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RADIATION ENHANCED MICRO CRACKING AND POROUS FORMATION IN DOPED GLASSY POLYMERS

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Abstract

Glassy polymers like Poly Mathyel Metha Acrylate are usually classified as non-porous materials; they are almost considered as fully transparent. Thin samples of these materials reflect color changing followed by porous formation and consequently cracking when exposed to certain level of γ-irradiation. The more the dose is the higher the effect have been observed. The optical microscope and UV-VIS spectroscopy have clearly approved these consequences especially for doped polymers.

Key word:gamma ray ,dopedvglassy,radition application

Introduction

Methacrylic ester monomers have the general formula $CH_2 = C(CH_3)COOR$, and the nature of the R group that generally determines the properties of the corresponding polymers. α-Methyl group of the Poly methacrylic imparts the stability temperature, hardness, porous, and stiffness of mehacrylic polymers. The methacrylate monomers are usually versatile building blocks since they are moderate-to-high boiling liquids that readily polymerize or co-polymerize with variety of other monomers [1]. At room temperature, Polymathyelmethaacrylate (PMMA) is a hard, fairly rigid material when heated above its glass-transition temperature (T_g=105°C), it is a tough, pliable, and that can be molded or extruded [2].

PMMA is characterized by crystal clear transparency (non-porous), i.e. transmits light almost perfectly (92%) compared to (92.3%) theoretical at (360-100nm)[1,2].

Composite materials are essentially volumetrically formed special combination of two or more components dissimilar in form and properties, exhibiting clear boundaries between components, using the advantages of each component [3].

In the present work conductive composite has been achieved by the incorporation of macroscopic pieces of conducting material (Cu powder) into host polymers to form conducting composites [4].

Radiation processing using γ, electron beam has been demonstrated on a large commercial scale to be a very effective means of improving end use properties of various polymers[5]. When the radiation from source interacts with a polymer material, the polymer material absorbs its energy and active species such as radicals are produced, thereby, initiating various chemical reactions. The different responses to radiation for different polymers are intrinsically related to the chemical structures of the polymers. Crosslinking and degradation are two competing processes that always co-exist under radiation. The overall effect

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depends on which of the two is predominant at a certain time. Crosslinking is the most important effect of polymer irradiation and has the large number of applications because it can usually improve the mechanical and thermal properties and environmental and radiation stabilities for both preformed parts and bulk materials [6].

Beer-Lamberts law is fundamental for quantities absorption spectroscopic in the UV-VIS and constitutes a special case of the general law of absorption of radiation equation (1) in homogenous matter [7].

$$I = I_0 e^{-\alpha t} \qquad (1)$$

$where\ I_0$ is the intensity of the incident light and I is the intensity of light after traversing a thickness (t) of the sample material.

$Equation\ (1)$ implies that the decrease in light intensity (I) only depends upon the intensity at depth (t) and on a constant (α) characteristic of the substance (absorption coefficient)[8].

The absorption coefficient is defined by [4]:

$$\alpha(\omega) = \frac{1}{t}\ln\left[\frac{I_0}{I}\right] - - - - - - - - - - - - (2)$$

However equation (2) can be related to the absorbance by the following relation [9].

$$A - l\omega y_{10}\left[\frac{I_0}{I}\right] - - - - - - - - - - - - - (3)$$

Where A is the absorbance of the material. So the absorption coefficient α(ω) in terms of absorbance becomes

$$\alpha(\omega) = 2.303\,\frac{A}{t} - - - - - - - - - - - - - (4)$$

The aim of this work is to produce color change in visible region in PMMA composite when it are irradiated to low doses (10 -200) Gy from gamma ray source.

Materials and methods

The material is used in this work for polymer matrix is Polymethylmethacrylate (PMMA) from BDH chemicals (LTD), the average weight is (0.02315gm). One the filler used in this work is Copper powder from organic syntheses (LTD), England. The main characteristics of these materials are listed in the Table (1).

