The Effect of High Irradiation Energy (Gamma, UV- light) Radiation on the Energy Gap of Polymers Doped with Anthrancene

Ahmed K. Abdullah
Department of Physics, College of Science, Baghdad University, Baghdad-Iraq.

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Abstract

This research is related to the study of the energy gap of some glassy polymers (PC,PS and PMMA), we have studied the effect of gamma–ray and UV light radiation on the energy gap of these polymers and then the effect of dyes (anthracene) on the energy gap for these materials for exposure times (0 to 34 hr). It’s found that the energy gap of pure polymers and doped polymers measurement was changed depending on the gamma and UV dose and the mechanism of interaction between molecules of polymers and dye .It was found that the addition of anthracene to polymers leads to a reduction in the energy gap generally.

الخلاصة

تم دراسة تأثيراشعة كاما والاشعة فوق البنفسجية لبعض البوليمرات الزجاجية كبوليمر (البولي كاربونيت ، البولي ستايرين والبولي مثيل ميثا اكريليت) وتاثير هذه الاشعة على نفس البوليمرات بعد تطعيمها بصبغة (الانثراسين) من خلال حساب فجوة الطاقة لهذه المواد من طيف الامتصاص للاشعة فوق البنفسجية باستخدام جهازمطياف الاشعة فوق البنفسجية , حيث عرضت العينات لفترات زمنية مختلفة تتراوح بين(0− 34 ساعة تشعيع) ولكلا المصدرين ، لقد وجد ان فجوة الطاقة المقاسة للبوليمرات النقية والمطعمة بالصبغة تتغير أعتمادا على فترة التعرض للاشعة فوق البنفسجية واشعة كاما وميكانيكية التفاعل بين جزيئات البوليمرات وجزيئات الصبغة. حيث وجد أن تطعيم البولمرات المستخدمة بصبغة ألأنثراسين يؤدي الى نقصان فجوة الطاقة بصورة عامة.

Introduction

The effect of high- energy radiation on organic polymers is to produce ionization and excitation. Subsequent rupture of chemical bonds yields fragments of the large polymer molecules, which may retain unpaired electrons from the broken bonds. The free radicals thus produced may react to change the chemical structure of the polymer and alter the physical properties of the material. Ultraviolet radiation sources are widely employed to assess the weathering capability of polymeric materials, primarily because they can reduce the time required for evaluation [1, 2].

Theoretical Part

1. Photo degradation Mechanism of Polymers

One of the most important characteristics of a polymer is its molecular weight. Radiation can affect the molecular weight in two ways. It can increase it by linking molecules together (cross-linking) or it can decrease it, by inducing main-chain degradation .A third process is possible in principle: scission might occur in the main chain of the polymer, and at least one of the fragments might link to the main chain of a polymer [2].

The effect of high- energy radiation on polymers have been investigated by a number of workers [3,4]. Due to the nature of these materials, scissions and cross-links are most easily determined and polymers have catalogued as to whether they undergo one or the other of the two processes. Polymethyl methacrylate, polycarbonate and polystyrene were chosen for this study because one undergoes scission, while the others undergoes cross- linking , and in each case the alternative process is nearly absent .

2. The Role of Dyes in Photosensitized Degradation and Oxidation of Polymers

The wide applications of dyes to polymers are subject to many conditions [5]

1- Compatibility of dyes and polymer.
2- Formation of chemical and physical bonds between the dye and polymer molecule, e.g. salt formation, hydrogen bonding or van der waals forces.
3- Chemical structure of the polymer
4- Aggregation in the polymer material
5- Stability of the dye to heat, light, chemical agents, solvents, etc.
6- Photosensitizing effects of the dye.

3. Absorption Coefficient

The studying of the spectral dependence of the absorption coefficient is to distinguish between direct and indirect transition and estimate the energy gap.

The absorption coefficient is defined by [6]:

$\alpha\,(\omega) = 1/x \ln (I_o/I_T)$ ------1

Where I_o: is the intensity of the incident light and I_T is the intensity of light after transversing a thickness x of the sample material.

The absorbance can be determined by the relation

$A = \log_{10} (I_o/I_T)$ ---------2

So that the absorption coefficient in the term of absorbency becomes

$\alpha\,(\omega) = 2.303\, A/x$ -----3

4. Energy Gap

Insulators are characterized by completely filled valence band and empty conduction band. Thus no *intra* band transitions i.e., no classical IR absorption, takes place .Furthermore, the gap energy for insulators is fairly large (typically 5 eV or larger) so that *inter* band transitions do not occur in the IR and visible spectrum. They take place however in the ultraviolet region, and excitons may be created which can cause absorption peaks somewhat below the gap energy. [7].

