of the azo-dye (methyl red) and the photosensitive benzylidimethylketal (BDK) blend with polymethylmethacrylate (PMMA) have been studied using Variable Angle Spectroscopic ellipsometry (VASE), in the spectral range 300-1000 nm. The Lorentz model is reasonable accurate in representing the (PMMA/ Azo-dye (MR)/ BDK) with one oscillator centered at 4.15 eV. The curing process for polymerization affects the physical and optical properties of the polymer. The thin films material prepared by spin coating method has a strong and a broad absorption band and the transmittance was more than 85% in the visible region. Both azo-dye and BDK materials are known as photo sensitive substances and respond to UV light in two different mechanisms; the first one is photo polymerization using BDK as a photo initiator. The second mechanism is the isomerization process (cis- trans) transition. Changes in the optical properties were obtained in the (PMMA/BDK/MR) film during exposure to UV and Laser which indicates that this media may be used as an optical data storage media for READ/WRITE using UV light. The characterization data of the films include surface morphology of the films made by scanning electron microscopy (SEM), which shows improvement of nanoparicles initiated by short time of UV curing. The composition analysis for the films performed through the electron dispersive analysis of X-ray (EDAX) shows that they contain mainly carbon and oxygen and the ratio varies with respect to the curing time. This conclusion confirms the cis-trans and trans-cis transformation that occurs due to UV light curing. We conclude that although the film has not been affected by laser beam aging during exposure, the UV beam did make a dramatic change in the UV range centred at 3.75eV (330nm) which makes it so sensitive to such light energy. Changes in the optical properties were obtained in the (PMMA/BDK/MR) film during exposure to UV and Laser which indicates that this media may be used as an optical data storage media or UV and laser light sensors.

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