Table (1) the main characteristics of materials used in this work

Material	Chemical Formula of Reparative Unit	Molecular weight	Density ($gmlcm^3$)
PMMA	CH_3 $[CH_2 - C - COOCH_3]_n$	84000	1.2
Copper	Cu	63.546	8.96
Methylene Chloride	CH_2Cl_2	84.93	1.323

Sample preparation

Pure PMMA Film Casting

The purified polymer used to cast film, (0.5gm) of PMMA was dissolved in (5ml) methylene chloride, shacked until homogenous solution was

occurs. The solution was transferred to clean glass petri dish of (5cm) diameter. The dried film was then removed by using tweezers clamp. From the film weight and petri dish radius the average films thickness was accounted to be (0.01585cm) ±0.00165cm.

Composite Film Casting

The preparation of PMMA-Cu composite was made in different weight percentage of filler with observance of a total weight of sample (polymer+ filler) equal (0.5gm) its similar procedure of preparing purified sample, which mentioned above.

room temperature in a different time (10, 15, 20, 30, 60) mints or at different doses of radiation (34.16, 50, 68.33, 100, 200) Gy using (^{60}Co) cell (model 900 manufactured by Bhabha Atomic Research center / Bombay / India). The source ^{60}Co giving photons having energy (1.17, 1.33) MeV and the dose rate was 0.2 KGy/hr.

Results

The weight ratio known of polymer purified dissolved in (5ml) methylene chloride and handly skaked to give homogenous solution, then the filler were added with a continuation handly shaked to give adhesive solution, the particles of copper were bending to it and regular distribution, this solution transferred to petri dish and left overnight to dry, removed as similar as above.

Irradiation Processes

Samples were prepared by cutting each film to four identify portions and irradiated with γ-rays in the

For studying the effect of Cu content on PMMA samples, the ABS, α, Eg, and λg values of similar samples doped with Cu for these concentration (1, 2, 3, 4, 5)% were determined. Figs. (1 and 2) show the effect of Cu content on absorption coefficient α (ω) for the samples unradiated and irradiated for 60 mints (radiation dose equal 200Gy) respectively. Figs. (3-6) illustrated the effect of Cu content on their tendency of cracking the samples by the radiation.

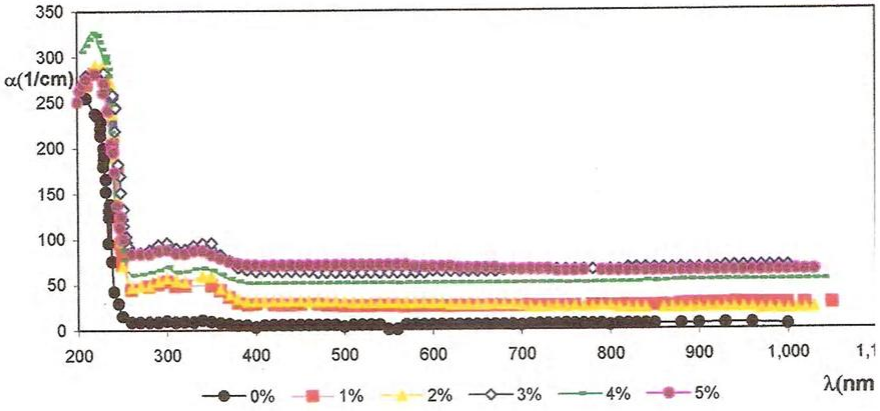

Fig.(1): Absorption coefficient (α) as a function of wavelength for the samples unradiated with (1, 2, 3, 4, 5)%Cu

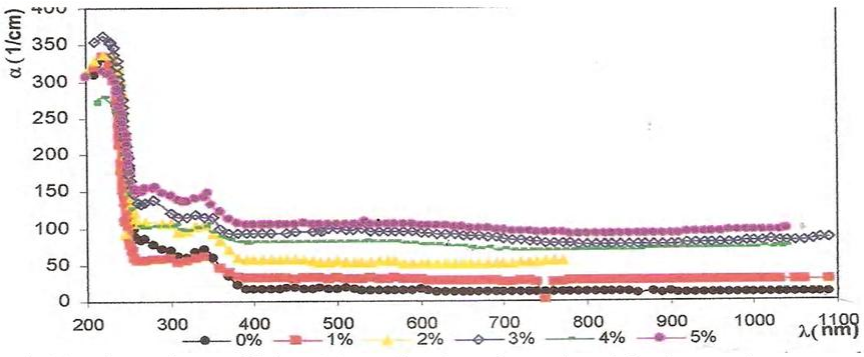

Fig.(2): Absorption coefficient (α) as a function of wavelength for the samples radiated (for 60 mint) with (1, 2, 3, 4, 5)%Cu

