MATERIALE PLASTICE
https://revmaterialeplastice.ro
https://doi.org/10.37358/Mat.Plast.1964

Study Effect Alpha Irradiation with Annealing on Chemical – Optical Properties of Poly (methyl methacrylate) Films

MUHANAD ALRAKABI[1], ZAHRAA SABAH RASHEED[1*],
MAYYADAH HASAN RHAIF AL-SAHLANEE[2], IBRAHEEM MUSA MOHAMMED[3]
[1]Department of Physics, College of Sciences, Mustansiriyah University, Baghdad, Iraq
[2]College of Medicine, Mustansiriyah University, Baghdad, Iraq
[3]Department of Physics, College of Education, Mustansiriyah University, Baghdad, Iraq

Abstract: *Polymers are commonly utilized sophisticated materials that may be found in nearly every item we use daily. Polymers' relevance has recently been highlighted due to their applications in several fields of science, technology, and industry, ranging from fundamental usage to biopolymers and medicinal polymers. The research aims to study the effect of annealing with irradiation on the optical properties of PMMA films used in many industrial and medical applications. Where UV-Vis spectroscopy was used to study the absorption and emission spectra in calculating the optical parameters, it was found that the optical energy gap of the indirect transmission type decreases with the increase in the thickness of the thin films. Also, the optical parameters such as the absorption coefficient, refractive index, attenuation coefficient, and dielectric constants increase with increasing thickness. The character of FTIR spectra and the locations of the bands have been demonstrated to change with different time annealing temperatures with irradiation. Irradiation has been demonstrated to change the shape of FTIR Spectra and the placement of the peaks.*

Keyword: *annealing, energy gap, irradiation, poly (methyl methacrylate), thin film*

1. Introduction

Polymers are generally used in electrical applications and the fields of microelectronics. Poly(methyl methacrylate) is a polymer used to manufacture light conductors, fiber optic filaments, and film, among other things. It has a refractive index of 1.49, making it ideal for optical product manufacturing [1]. poly(methyl methacrylate) PMMA as a transparent polymeric material, has outstanding transparency in the visible and near-infrared ranges, as well as dielectric constants that are usually lower than those of inorganic materials [2]. This noncrystalline polymer has excellent transparency in the visible range of (380–780) nm (92 percent light transmission). Because PMMA is hygroscopic, water absorbed acts as a plasticizer, changing the material's properties under extreme conditions. When corrosive compounds are present, such as alcohol or gasoline, this behavior is increased. The polymer is brittle, and the shock resistance is minimal. This resistance can be boosted by adding an anti-shock agent [3]. Polymer characteristics are mostly determined by the attractive forces between polymer chains. Because polymer chains are so long, they contain a lot of these inter-chain interactions per molecule, magnifying the effect of these interactions on polymer attributes compared to normal molecule attractions. Different side groups on the polymer can allow it to form ionic or hydrogen bonds with its chains. Higher tensile strength and crystalline melting points are usually the results of larger forces. The use of infrared measurements to determine the degradation and recombination of different PMMA group bands has shown to be a successful strategy. The interaction of radiation with materials depends on the radiation dose, the type of radiation, and the physical and chemical properties of the materials. Irradiation helps to improve the properties of materials reduce their negative impact on the environment and increase their usefulness in the field of nanotechnology applications and medicine [4]. The photodegradation of PMMA is caused by a radical process that results in a random scission of the polymer chain backbone.

Three key processes were reported to occur simultaneously: random hemolytic scission of main-chain carbon-carbon bonds, photolysis of the ester side groups, and photodissociation of the methyl side

---

**email: sci.phy.zsr@uomustansiriyah.edu.iq* groups. The main cause of monomer formation during irradiation is chain de-polymerization following photolytic scission of main chains [5]. The characterization and analysis of the optical properties and the infrared (IR) absorption spectrum of poly (methyl methacrylate) PMMA films will be discussed in detail in this study. The investigation of these compounds is of different Annealing times with irradiation by Alpha rays. The optical parameters such as extinction coefficient (k), refractive index (n), optical band gap E_g, dielectric constant (ε_1), and dielectric loss (ε_2) will be evaluated at annealing and irradiation. This sheds light on how to improve these properties and use them in new industrial applications.

