التغيرات في الخواص الفيزيائية لبلمرات عديد الكربونات نتيجة للتشعيع

Radiation induced changes in the physical properties of polycarbonate

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الملخص العربـــي

لقد أصبحت دراسة تأثير الإشعاع على البلمرات، موضوع ذو أهمية كبيرة وذلك نظراً لانتشار استخدام البلمرات في التطبيقات التي تتعرض لمستويات عالية من الإشعاع ، مثل محطات القوى النووية و المعجلات الالكترونية و سفن الفضاء... الخ.

ومن ثم كان الهدف من هذا البحث دراسة تأثير التشعيع على الخواص الفيزيائية للكاشف النووي Makrofol-DE 1-1CC. وذلك بتعريض الكاشف النووي لجرعات مختلفة من البروتونات في المدى من 10^{11}-10^{15} ions/cm^2 ذات الطاقة 1 MeV.

و قد تم هذا البحث باستخدام العديد من التقنيات مثل تقنية حيود الأشعة السينية XRD والتحليل الحراري الوزني TGAو معدلات فقد الوزن .DTG

* **أظهرت نتائج حيود الأشعة السينية أن عينات Makrofol** تتصف بهالة halo تمتد في المدى 2θ =14°-32° تشير إلى أن البوليمر شبه بلوري، و لكن الطور الأمورفي هو الطور السائد. كما أظهرت النتائج أن التشعيع بالبروتونات حتى $5x10^{11}$ ions/cm^2 يسبب تكسير لسلاسل البوليمر مما يؤدي إلى زيادة درجة الترتيب لسلاسل البوليمر، ولكن بزيادة الجرعة الإشعاعية في المدى $5x10^{11}$ ions/cm^2- $1x10^{15}$ ions/cm^2. يسبب تكوين الروابط التي تسبب زيادة درجة التفرع في البوليمر branching و التي تقلص الأجزاء البلورية مما يؤدى إلى زيادة العشوائية فيميل البوليمر إلى الشكل الأمورفي، و تزيد صرامته، فيصبح ملائم للأغراض الصناعية التي تتطلب ثنيه دون كسره.

***تم تتبع التغيرات التي تطرأ على العينات نتيجة تسخينها من خلال التحليل الحراري الوزني TGA و معدلات فقد الوزن DTG**، وتم استخدام المنحنيات الناتجة في حساب كلاً من طاقة تنشيط الانحلال الحراري E_a و درجة حرارة بداية الانحلال T_o.

و أظهرت النتائج أن عينات Makrofol تنحل حرارياً في مرحلة رئيسية وحيدة، وأن التشعيع بالبروتونات حتى $5x10^{11}$ ions/cm^{2}قد قلل من درجة الثبات الحراري نتيجة للتكسير الذي يحدث في العينات. وعند زيادة الجرعة حتى$1x10^{15}$ ions/cm^2 تحدث زيادة في الثبات الحراري للبوليمر مما يطيل من عمر استخدام الأدوات المصنوعة من هذا البوليمر.

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Abstract

Makrofol-DE 1-1 CC Polycarbonate is a class of polymeric solid state nuclear track detector which has many applications in various radiation detection fields.

Structural property studies using X-ray diffraction were performed on the non-irradiated and irradiated Makrofol samples. The intensities of the characteristic absorption bands were found to decrease predominantly with increasing the proton fluence in the ranges 0-5x10^{11}ions/cm^2 indicating that the degradation is the dominant mechanism.

Non isothermal studies were carried out using thermo-gravimetric analysis (TGA) and differential thermo-gravimetric (DTG) to obtain information concerning the thermal stability for Makrofol detector. The obtained TGA thermograms indicated that the Makrofol detector decomposes in one main weight loss stage.