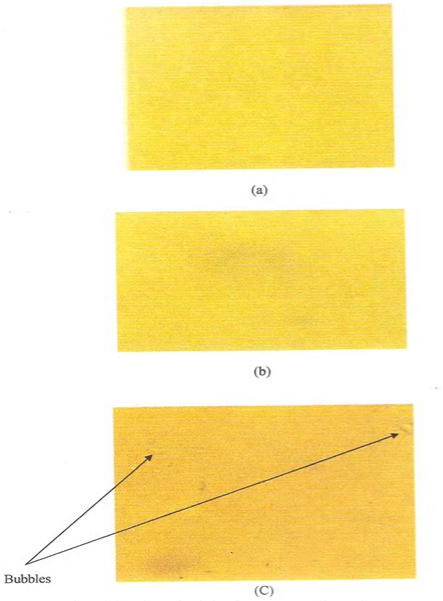

Fig.(3): Optical micrographs of pure PMMA before irradiation (×200) (a), and after irradiation with (34.16 Gy) (b), and (68.33 Gy) (c) doses.

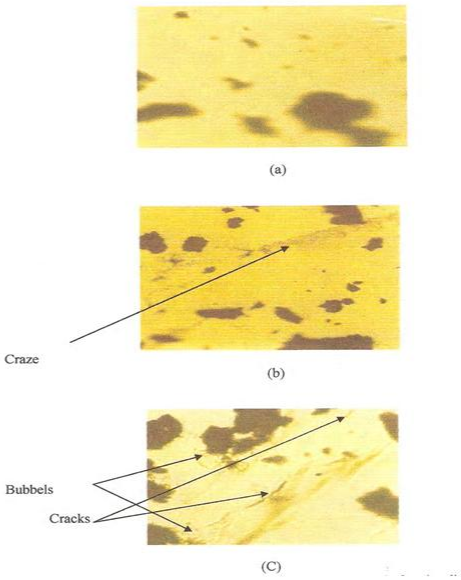

Fig.(4): Optical micrographs of doped PMMA with 1% Cu before irradiation (×200) (a), and after irradiation with (34.16 Gy) (b), and (68.33 Gy) (c) doses.

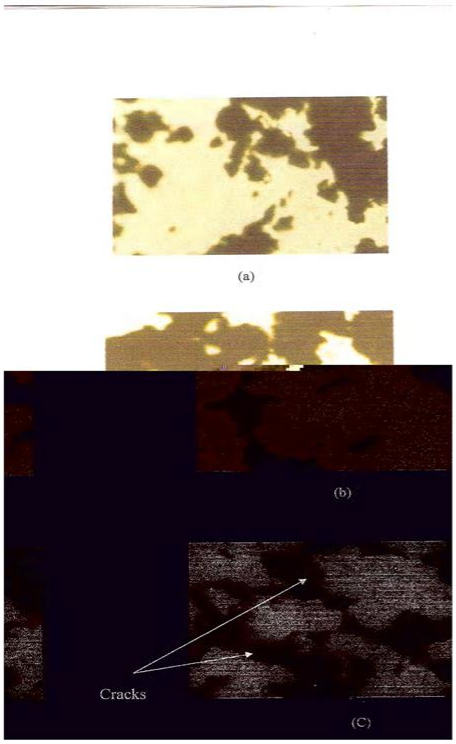

Fig.(5): Optical micrographs of doped PMMA with 3% Cu before irradiation (×200) (a), and after irradiation with (34.16 Gy) (b), and (68.33 Gy) (c) doses.