2. Materials and methods

2.1. Preparation Poly(methylmethacrylate) PMMA Films

The polymer utilized in this work was Poly(methylmethacrylate) PMMA, which was given by ICI and has the chemical formula $(C_5O_2H_8)$ n, (Mw = 100.12 g.mol^{-1}), the chemical structure of which is shown in Figure 1 [6]. Chloroform was employed as a common solvent for pure PMMA (purity of 99.8% HPLC). In a consistent volume of solvent chloroform (20) mL, a certain weight of the polymer was dissolved. The polymer PMMA weight (0.5) g was chosen. To make polymer film, the casting method was adopted [7]. The liquid will be shaken vigorously before being put onto a 10cm diameter glass Petri dish and allowed for 24 h at room temperature (25-30)^{o}C to obtain homogenous films. Also, annealing PMMA films at 175^{o}C for half an hour.

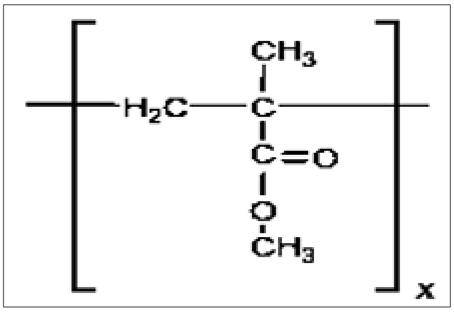


Figure 1. The chemical structure of PMMA polymer

2.2. Irradiation Poly(methylmethacrylate) PMMA Film

For user-irradiated source research, the americium-irradiated source was positioned one centimeter above the annealing PMMA film at 175^{o}C for one hour. The material was irradiated with Alpha particles for two minutes. Table 1 contains all information for irradiation sources.

Table 1. information for irradiated source [8]

Isotope	Activity	Date of Manufacture	T_{1l2}	E(Kev)	I(%)	Notes
$^{241}Am_{146}$	9 µCi	1976	432.2Y	59.54 5485.6 5442.8	I_r=35.9 I_α=84.5 I_α=13.0	Manmade (Neutron Activation) Q[α (100%)=5637.8Kev v+S.F.

3. Results and discussions

3.1. Optical properties

At room temperature, thin poly(methyl methacrylate) PMMA films were formed onto the glass substrate. Between (300-900) nm, the transmittance and absorbance spectra were measured. The T70/T80 UV-visible spectrophotometer was used to measure the results.

3.1.1. The Absorption spectrum for PMMA polymer films

The lower energy region of the absorption spectrum provides information about atomic vibrations, while the higher energy section of the spectra provides information about electronic vibrations. The separation energies of the bonds between the atoms in many polymers are extremely similar to the quantum energy found in UV radiation, as documented in references [9,10]. Figure 2 indicates that the polymer PMMA exhibits high absorption below 250 nm, followed by a sharp reduction in absorption values above this limit. The intensity of the absorption spectrum of all samples increased with increasing annealing time and irradiation.

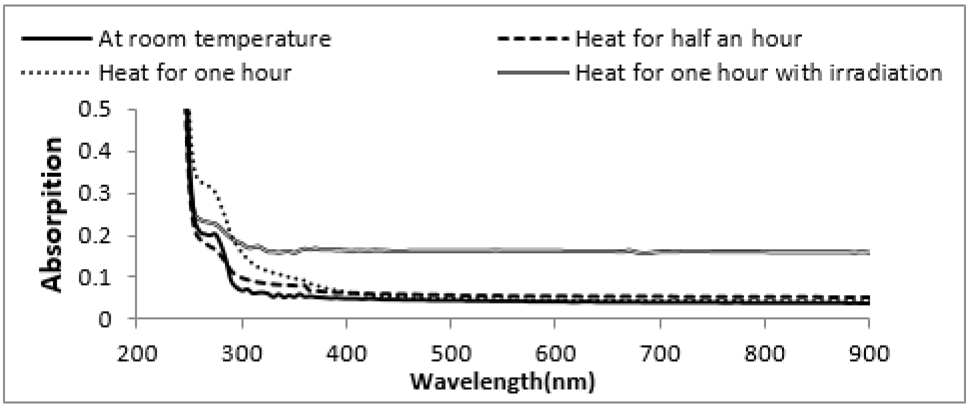


Figure 2. The absorption spectrum of PMMA thin films at annealing temperature and irradiation

3.1.2. The Optical Transmittance Spectrum

The thin films were exposed to irradiation and were treated for annealing temperature. Figure 3 shows the transmittance for Poly(methyl methacrylate) PMMA thin films in the over range (200-800) nm and from the diagram, where the maximum transmittance range is 90%, where the PMMA films annealed at 175°C for half and one- hour exhibits transmittance in the (250nm-900nm) shows high transmittance above 80 percent initially expressions the lowest transmittance and gradually increases, while its highest transmittance 60 percent for annealing. The typical transmittance of annealing with irradiation film is less than 70%, however, the transmittance increases when the annealing film is exposed to irradiation.