Using the TGA curves, both the onset temperature of decomposition and the activation energy of thermal decomposition were calculated. The results indicated that the proton irradiation of Makrofol detector in the fluence range 0-5x10^{11}ions/cm^2causes an initial scission that reduces the thermal stability of the Makrofol samples. The proton irradiation in the fluence range 5x10^{11}-1x10^{15}ions/cm^2 led to a more compact structure of Makrofol polymer, whichresulted in an improvement in its thermal stability with an increase in the activation energy of thermal decomposition.

Introduction

Radiation-induced modification of polymers is a promising technique for the production of new polymeric materials which can be engineered with specific physical and optical properties. In particular, the interaction of protons with polymers leads to specific changes in the polymer properties due to induced chain scissions and cross-linking. In other words, radiation processing is a useful technology to induce suitable modifications of polymers. It is an important way to achieve some desired improvements that promise many applications in a wide range of industrial fields. Also, the action of radiations on polymeric solid state nuclear

track detectors (SSNTDs) leads to several changes in their properties due to the induced chain scissions and cross-links[1]. Crosslinking generally improves the physical properties of polymers and reduces crystallinity, therefore increases the light transmission of the polymer. Degradation has the opposite effect and can be considered as a prompt way to study the aging of polymers and their radiation stability[2].

The aim of work

From literature survey it can be concluded that the effects of protons irradiation on properties of polycarbonate have received little attention. The present study deals with the investigation of the effect of proton irradiation on the structural and physical properties of Makrofol polycarbonate .

Samples

The present study is performed using Makrofol DE 1-1 CC. It is a bisphenol-A polycarbonate of chemical composition ($C_{16}H_{14}O_3$) manufactured by Farbenfabriken Bayer A. G., Leverkusen (Germany), with an average thickness of 300µm and density 1.2 g/cm^3 (its physical properties are given in Table 1). A set of ten samples each having sizes of 2 x 2 cm^2 are cut from commercially available sheets.

Table 1 Physical Properties of MakrofolDE 1-1 CC

Property	Guide Data	Units	Test Conditions
Density	1.23	g/cm^3	20 ˚C
Ultimate tensile strength	70	MPa	23 ˚C
Tensile strain at break	140	%	23 ˚C
Young's modulus	2300	MPa	23 ˚C
Glass transition temp.	150	ºC	
Light transmission	>80	%	

Irradiation Facilities

The Makrofol samples were exposed to a 1 MeV proton beam at the IonBeamCenter, University of Surrey, UK. The current density of the proton beam was 0.05 μA/cm^2 and the beam diameter was 0.2 mm. The irradiation was carried out at fluences in the range 10^{11}-10^{15}ions/cm^2, with the sample held at a vacuum of 10^{-6} Torr.

- **Polymer Characterization**

After irradiation, the samples were characterized by different techniques,

namely, X-ray diffraction,Thermal techniques (Thermo- gravimetric analysis).

1.X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is one of the most powerful techniques for qualitative and quantitative analysis of crystalline compounds. The technique provides information that cannot be obtained by other ways. The information obtained includes types and nature of crystalline phase present, structural make-up of phases, degree of crystallinity, and amount of amorphous content, micro-strain, size and orientation of crystallites[(3)].

2.Thermal Analysis

Thermal analysis refers to a variety of techniques in which physical property of a sample is continuously measured as a function of temperature, whist the sample is subjected to a pre-determined temperature profile.

Thermal Analysis techniques are used in virtually every area of modern science and technology. The basic information that these techniques provide, such as crystallinity, specific heat and expansion, are relied on heavily for the research and development of new products. Thermal Analysis techniques also find increasing use in the area of quality control and assurance, where demanding requirements must be met in an increasingly competitive world [(4)].

Results& Discussion

In the present work, Makrofol samples were irradiated using different fluences(10^{11}-10^{15} ions/cm^2)of 1MeV protons. The structural modifications in the proton irradiated Makrofol samples have been studied as a function offluence using different characterization techniques

such as X-ray diffraction ,thermo gravimetric analysis, differential thermal analysis, refractive index,electrical properties.