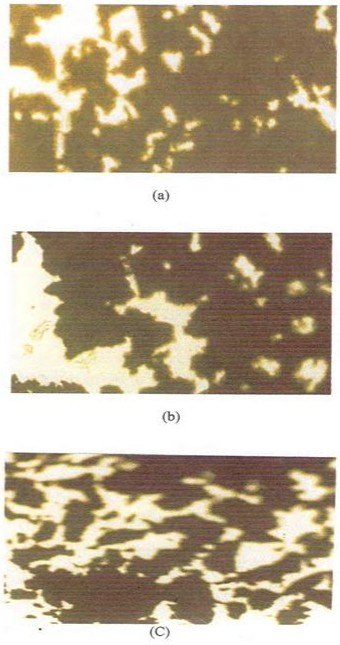

Fig.(6): Optical micrographs of doped PMMA with 4% Cu before irradiation (×200) (a), and after irradiation with (34.16 Gy) (b), and (68.33 Gy) (c) doses.

Discussion

In the visible region PMMA is transparent [9]. It's well known that the exposure of solid materials to γ-rays and impurities induces structural defects known as color centers. The presence of such color centers in the materials caused absorption which occurs in the visible region. This fact can be seen in dose (68.33Gy) located peak at 775nm, at (100, 200)Gy peaks observed at $(\lambda g)_{meas}$ =811, 825)nm, for (1, 2, 3, 4, and 5)% Cu at different dose of some concentration of Cu and radiation dose, which expanded to high value so as in the 4% Cu content and dose of radiation = 100Gy, $(\lambda_g)_{cal}$ = 1034nm this located in IR region, with 5% content and radiation dose (34.16, 68.33)Gy, $(\lambda_g)_{cal}$ =(428, 776)nm respectively, then peaks observed for pure PMMA at dose 50Gy in wavelength (761, 1047)nm, at radiation can be see the peak at wavelength more than 1000nm such as the values illustrated in Tables (3-7).

Table (2): Illustrated the values of λ_g(nm), E_g and peaks observe for pure PMMA.

Radiation Time (min.)	Dose (Gy)	Intensity of Absorption for Peaks Observe and Their Wavelengths						Direct trans.		Indirect trans.	
								E_g (eV)	$\lambda_{g\ cal.}$ (nm)	E_g (eV)	$\lambda_{g\ cal.}$ (nm)
0	0	$\lambda_{g\ meas}$ (nm)	219	345				5.1	243	4.8	258
		abs	1. 898	0.124							
10	34.16	$\lambda_{g\ meas}$ (nm)	219	300	343			5	248	4.6	270
		abs	1. 507	0. 276	0. 321						
15	50	$\lambda_{g\ meas}$ (nm)	220	349	761	1047		4.5	276	3.8	327
		abs	2. 316	0. 591	1. 076	0. 599					
20	68.33	$\lambda_{g\ meas}$ (nm)	219	301	343	775		4.9	253	4.3	289
		abs	1. 532	0. 34	0. 392	0. 056					
30	100	$\lambda_{g\ meas}$ (nm)	223	345	811			4.9	253	4.4	282
		abs	2. 018	0. 361	0. 085						
60	200	$\lambda_{g\ meas}$ (nm)	225	345	825			4.9	253	4.6	270
		abs	2. 06	0. 453	0. 069						

Table (3): Illustrated the values of λ_g(nm), E_g and peaks observe for composite PMMA with 1% Cu

Radiation Time (min.)	Dose (Gy)	Intensity of Absorption for Peaks Observe and Their Wavelengths						Direct trans.		Indirect trans.	
								Eg (eV)	$\lambda_{g\ cal.}$ (nm)	Eg (eV)	$\lambda_{g\ cal.}$ (nm)
0	0	$\lambda_{g\ meas}$ (nm)	220	301	345	925		4.95	251	4.6	270
		abs	2. 032	0. 302	0. 322	0.186					
10	34.16	$\lambda_{g\ meas}$ (nm)	219	300	343	903		4.9	253	4.3	289
		abs	1. 557	0. 491	0. 557	0.147					
15	50	$\lambda_{g\ meas}$ (nm)	218	349	725	1031	1046	4.9	253	4.4	282
		abs	2.162	0. 698	1. 4	0. 929	0. 877				
20	68.33	$\lambda_{g\ meas}$ (nm)	220	300	343	745	900	4.9	253	4.2	295
		abs	1. 589	0. 654	0.736	0. 21	0. 215				
30	100	$\lambda_{g\ meas}$ (nm)	220	0.305	348	1081		4.9	253	4.6	270
		abs	2. 071	0. 401	0. 416	0. 2					
60	200	$\lambda_{g\ meas}$ (nm)	221	304	345	895		5	248	4.5	276
		abs	2. 036	0. 362	0. 381	0.174					