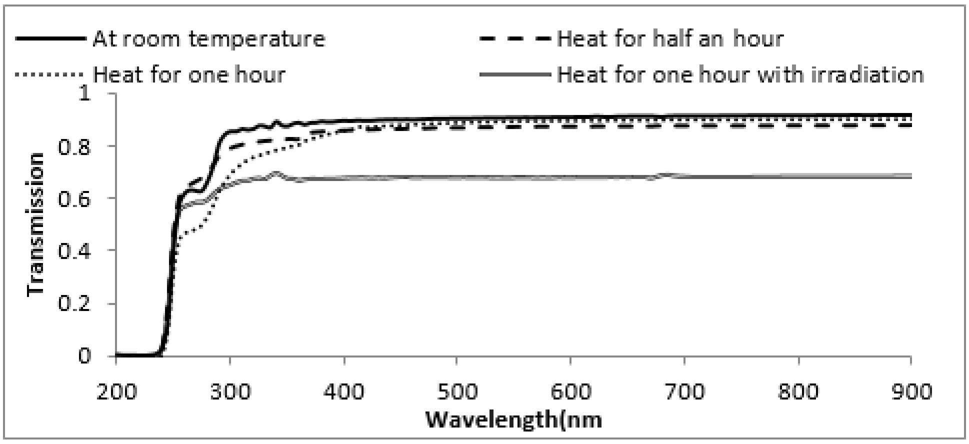


Figure 3. Transmission spectrum of PMMA thin films at annealing temperature and irradiation

3.1.3. Absorption Coefficient α

The reason for the fading intensity of falling light is reflected in the limitations surface between them, desperation suffered by the beam due to matter in the media, or direct absorption by the matter when light passes through a specific medium. If light of intensity I_o is incident on films of thickness x and transmits intensity I, Lambert-Beer Law is stated as equation 1 [11]:

$$I = I_0 e^{-\alpha x} \tag{1}$$

The absorption coefficient α (cm^{-1}) can be calculated from the Lambert's formula according to the following equation 2 [12]:

$$\alpha\, x = 2.303 \log \frac{I}{I_0} \tag{2}$$

The absorption coefficient can be calculated by equation 3 [13]:

$$\alpha = 2.303 \ \frac{A}{X} \tag{3}$$

The ability of a substance to attenuate light of a certain wavelength per unit length is characterized by its absorption coefficient [14]. The absorption coefficient as a function of wavelength is depicted in Figure 4. A high energy (very low wavelength) absorption coefficient is observed ($\alpha > 10^4$ cm^{-1}) due to the dominance of the fundamental band-gap, and the high values of absorption coefficient owing to direct electronic transitions of the energy and momentum of the electron and photon, and low energies (for higher wavelength) absorption coefficient is observed ($\alpha < 10^4$ cm^{-1}), the low values of the absorption coefficient due to indirect electronic transitions of the energy and momentum of the electron and photon. The absorption coefficient values for PMMA thin films in this investigation are indirect electronic transitions, as in the prior study. The trend in Figure 4 was identical to the absorption spectra, indicating a direct relationship between absorption and absorption coefficient, as shown in equation 3.

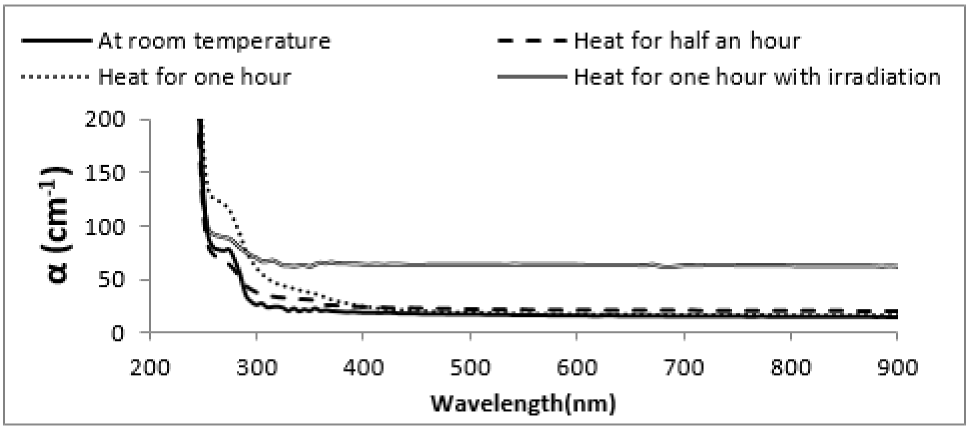


Figure 4. Optical absorption coefficient α as the wavelength for PMMA thin films at annealing temperature and irradiation