The large band gap of insulators means that no visible light is absorbed and therefore passes right through the material. The material is transparent as long as there are no impurities

Introduction of an impurity places an intermediate level in the large band gap of an insulator. A donor level can absorb light by kicking electrons into the conduction band. An acceptor level can absorb light by receiving electrons from the valence band. This can result in the absorption of a visible frequency of light. The remaining transmitted light gives the material its color [6].

The developed power law which identified optical property is:

$(\alpha h\ \upsilon)^{1/r} \sim (h\ \upsilon - Eg)$ ----4

Where α: is the absorption coefficient (cm^{-1})

υ: is the frequency (sec^{-1})

Eg: is the optical energy gap (eV)

The value of r is 0.5 for direct transition, 3/2 for forbidden direct transition 2, 3 for indirect transition , the value of r for this research were chosen to be (2) for the best straight line i.e. indirect transition will happened.

By plotting (α h υ)$^{1/r}$ versus h υ for fixed r value , the extrapolation of the linear part with the x- axis could be used to define Eg [8] .

Experimental Part

1. Samples Preparation

Each of the three types of homo polymers (PMMA,PS and PC) were dissolved in methylene chloride and handily shacked to achieve better , the solution then transferred to clean petri dish of 6 cm diameter and leaves it for 24 hours in room temperature . The procedure repeated again by doping anthracene by dissolving it with methylene chloride solvent and then with each polymer to get the mixture, the concentration of the dopant to matrix (wt/wt) was then choose as 3.7×10^{-3} wt. /wt.

2. Gamma - Ray samples irradiation

The sample under study, were irradiated in air to energetic Gamma- ray, using ^{60} Co source (Gamma cell 900) manufactured by BHA Atomic Research Center /Trombay / Bombay /India. The dose rate was (0.59 kGy/hour). The samples were irradiated to different doses using different irradiation time ranging from (0 up to 34 h).

3. UV sample irradiation

The prepared film was irradiated with UV source (OHD – 300 watt high pressure Hg- lamp of the main emission lines at 254, 290 and 365 nm, for irradiation time ranging from (0 to 34 h).

4. Materials characterization

The UV/VIS spectroscopy measurements were carried out by using UV/160/Shimadzu spectrophotometer, which operating in the wavelength range of 200nm to 1100 nm and scanning speed of 1500 mm/min. , the instrument is computerized and it features on a CRT screen and a keyboard for operator input . This Shimadzu spectrophotometer has a full scale absorbency up to 2.5 .

Optical spectra are the principal means to obtain experimentally the band gaps and energies for inter band transitions .

Results and Discussion

1. γ – ray irradiation

In the Fig.(1,2,3) ,the energy gap of PMMA , PC and PS are very sensitive to radiation and hence one say its unstable polymers to radiation (effectively there is a radiation damage) ,while this means that there is less possibilities to form intermediate stable (impurity state), the adding of Anthracene act as photo stabilizer , because in the using of dyes in polymers, it is possible to extend the spectral range for the photo degradation of polymers into the visible region .

The characteristic feature of aromatic compound is their relative stability on irradiation, if aromatic compounds are mixed with other substances; they sometimes appear to absorb energy initially absorbed in the other component and so protect them from the effect of radiation (sponge- type protection).

In PMMA, the behavior of this materials suggests an energy transfer to the benzene ring , the effect of additives on the rate of scission under irradiation is to reduce the molecular weight of the films contains the protective substrate compared to the pure polymer. Polymethyl methacrylate becomes colored on irradiation because of the formation of stable free radicals or trapped electrons and partly because of the formation of conjugated double bonds.

The UV- absorption spectrum of PS is due to the transitions of the benzene ring, PS photoluminescence is due to the carbonyl groups presented in the polymer and styrene monomer. Oxygen causes linking of polystyrene because it diffuses into polystyrene after irradiation causes carbonyl and hydroxyl groups by the reaction with free radicals or double bonds . Anthracene , if present during irradiation become link to polystyrene because, for PS, the energy is dissipated per cross link, the effect of additives for PS shows a stabilizing effect due to the low mobility of the molecular segments in the solid and the cross linking is retarded considerably by the irradiation of PS films, Fig (6). i.e. the material demonstrates the stabilizing effect of a regularly occurring phenyl group on the main chain [9].

PMMA doped with anthracene shows highly sensitized to uv degradation as shown in Fig. (4). The exposed surfaces of anthracene doped PMMA were therefore severely damaged by uv degradation.