1.X-ray Diffraction

Figure (1) shows the X-ray diffraction patterns of the non-irradiated and irradiated Makrofol samples. From the figure we see that the X-ray diffraction patterns of the Makrofolsamples are characterized by halos extending in the 2θ range 14˚-32˚ with maximum diffraction intensity (peak) has been observed at 2θ=17˚. The profile of the halos shows that the Makrofol polymer is a partly crystalline polymer with a dominant amorphous phase. The area under these halos is proportional to the integral scattering intensity of the X-rays. The integral intensity of the halos was calculated; approximate indicative values are given in Table (2) and plotted in figure (1) as a function of the protonfluence[5].

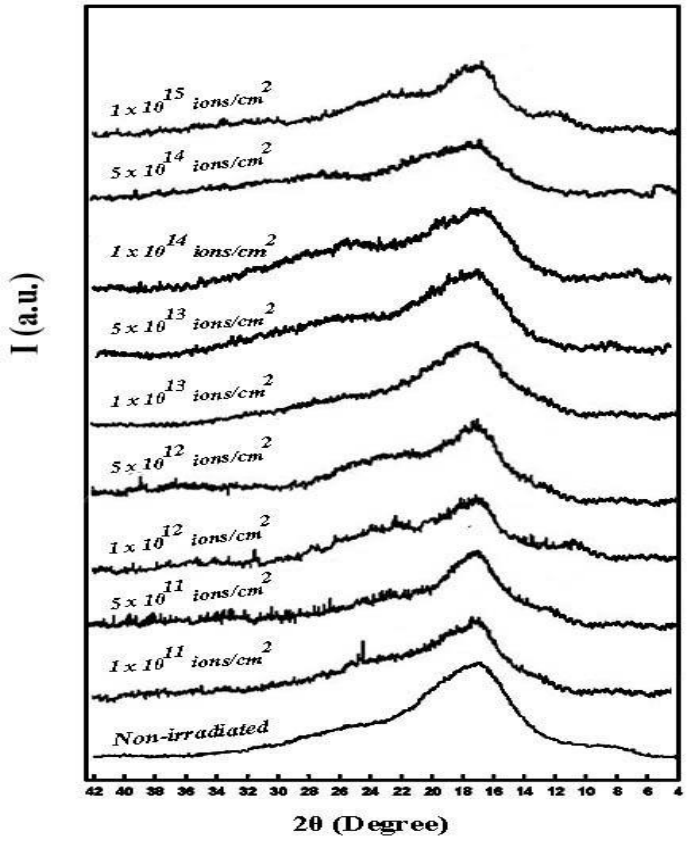

Fig 1: X-ray Diffraction Patterns of the non irradiated and proton irradiat

samples

Fig 1: X-ray Diffraction proton of the non irradiated and proton irradiated Makrofol samples.

Table 2 Values of integral intensity (I) and full width at half maximal intensity (ΔW) as a function of proton fluence

Proton fluence (ions/cm^2)	**I (a.u.)**	**ΔW (Radian)**
0.00	12.8	7
1.00E+11	17.2	6.5
5.00E11	19.3	5.6
1.00E+12	16.4	6
5.00E+12	12.7	6.2
1.00E+13	10.4	6.6
5.00E+13	9.8	6.8
1.00E+14	9.1	6.8
5.00E+14	8.5	7.2
1.00E+15	7.1	7.4

The figure shows that the integral intensity increases up to a maximum value around the 5x10^{11}ions/cm^{2}irradiated sample, then decreases with increasing the proton fluence up to 1x10^{15} ions/cm^2.

Since the halo's width at the half of maximal intensity, ΔW, is inversely proportional to the crystallite size, approximate indicative values of ΔW were calculated and are given in Table (2). Figure (2) shows the variation of ΔW with the proton fluence. The results indicated that the half width, thus the thickness of the lamella shows an opposite trend to that of the integral intensity, where it decreases until a minimum value around the $5x10^{11}$ions/cm^2irradiated sample, then increases with increasing the fluence up to $1x10^{15}$ ions/cm^2.