3.1.4. Optical Energy Gap E_g :

Excitation of the electron from the valence band to the conduction band can result in photon energy absorption in one of two ways: direct or indirect transitions. Tauc connection describes these transitions in equation 4 [15,16]:

$$\alpha\, h\upsilon = B(h\upsilon - E_g)^r \tag{4}$$

where $h\upsilon$ is the photon energy, B is constant and has different values for different transitions, E_g is the energy gap, and r is exponential constant, its value depended on the material and type of optical transition where r =1/2 for allowed direct transition, r =3/2 for the forbidden direct transition, r =2 for allowed indirect transition and r =3 for the forbidden indirect transition [17]. Because it was the most likely transition and the diagram produced the greatest line fit, the value of n was decided to be 2 (for allowable indirect transition band gap) in this study. The energy gap was discovered to decrease with annealing temperature shown in Figure 5. In addition, after irradiation, a drop in the energy gap values due to the development of local levels between the valence band and the conduction band has eliminated structural flaws in the films and boosted their conductivity [18]. Table 2 shows the indirect band gap variation with annealing temperature and irradiation.

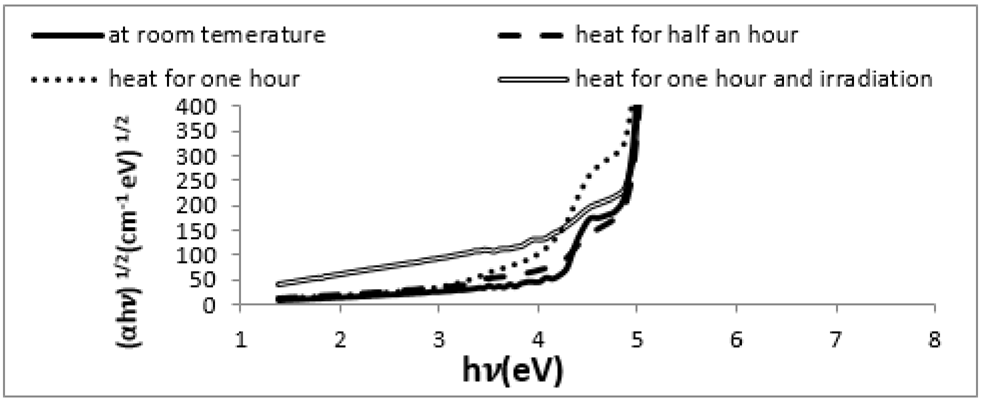


Figure 5. The plot of $(\alpha h\nu)^n$ against photon energy for PMMA thin films at annealing temperature and irradiation

Table 2. The energy gap for Poly(methyl methacrylate) PMMA thin films with annealing at 175°C and irradiated

Energy gap Eg (eV)	At room temp.	Annealing half hour	Annealing one hour	Annealing one hour with irradiation
	4.8	4.7	4.6	4

3.1.5. Reflection spectrum

The reflection spectrum is calculated from the absorption and transmission spectrum according to equation 5 [19, 20]:

$$R+A+T=1 \tag{5}$$

The reflection spectrum of Poly(methyl methacrylate) PMMA films at annealing temperature and irradiation is shown in Figure 6. PMMA films at annealing temperature have the same behavior as other polymer films, however, PMMA films at annealing temperature with irradiation have the highest reflection.

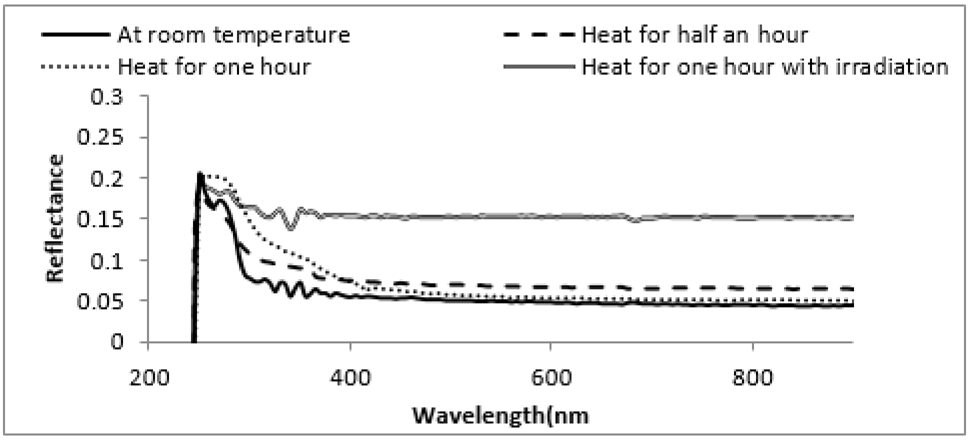


Figure 6. The reflection spectrum of PMMA thin films at annealing temperature and irradiation