In the Fig.(5)the irradiation of PC shows a broad absorption peaks such peaks were reported to change in the structure of PC due to photo – fries rearrangement .

The PC self stabilization action caused by 2,2 dihydroxybenzophenone formed by photofries rearrangement prohibited the formation of the main chain scission and gel formation.

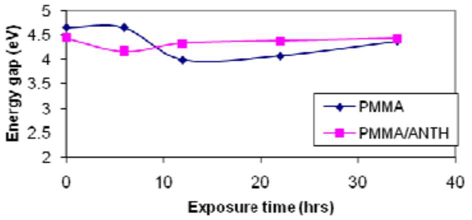
Increasing the irradiation time a slight changes in the absorption edge, Eg value and no change in the transition mechanism were observed. These results indicates that the used polymer are generally photo – stabilized.

Decreasing of absorption was also founded for the cases in which photodegradation caused surface damage .PS is more stabilized.

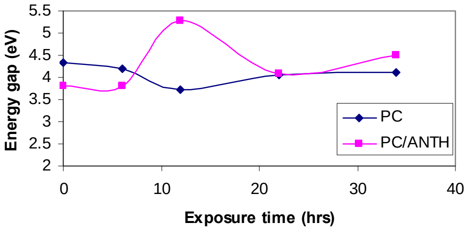
2. UV light irradiation

For doped PMMA, samples doped with anthracene showed low level effect of photo degradation. With anthracene, however PMMA was more sensitized to UV degradation as shown in Fig. (4). With increasing the irradiation time, the structured spectrum of PMMA / anthracene composites was gradually disappeared and the photo oxidation process was not efficient for this polymer matrix.

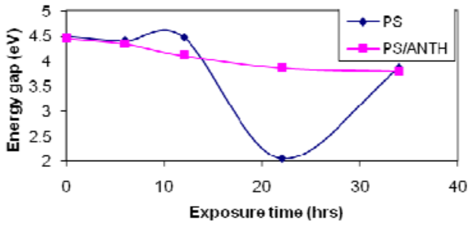
Polycarbonate (PC) has high optical clarity and excellent impact strength. However, under exposure it will yellow and becomes brittle. Recently, stabilized versions of polycarbonate have been developed. For example, Bayer has two products designated APEC 5391 and APEC 5393. The first is finally, several commodity polymer materials are being considered based upon their very low cost.



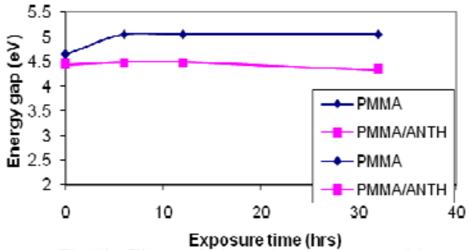
Fig(1) : The variation of energy gap with exposure time γ-radition for PMMA



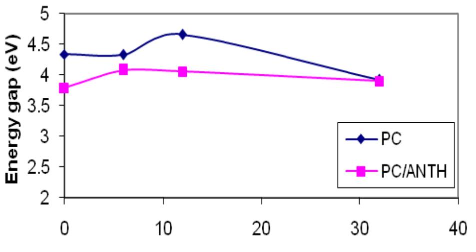
Fig(2) : The variation of energy gap with exposure time γ-radition for PC



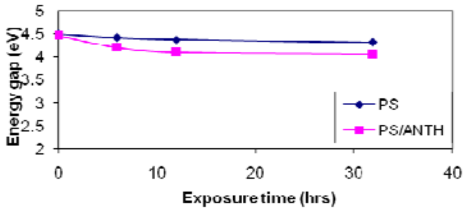
Fig(3) : The variation of energy gap with exposure time γ-radltion for PS



Fig(4) : The variation of energy gap with exposure time UV-radiation for PMMA



Fig(5) : The variation of energy gap with exposure time UV radiation for PC



Fig(6) : The variation of energy gap with exposure time UV radiation for PS

Conclusions

1- The energy gap for PC is stable against radiation, while the energy gap of PMMA and PS is very sensitive to radiation.
2- The addition of dyes to PC produced stabilization against radiation, while PMMA and PS is sensitive to dyes.
3- PMMA – Anthracene Composite showed UV photosensitivity and consequently UV photo degradation and photo oxidation higher than the other anthracene /polymer composites.
4- Self stabilization of PC of uv irradiated by photo-fries rearrangement did not significantly altered by doping.
5- Decreasing of absorption was also founded for the cases in which photodegradation caused surface damage .PS is more stabilized.
6- UV -Photodegradation increases the absorption of degraded samples and this cause high energy gap as compared with the energy gap of samples degraded by gamma radiation.

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