The increase in integral intensity indicates an increase in the crystallinity (ordering character) of the polymer samples which can be attributed to degradation (chain scission) induced by proton irradiation. This scission can reduce the number of entanglements per molecule. Chain scission can also act to relieve intermolecular stress in the amorphous region, thus increasing chain mobility. The increase

in mobility permits some molecules to re-crystallize because crystalline state is thermodynamic stable state [6-9].

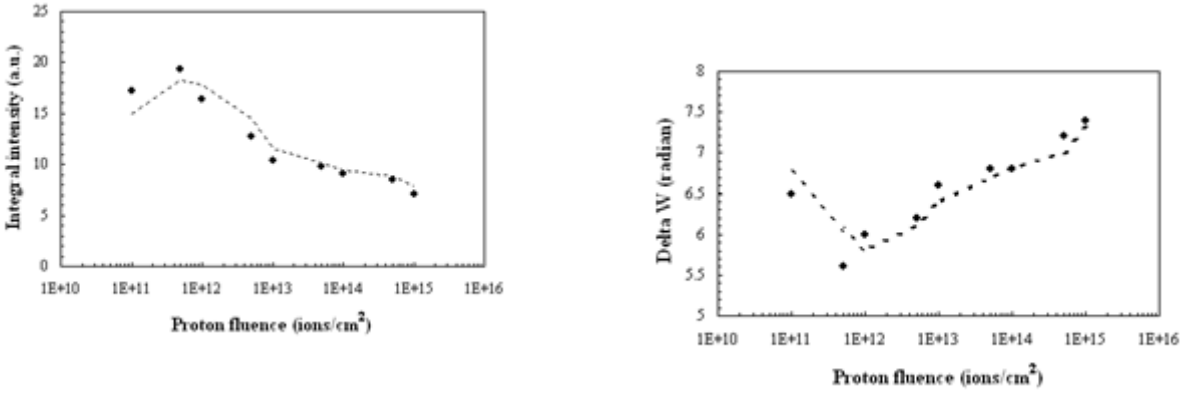

Fig 2 Variation of the integral intensity (I) and the full width at half maximal intensity (ΔW) of the main diffraction peak of Makrofolsamples with the proton fluence.

On the other hand, the decrease in integral intensity in the fluence range $5x10^{11}$-$1x10^{15}$ ions/cm^2 denotes a decrease in the amount of crystalline phase in the samples, indicating that the crystalline structure (lamella) has been destroyed. This could be attributed to the crosslinking which change the previously regularly arranged portions into non-arranged ones by forming new bonds between chains. This means that crosslinking is the predominant effect in this fluence range.

2. Thermal Analysis Techniques

The study of the thermal properties is useful for determination of several important parameters such as heat of reaction, heat of transition, sample purity, phase diagram, specific heat, reaction rate, activation energy, thermal resistance, etc. All of these properties are strongly dependent on the structure of polymers. Since radiation is one of the major factors that change the structural properties of polymers, it would be worthwhile to study the modifications on thermal properties due to irradiation[10].

.Thermogravimetric analysis (TGA)

Thermo-gravimetric analysis TGA and differential thermo gravimetric DTG were performed on Makrofol samples to get a better understanding of the changes in its thermal stability due to the proton irradiation. TGA was performed for non-irradiated and irradiated samples in the temperature range from room temperature up to 600 ˚C, at a heating rate of 10 ˚C/min and the obtained thermograms are shown in Figure (3). It is clear that the Makrofol samples decompose in one main weight loss stag[10]