3.1.6. Optical Constants: Refractive Index *n* and Extinction Coefficient *k*

The most essential optical properties of Poly(methyl methacrylate) PMMA thin films are the refractive index n and the extinction coefficient k, which are derived from transmission and reflectance spectra. The following equation [21] can be used to get the refractive index n:

$$n = \left[\left(\frac{1+\mathrm{R}}{1-\mathrm{R}}\right)^2 - (K^2+1)\right]^{1/2} + \frac{1+\mathrm{R}}{1-\mathrm{R}} \qquad (6)$$

R is the reflectance, while n is the refractive index for thin film refracted index. k is the extinction coefficient, which is defined as the amount of energy lost as a result of the reaction between the light and the medium charge. Equation 7 can be used to get the excitation coefficient k for thin films [22]:

$$K = \frac{\alpha\lambda}{4\pi} \qquad (7)$$

The refractive index and extinction coefficient as a function of wavelength are shown in Figure 7 and Figure 8 respectively. The refractive index n of Poly(methyl methacrylate) PMMA thin films grow with increased time annealing temperatures and with effect irradiation, as can be seen. The extinction coefficient k for Poly(methyl methacrylate) PMMA thin films increased with increased time annealing temperatures and irradiation for 2 min. All curves behave similarly to the absorption spectrum because the extinction coefficient is proportional to absorbance.

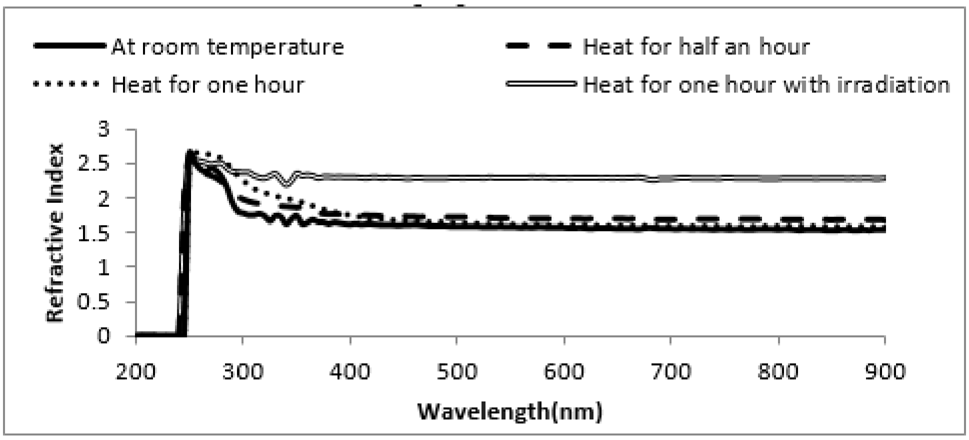


Figure 7. Dispersion of refractive index of PMMA thin films at annealing temperature and irradiation