Table (4): Illustrated the values of λ_g(nm), E_g and peaks observe for composite PMMA with 2% Cu.

Radiation Time (min.)	Dose (Gy)	Intensity of Absorption for Peaks Observe and Their Wavelengths						Direct trans.		Indirect trans.	
								E_g (eV)	λ_g cal (nm)	E_g (eV)	λ_g cal (nm)
0	0	$\lambda_{g\ meas}$ (nm)	222	283	345	760		4.9	253	4.5	276
		abs	2. 099	0. 454	0. 488	0. 237					
10	34.16	$\lambda_{g\ meas}$ (nm)	218	300	343	851		4.9	253	4.3	289
		abs	1. 565	0. 605	0. 67	0. 402					
15	50	$\lambda_{g\ meas}$ (nm)	222	283	345	701		4.9	253	4.4	282
		abs	2.157	0. 671	0. 663	0. 334					
20	68.33	$\lambda_{g\ meas}$ (nm)	219	300	343	849		4.9	253	4.3	289
		abs	1. 571	0. 647	0.705	0. 435					
30	100	$\lambda_{g\ meas}$ (nm)	222	283	345	1037		4.9	253	4.6	270
		abs	2. 215	0.772	0.776	0. 388					
60	200	$\lambda_{g\ meas}$ (nm)	223	283	345	932		4.9	253	4.4	282
		abs	1.764	0. 599	0. 596	0. 298					

Table (5): Illustrated the values of λ_g(nm), E_g and peaks observe for composite PMMA with 3% Cu.

Radiation Time (min.)	Dose (Gy)	Intensity of Absorption for Peaks Observe and Their Wavelengths						Direct trans.		Indirect trans.	
								E_g (eV)	λ_g cal. (nm)	E_g (eV)	λ_g cal. (nm)
0	0	$\lambda_{g\ meas}$ (nm)	219	282	345	781	994	4.9	253	4.4	282
		abs	2.181	0. 684	0. 648	0. 447	0. 453				
10	34.16	$\lambda_{g\ meas}$ (nm)	220	300	342	1010		4.9	253	3.9	318
		abs	1. 598	0.738	0.789	0. 553					
15	50	$\lambda_{g\ meas}$ (nm)	219	282	345	903		4.9	253	4.6	270
		abs	2.107	0. 565	0. 537	0. 385					
20	68.33	$\lambda_{g\ meas}$ (nm)	221	300	343			4.9	253	4.1	303
		abs	1. 604	0.771	0. 875						
30	100	$\lambda_{g\ meas}$ (nm)	222	275	344	925		4.8	258	4.3	289
		abs	2. 259	0. 894	0. 832	0. 661					
60	200	$\lambda_{g\ meas}$ (nm)	219	279	348	534	1037	4.8	258	4.1	303
		abs	2. 214	0. 844	0.757	0. 612	0. 506				

Table (6): Illustrated the values of λ_g(nm), E_g and peaks observe for composite PMMA with 4% Cu.