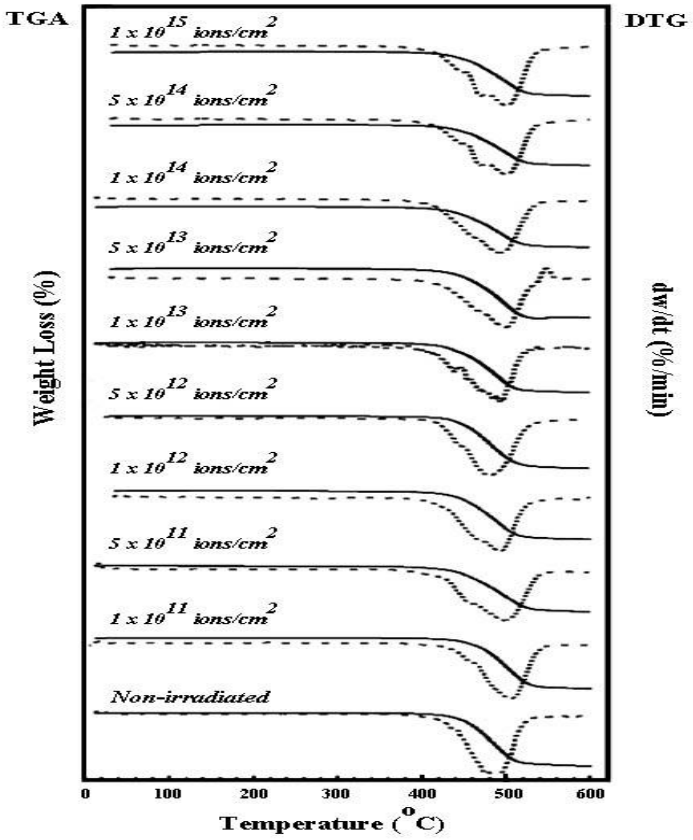

Fig 3 TGA and DTG thermograms measured in the temperature range from room temperature up to 600 ˚C, at a heating rate of 10˚C/min, of non-irradiated and irradiated Makrofol samples

Using the TGA thermograms, the values of onset temperature of decomposition T_o, the temperature at which the decomposition starts, were calculated and given in Table 3. Figure (3) shows the variation of T_o with the protonfluence. From the figure it is clear that T_o decreases until a minimum value around the $5x10^{11}$ ions/cm^2 irradiated sample followed by an increase on increasing the protonfluence up to $1x10^{15}$ ions/cm^2.

These results support that the degradation is the dominant phenomenon in the fluence range 0-$5x10^{11}$ ions/cm^2. Degradation led to formation of low molecular weight products, which decrease the strength of the polymer, thereby decreasing its ability to withstand high temperatures . At the fluence range $5x10^{11}$-$1x10^{15}$ ions/cm^2, the opposite effect was observed indicating that samples re-gain their thermal stabilities due to crosslinking process which strength the polymer against thermal degradation [11].

Proton fluence (ions/cm^2)	T_o (˚C)	E_aKJ/mol)
0.00	395	394
1.00E+11	388	385
5.00E11	373	370
1.00E+12	382	375
5.00E+12	398	382
1.00E+13	401	394
5.00E+13	406	397
1.00E+14	412	408
5.00E+14	418	418
1.00E+15	423	423