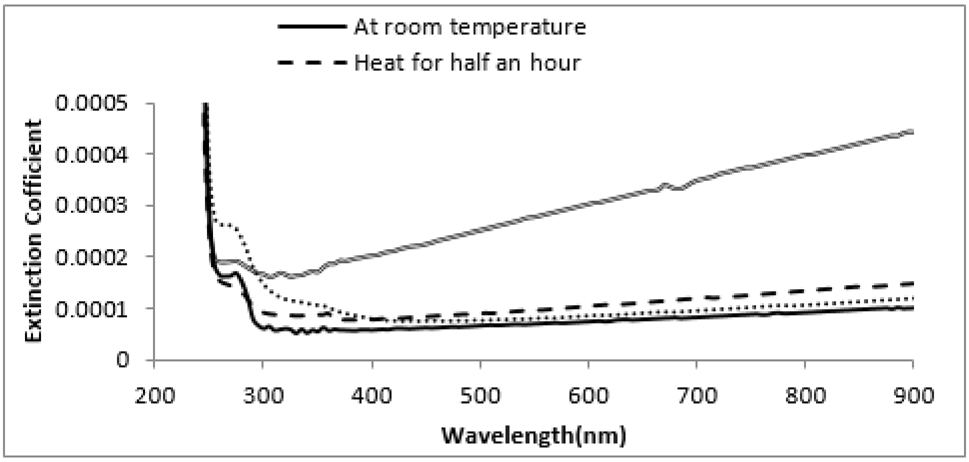
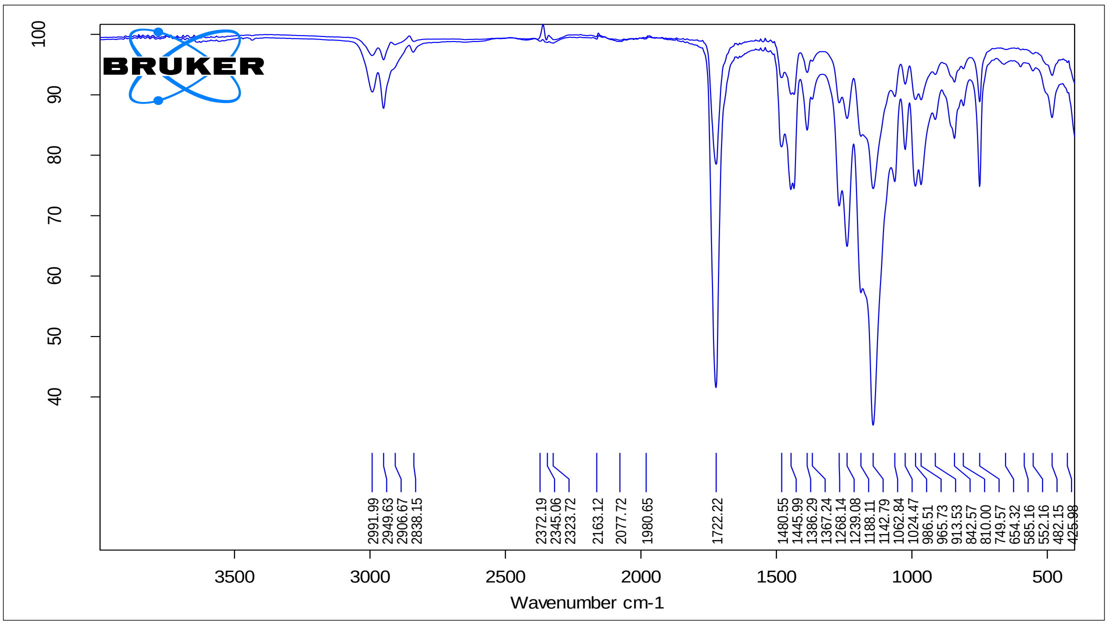


Figure 8. Dispersion of extinction of PMMA thin films at annealing temperature and irradiation coefficient *k* with wavelength

3.2. Fourier Transformation Infrared properties

In the frequency range (400-4000) cm^{-1}, Fourier transmission infrared spectroscopy (FTIR; Bruker-Equinox 55; Bruker Optics, Billerica, MA) was utilized to analyze the samples in transmission mode. The phase composition and the way elements relate together are revealed by FTIR analysis Figure 9 shows the FTIR spectrum of PMMA thin films generated by casting at various time annealing temperatures with irradiation, displays the transmission bands of (PMMA) thin films before and after annealing temperature for half hour shown in Figure 9a. The peaks correspond to CH_2 twisting, wagging, and rocking modes of PMMA appear at 987.47 cm^{-1} and 749.24 cm^{-1} and C-O stretching vibrations of ester groups 1239.45 cm^{-1} and 1299.44 cm^{-1}. The prominent peak at 1396.73 cm^{-1} was created by the O-CH_3 deformation of PMMA. The (C-CH_3) and (C-CH_2) bonds have asymmetric bending vibrations with transmissions of 1435.01 and 1473.92 cm^{-1}, respectively [23]. The C=O stretching vibration of the ester group appears at 1720.36 cm^{-1}, and –CH_3 asymmetric stretching appears at 2949.50 cm^{-1}. In addition, the amine group is represented by three bands at 2990.13 cm^{-1}, 2949.59 cm-1, and 3550. 99 cm^{-1}, When comparing the effect of annealing for one hour with irradiation shown in Figure 9b the intensity of transmission of most of the peaks increased with increased time-annealing and irradiation [24], and the reason for this is that annealing aging and irradiation promotes the oxidation process. This leads to a rise in free - radicals, which increases the quantity of space charge [25].