Radiation Time (min.)	Dose (Gy)	Intensity of Absorption for Peaks Observe and Their Wavelengths						Direct trans.		Indirect trans.	
								E_g (eV	λ_g cal. (nm)	E_g (eV)	λ_g cal. (nm)
0	0	$\lambda_{g\ meas.}$ (nm)	215	304	345	961		4.95	251	4.6	270
		abs	2. 074	0. 578	0. 596	0. 488					
10	34.16	$\lambda_{g\ meas.}$ (nm)	215	300	342	1033		4.8	259	3.9	318
		abs	1. 596	0.716	0.771	0. 381					
15	50	$\lambda_{g\ meas.}$ (nm)	218	304	345	1037		4.9	253	4.3	289
		abs	2. 221	0. 932	0. 981	0. 569					
20	68.33	$\lambda_{g\ meas.}$ (nm)	220	300	342	702		4.8	258	3.7	335
		abs	1. 693	0. 951	1. 031	0. 62					
30	100	$\lambda_{g\ meas.}$ (nm)	222	356	806			3.8	258	1.2	1034
		abs	1. 281	1. 08	1. 247						
60	200	$\lambda_{g\ meas.}$ (nm)	218	304	345	534	1022	4.9	253	4.1	303
		abs	2.196	0. 832	0. 848	0. 652	0. 569				

Table (7): Illustrated the values of λ_g(nm), E_g and peaks observe for composite PMMA with 5% Cu.

Radiation Time (min.)	Dose (Gy)	Intensity of Absorption for Peaks Observe and Their Wavelengths						Direct trans.		Indirect trans.	
								E_g(eV)	λ_g cal. (nm)	E_g(eV)	λ_g cal. (nm)
0	0	$\lambda_{g\ meas.}$ (nm)	219	345	1034			4.9	253	4.3	289
		abs	2. 205	0.772	0. 536						
10	34.16	$\lambda_{g\ meas.}$ (nm)	220	299	341	1009	1034	4.5	276	2.9	428
		abs	1.723	1. 36	1. 466	1. 269	1. 282				
15	50	$\lambda_{g\ meas.}$ (nm))	221	283	344	663		4.95	251	4.2	295
		abs	2.187	0. 784	0.734	0. 512					
20	68.33	$\lambda_{g\ meas.}$ (nm)						4.7	264	1.6	776
		abs									
30	100	$\lambda_{g\ meas.}$ (nm)	219	281	344	534		4.1	303	4.9	253
		abs	2. 301	1. 054	1 .018	0. 867					
60	200	$\lambda_{g\ meas.}$ (nm)	220	281	345	534	1037	4.7	264	4	310
		abs	2.298	1.134	1. 085	0.789	0.711				

The value of absorption coefficient $\alpha(\omega)$ which is calculated by equation (4) was changed depending on the thickness of the sample and the intensity of absorption. In this work the thicknesses of the samples are constant, therefore the value of $\alpha(\omega)$ will be changed when the intensity of absorption are changed. For pure sample, Fig(7) represented absorption coefficient $\alpha(\omega)$ as a function of wavelength. This figure shows that increase the dose of radiation leads to increase or decrease on the value of α depending on the absorbance dose, as a result to increase or decrease the intensity of absorption which is studied above and the value of α very low on the visible region compared with doped samples with Cu consequence to ability of copper for absorption the radiation on this region. This fact illustrated in Fig (1) for unradiated sample, the value of $\alpha(\omega)$ in the visible region has been increased with increase

the concentration of Cu as in 5% Cu content, the value of $\alpha(\omega)$ equal twice the value for pure sample. The curves on Fig (2), for radiated sample with dose 200 Gy or time of radiation (60mint), show that similar behavior for curves in Fig (1) but the value of α for radiated sample higher than the value for unradiated sample at the same concentration because increase the disorder occurs by irradiated sample leads to increase the absorbance.

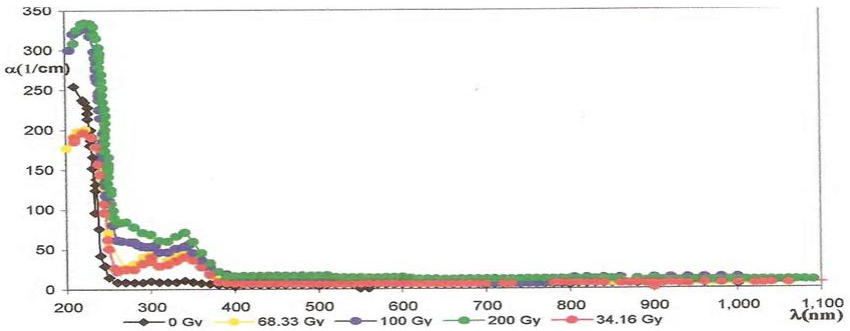

Fig.(7): Absorption coefficient (α) as a function of wavelength for pure PMMA with radiation dose (0, 34.16, 68.33, 100, 200)Gy.