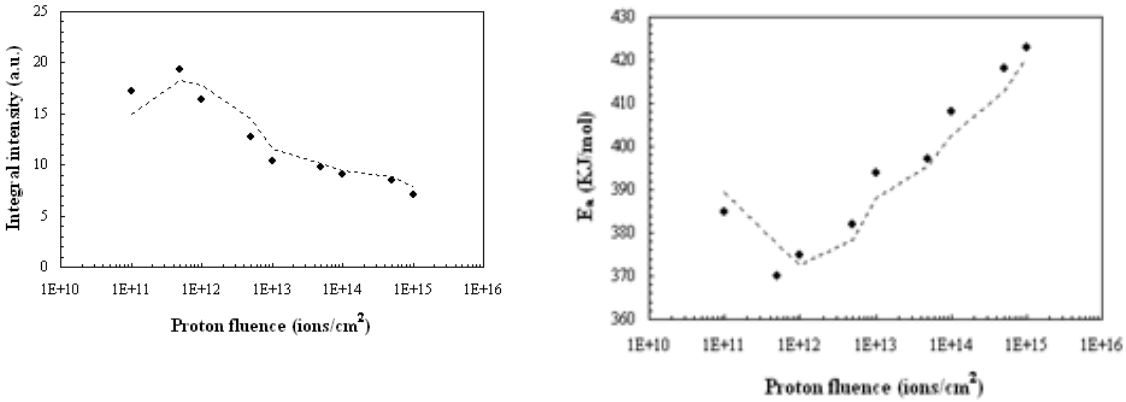

Fig 4 Variation of onset temperature of decomposition (T_o) and activation energy of thermal decomposition (E_a) with the proton fluence.

.Activation Energy of Thermal Decomposition (E_a)

Various thermogravimetric mathematical methods based on either the rate of conversion or the heating rate have been reported to determine the kinetic parameters of thermal degradation. The method proposed by Horowitz and Metzger[12] has been used in the present study for the measurements of the thermal activation energies.

Using the TGA data, values of activation energy of thermal decomposition E_a were calculated and are given in Table 3.4. Figure (4) shows the variation of E_a with the proton fluence. The figure shows that E_a exhibited a similar trend to that of T_o, where it decreases until a minimum value around the $5x10^{11}$ ions/cm^2 irradiated sample, indicating an increase in the thermal degradation rate. Above $5x10^{11}$ and up to $1x10^{15}$ ions/cm^2, it increases leading to an increase in the thermal decomposition rate.

At the fluence range 0-$5x10^{11}$ ions/cm^2, the proton irradiation leads to an acceleration of thermal degradation; this can be attributed to the change in structure which causes the thermal degradation to go through another pathway with higher rate of degradation. The opposite effect was observed in the fluence range $5x10^{11}$-$1x10^{15}$ ions/cm^2. This may be due to re-formation of the initial structure in the polymer[6].

Conclusion

From the study of the changes of the physical properties of Makrofol detector one can draw the following conclusions:

The Makrofol samples exhibit degradation under the effect of proton irradiation up to $5x10^{11}$ ions/cm^2, where crosslinking mechanism starts and continues until $1x10^{15}$ ions/cm^2. It should be noted that the samples are more crosslinked than the initial one.

When polycarbonate was irradiated with gamma radiation or electrons, the observed effect was only degradation of the polymer, while when irradiated with heavy ions, Makrofol undergoes degradation at first and with increasing fluence (dose) the crosslinking of chains starts to occur. It can be concluded that the behavior of Makrofol under proton irradiation is the same as that under heavy ions irradiation.

The degree of ordering in Makrofol detector was found to be dependent on the proton fluence. The irradiation of Makrofol detector at the fluence range ($5x10^{11}$-$1x10^{15}$ ions/cm^2) causes crosslinking which reduces crystallinity and increases the amorphous regions that enhance polymer resilience. Thus the Makrofol polymer may be suitable candidate for industrial application requiring it's bending without breaking.

The X-ray diffraction and differential thermal analysis measurements of irradiated Makrofol polymer show significant changes in its melting properties. This indicates that at the proton fluence range 0-$5x10^{11}$ ions/cm^2, the thickness of crystalline structures (lamellae) increases, thus the melting temperature increases, whilst at the fluence range $5x10^{11}$-$1x10^{15}$ ions/cm^2, defect generated splits the crystals so depressing the melting temperature.

Thermogravimetric analysis indicate that the irradiation of Makrofol detector by protons in the fluence range ($5x10^{11}$-$1x10^{15}$ ions/cm^2) led to a more compact structure of Makrofol polymer, whichresulted in an improvement in its thermal stability with an increase in the activation energy of thermal decomposition.This increase in thermal stability enhances the scope of this polymer in high-temperature applications and prolongs the service lifetime of articles made from this polymer.

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