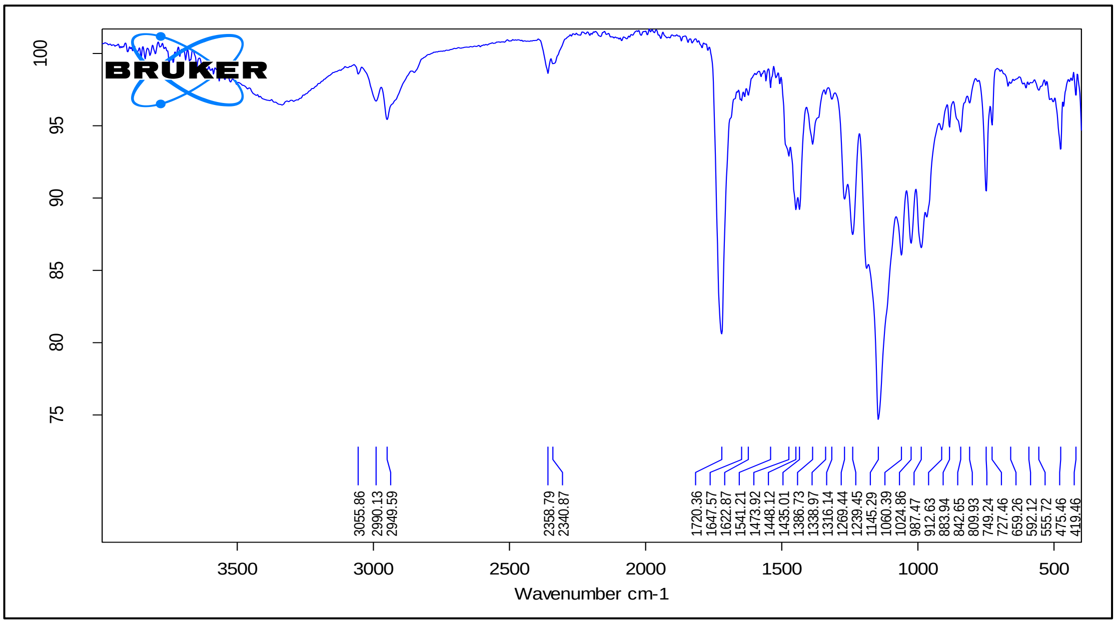


Figure 9. FTIR spectrum of PMMA thin films at: (a) room temperature and annealing for half hour, (b) annealing for one hour with irradiation

4.Conclusions

Poly(methyl methacrylate) PMMA thin films were made using a simple casting method. The structural and optical characteristics of PMMA thin films were investigated using time-annealing temperatures and irradiation. With varying time annealing temperatures, the character of the FTIR spectra and the placement of the bands have been shown to alter. Irradiation has been shown to alter the shape of FTIR spectra and the placement of the peaks, which affects their performance. The greatest transmittance was 90 percent for annealing PMMA thin film at 175°C with irradiation, according to the UV-VIS spectrophotometer. In varied time-annealing temperatures, the average transmittance of PMMA thin films is less than 70%. With annealing temperatures and irradiation, the extinction coefficient k for PMMA thin films was found to be quite modest. The energy gap for the sample at ambient temperature was 4.8 eV, while the energy gap for the sample annealed at 175°C with irradiation was 4 eV.

References

1.HAMMANI, S., BARHOUM, A., BECHELANY, M., Fabrication of PMMA/ZnO nano-composite : effect of high nanoparticles loading on the optical and thermal properties. *J. Mat. Sci.*, 53 (3), 2017, 1911-1921. https://doi.org/10.1007/s10853-017-1654-9.

2.ZAHEDI, S., DORRANIAN, D., Effect of laser treatment on the optical properties of poly(methyl methacrylate) thin films. *Opt. Rev.*, 20 ,2013, 36-40. https://doi.org/10.1007/s10043-013-0007-4

3.AL-BATAINEH, Q., M., AHMED, A., A., ALSAAD, A., M., TELFAN, A., D., Optical characterizations of PMMA/metal oxide nanoparticles thin films: bandgap engineering using a novel derived model. *Heliyon*, 7(1),2021, 5-9. https://doi.org/10.1016/j.heliyon.2021.e05952

4.RASHEED, Z., S., MAHAMMED, R., S., SALIM, S., R., HASSAN, A., S., R, Compared Effect Exposure of Radiation to the Compounds Blood, *Res. J. Pharm. Tech.* 12(2), 2019.

5.BABO, S., FERREIA, J., L., RAMOS, A., M., MICHELUZ, A., PAMPLONA, M., CASIMIRO, M., H., FERREIRA L., M., Melo, M., J., Characterization and long-term stability of historical PMMA: impact of additives and acrylic sheet industrial production processes. *Polymers*, 12(10), 2020, 2198. https://doi.org/10.3390/polym12102198

6.VAN De WALLE, E., Youth Views on Sustainability: PMMA, from plexiglass window to a packaging for an implantable glucose sensor, *J. Chem. Int.*, 37, 2015. https://doi.org/10.1515/ci-2015-0305

