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The effect of annealing on the energy gap of Polyimide (PI) and Polyethylene terephthalate (PET) Polymers

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Abstract

The effect of annealing on the energy gap of PET and PI has been investigated. The annealing temperature were set at (75, 150, 200 and 240) °C which are less than the Tm of both polymers.

The energy gap are decreasing for PET and PI at different temperatures, the experimental results showed that the thermal energy and oxidation are the major factors responsible for the change in the energy gap of PET and PI.

الخلاصة

تم في هذا البحث دراسة تأثير التلدين على فجوة الطاقة لبوليمري البولي امايد والبولي اثيلين تيرافثليت. تراوحت درجات حرارة التلدين بين (75، 150، 200 و 240) درجة مئوية وهي بدرجات حرارة اقل من درجة حرارة الانصهار لكلا البوليمرين. لوحظ ان فجوة الطاقة تتناقص بزيادة درجة الحرارة ولقد اثبتت الدراسات التجريبية ان الطاقة الحرارية والاكسدة هما من اهم العوامل المؤثرة على تغير فجوة الطاقة لكلا البوليمرين.

Introduction

The degradation of polymers under normal use conditions is a major factor limiting application of these remarkable and versatile materials. Without exceptions, all polymers are regarded eventually within the environment to which they are exposed during their life cycle .though there is considerable variation between polymers in their resistance to degradation, eventually important properties of every polymer are effected adversely as those chemical reaction responsible for degradation proceed. Loss in mechanical strength, dielectric quality and aesthetic appearance often lead to failure of polymeric materials, as a result of degradation reactions, critical mechanical, dielectric aesthetic and optical properties may change beyond acceptable limits [1], Aymen studied the effect of uv radiation on the optical properties of polymers and composites [2]. Giesse and Maerco studied the surface and photooxidation of PE under uv radiation [3].

Polyimides are polymers that usually consist of aromatic rings coupled by imide linkages that is, linkages in which two carbonyl (CO) groups are attached to the same nitrogen (N) atom. There are two categories of these polymers, condensation and addition. The former are made by step growth polymerization and are linear in structure, the latter are synthesized by heat – activated addition polymerization of dimides and have network structure. Polyimides are amorphous plastics that characteristically exhibit great temperature stability and high strength, especially in the form of composites. They are used in aircraft components, sporting goods and adhesives [4].

The polyesters all have the ester group in their repeated structures. Due to this ester group polyesters are subject to hydrolysis at high temperature. Therefore, they must be extremely dry when they are processed in the melt. There are many types of polyesters which cover a wide range of properties. Only commercially well established polyesters are presented here. Most of the polyesters are crystalline with high melting temperatures. They have high densities compared to polyolefins but low densities compared to the fluorocarbons. The major industrial polyester include Polyethylene terephthalate, Polycarbonate, alkyds and unsaturated polyesters [5] .

Theoretical Part

1. Absorption Coeffient

The fundamental absorption edge of semicondutors and insulators corresponds to electron transition between the highest nearly filled band and the lowest nearly empty band was the objet of some of the earliest investigations of the optical properties [6].

The decrease of light intensity during transmission –dI/ Id, is proportional to the light intensity, I:

$-dI/Id = \alpha I$ ----- (1)

where α is the absorption coefficient, or

$I = I_o e^{-\alpha \iota}$ -------(2)

$I_o/I = e^{-\alpha \iota}$ --------- (3)

$\alpha \iota = \ln (I_o/I)$ ----(4)

$\alpha \iota = 2.303 \log (Io/I)$ -----(5)

$\log (I_o/I) = A$ -------(6)

$\alpha \iota = 2.303 A$ ------(7)

The absorption coefficient α in term of absorbancy becomes

$\alpha = 2.303 A / \iota$ -----(8)

2. Optical energy gap

The developed power law which identify optical property is [7]

$(\alpha h\upsilon)1/r \sim (h\upsilon - Eg)$ ----(7)

where a: is the absorption coefficient, u: is the frequency (Hz) and Eg: is the optical energy gap(eV).

r: is constant for field electronic transition (the value of r is 0.5 for direct transition, 3/2 for forbidden direct transition, 2 and 3 for indirect transition [8].