Figs (3-6) a, b, c, illustrated the optical micrographs of PMMA and its composite before and after irradiation with γ-rays for doses (34.16)Gy and (68.33)Gy, the part of these figures for unradiated samples shoe that these samples are free from any bubbles but when PMMA and its composite irradiated with γ-ray, degradation products are formed causing changes in the colour of the sample leads to change the optical absorbance which is increased by this change, Fig(3) c, shows the bubbles produced by increases the dose of radiation as a result to liberation the hydrogen, these bubbles may be burst as in Fig ((4) and (5) c) and caused cracks in the structure and almost the radiation may be transmitted, the absorption will be decrease but at high concentration of Cu, cracks will be decreased as in Fig(6) b,c and reflect the light increase by increasing Cu content, any changing occurs in transmission or reflectance leads to change in absorbance depending on the relation R+A+T=1.

Conclusions

1- The number of absorbance band changed depending on Cu content and absorbance dose.
2- The value of absorption intensity increase with increasing the concentration of Cu.
3- The reduction in optical energy gap was markedly reduced to give a chance of using the prepared samples as dosimeter especially in 4% Cu content.
4- For tendency of cracking the samples decrease with increasing the concentration of copper.

References

1- Encyclopedia of Polymer-Science and Engineering, (1988); 2nd Ed, Vol.15 P. (377-397).
2- Urich, H., (1992); "Introduction to Industrial Polymers", New York.

3- Hollaway, H., (1978); "Glass Reinforced Plastics in Construction", Surrey University Press.
4- Al-Delaimi M.N., (1996) Ph.D. Thesis; "The Effect of Ni, Cu, and CB additives on the Electrical, Optical and Mechanical Properties of PMMA", University of Baghdad, College of Science.
5- El-Salmaway K.M., (2007); "Gamma Radiation Induced Crosslinked PVA/Chitosan Blends for Wond Dressing", Journal of Macromolecular Science; Part A, Vol. 44, P(541-545)
6- Mishra S., Bajpai, R., Katare, R,. Bajpat, A.K.(2007); " Radiation Induced Crosslinging Effect on Semi-Interpenetrating Polymer Networks of Poly(vinyl alcohol)" Polymer Letters, Vol. (7) P(407-415).
7- Klobffer, W., (1984); "Introduction to polymer Spectroscopy ", New York.
8- Al-Mashhadani, N.J.H., (2004) Ph.D. Thesis, "Structure and Spectrometric (UV/VIS) Study of γ-Irradiated Polymer Composites" University of Baghdad, College of Science.
9- Osaka, Z, and Fukuda, (1970) "Polymer Degradation and Stability" Oxford University Press, New York.

الاشعاع يحث تولد شقوق مجهرية ومسامية في البوليمرات المطعمة

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الخلاصة:

تصنف المواد البلورية الزجاجية مثل بولي مثيل ميثا أكرليت (PMMA) على أنها مواد غيرمسامية وشفافة جداً. وعند تشعيع هذه المواد بجرع معينة من أشعة كاما يحصل فيها تكسر وتتحول إلى مواد مسامية لذلك ستظهر تغير باللون يتبعه تولد المسامية وظهور شقوق. كمية التكسر الحاصلة في هذه المواد تعتمد على جرعة الأشعاع الساقط عليه، حيث لوحظ عند زيادة جرعة الإشعاع تؤدي إلى زيادة بالتأثير (التغير باللون وزيادة في عدد الشقوق الحاصلة والمسامية) في هذه المواد. ولغرض الحصول على تأثير أوضح في المواد البوليميرية المدروسة تم تطعيم البوليمر بمادة موصلة مثل النحاس. و قد استخدم المجهر الضوئي ومطياف الأشعة فوق البنفسجية والمرئية في دراسة وفحص تأثير أشعة كاما على العينات المدروسة.