7.ABDUALLAH, M., H., Study of optical properties of (PMMA) doped by methyl red and methyl blue films, *Iraq. J. Phy.*, 12, 2014 ,47-51.
8.RASHEED, Z., S., ALRAKABI, M., H., SALIM, S., R.., Effect Annealing and Irradiation on Structural - Optical Properties of Tin Oxide Thin Films, *J. Eng. Appl, Sci.*, 13(23), 2018, 9838-9843.
9.DIAB, M., A., AL GHAMAZ, N., A., Conducting polymers VIII optical and electrical, *poly. Test.* ,63, 2017, 440-447. https://doi.org/10.1016/j.polymertesting.2017.09.001
10.SUN, S., WANG, Y., In situ synthesis of poly nano composites and their optical properties, *Poly. Sci.*, 59, 2017, 630-638. https://doi.org/10.1134/S156009041705013X
11.KIM, KIBU, KUO, YUE, Light Sensing of a-Si: H pin DiodeMechanism of Asymmetric Charge Carrier Transfer, *Sen. Let*., 1.1,2017, 1-4.
12.ABDULLAH, A., K., The effect of high irradiation energy (Gamma, UV-light) Radiation on the energy gap of polymers doped with Anthrancene, Iraq. J. Sci., 2006,99-103.
13.RASHIDIAN, M., DORRANIAN, D., Low-intensity UV effects on optical constants of PMMA film, *J. Theor. Appl. Phy.*, 8, 2014, 1-7. https://doi.org/10.1007/s40094-014-0121-0
14.MUSA, W., A., HAMAD, T., K., The optical properties of Poly methyl methacrylate (PMMA) polymers doped by Potassium Iodide with different thickness. *Bag Sci. J.*, 8,2011, 538-542.
15.INDOLIA, A., P., GAUR, M., S., Optical properties of solution grown PVDF-ZnO nanocomposite thin films, *J. Poly. Res.*, 20, 2013, 1-8. https://doi.org/10.1007/s10965-012-0043-y
16.UEDA, J., G., LIU, M., High refractive index polymers: fundamental research and practical applications, J. *Mater.Chem.*, 19, 2009, 8907-8919. https://doi.org/10.1039/B909690F
17.STENZEL, O., The Physics of Thin Film Optical Spectra- An Introduction, Springer, ISBN 978-3-540-27905-1, 2005, 214.
18.MISHRA, R., TRIPATHY, S., P., SINHA, D., DWIVEDI, K., K., GHOSH, S., KHATHING, D., T., MÜLLER, M., CHUNG, W., H., Optical and electrical properties of some electron and proton irradiated polymers. *Nucl. Inst. Meth. Phy. Res. Sec. B*, 168,2000, 59-64.
https://doi.org/10.1016/S0168-583X(99)00829-0
19.ZIDAN, H., M., ABU-ELNADER, M., Structural and optical properties of pure PMMA and metal chloride-doped PMMA films. *Physica B*, 355,2005, 308-317.
https://doi.org/10.1016/j.physb.2004.11.023
20.LINK, STEPHAN, MOSTAFA, A., EL-SAYED, Shape and size dependence of radiative, non-radiative and photothermal properties of gold nanocrystals, *Int. rev. phy. Chem.*, 19,2000,409-453.
https://doi.org/10.1080/01442350050034180
21.HAMAD, T., K., Refractive Index Dispersion and Analysis of the Optical Parameters of (PMMA/PVA) Thin Film, *ANJS*, 16, 2018, 164-170.
22.Luay, HUSSEIN, NOOR, ZAINAB AL-BAWI, Microfluidic sensors platform technology to enhancement fluores-cence, *Lat.Amer.J.Bio.Lif.Sci.*, 3, 2023, 1-5.
http://dx.doi.org/10.21931/RB/CSS/2023.08.03.52
23.AHMAD, S., SAXENA, T., K., AHMAD, S., AGNIHOTRY, S., A., The effect of nanosized TiO2 addition on poly (methylmethacrylate) based polymer electrolytes, *J.Pow.Sou.*, 159, 2006, 205-209. http://dx.doi.org/10.1016%2Fj.jpowsour.2006.04.044.
24.NAMOUCHI, F., SMAOUI, H., FOURATI, N., ZERROUKI, C., GUERMAZI, H., BONNET, J., J., Investigation on electrical properties of thermally aged PMMA by combined use of FTIR and impedance spectroscopies, *J. All.Comp.*, 469, 2009,197-202.
https://doi.org/10.1016/j.jallcom.2008.01.148.
25.SZILASI, S., Z., HUSZANK, R., SZIKRA, D., VACZI, T., RAJTA, I., NAGY, I., Chemical changes in PMMA as a function of depth due to proton beam irradiation, *Mat. Chem. Phy.*, 130(1-2), 2011, 702-707. https://doi.org/10.1016/j.matchemphys.2011.07.048

Manuscript received: 8.03.2023