Experimental Part

1. Materials

Two types of thermoplastic polymers was used, PET and PI polymers

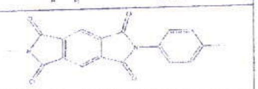
Mate rials	T_g (°C)	T_m (°C)	Chemical Structure
PET	80	250	
PI	320	385	

Table (1): Some properties of PET and PI [9]

2. SPECTROSCOPIC MEASUREMENTS

The UV-VIS spetrosopy measurements were carried out using UV/160 Shimadzu spetrophotometer which is operating in the wavelength of 200 nm to 1100 nm and scanning speed of 1500 mm/min. The instrument is computerized and its features on a RT screen and a keyboard for operator input. The full sale absorbency up to 2.5 .

3. Annealing process

Annealing was carried out by placing the specimens in an oven of temperature varied between 75, 150, 200 and 240 oC for one hour.

Results and discussion

To investigate the electronic transition for PET and PI, UV-Visible spectroscopy was used to determine the type of electronic transition for the two polymers. The experimental results to determine the value of (r) for PET and PI represent a transition of a direct type (r=0.5) for both annealed and un annealed sample [10].

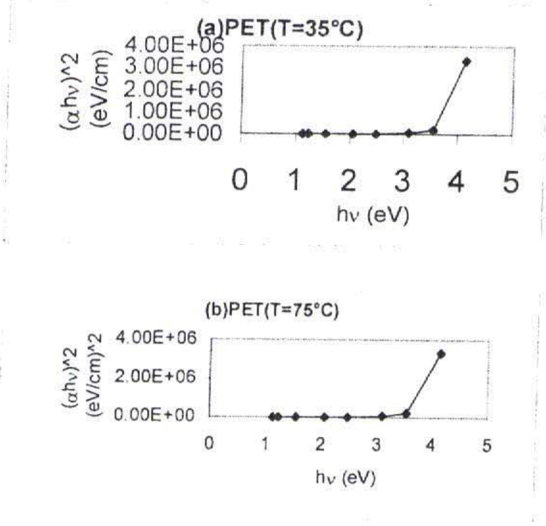
By plotting $(\alpha h\upsilon)^{1/r}$ versus hυ, the extrapolation of the linear part could be used to determine the energy gap as in fig(1), the energy gap for insulators is larger than that of semiconductors and metals, because the valance band states is filled with electrons, while the conduction band is empty, thus no transition of electrons is done without any excitation bands. The thermal energy are the major factor responsible for the change of energy gap of PET and PI , heat treatment were carried out under different annealing temperature range from (75, 150, 200 and 240)°C respectively, fig (2) which shows a decrease in the energy gap for PET, we observed that the energy gap of PET is approximately constant for different temperatures. The stability of many plastics is limited by the carbon – hydrogen bond and it can be increased by replacing the hydrogen with an atom or groups of atoms with greater combining strength.

The thermal stability for PI is also conferred by the incorporation of aromatic (benzene) ring into the polymer chain. The extra bonds provided by the ring structure make the polymer more resistant to thermal degradation and in the case of PI, this polymer contain aliphatic chains between aromatic nuclei in the diamene portion, thermal oxidation began at temperatures as low as 230 °C [11].

All commercially important polymers undergo reactions with oxygen leading eventually to changes in molecular structures or in morphology [9], the rate of oxidation increases with temperature and excessive oxidation is quite likely to occur under these condition unless the polymer has been adequately stabilized.

The combination of oxygen as the reactant and heat as the energy source is a major factor in polymer degradation [3]. Thermal energy is the major factors responsible for accelerating oxidative degradation, for the polymer which contains significant hydrocarbon segment, oxidation by radical – initiated chain mechanism can contribute to the overall degradation mechanism. In other non hydrocarbon polymers, different reaction mechanisms are primarily responsible for degradation, The free radical–initiated, chain reaction mechanism developed to explain thermal oxidation is similar to reactions which take place during photo oxidation.

The thermal energy and oxidation are the major factors responsible for the change in the energy gap of PET and PI.



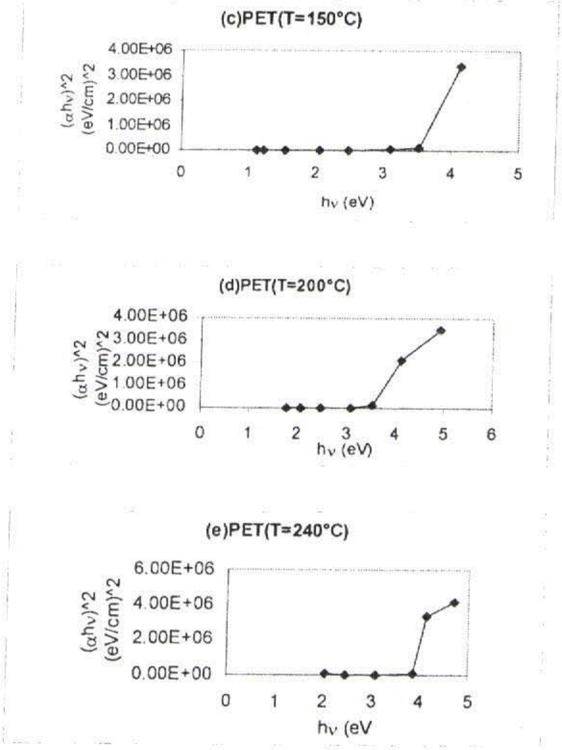
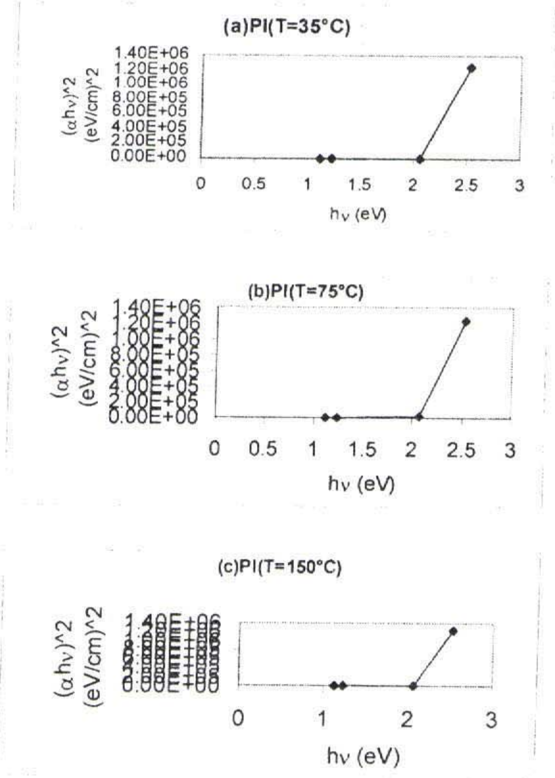


Fig.(1) :Energy gap calculation for PETat different temperatures



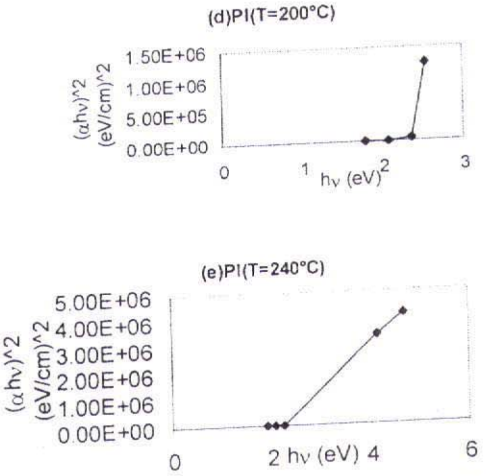


Fig.(2) :Energy gap calculation for PI at different temperatures

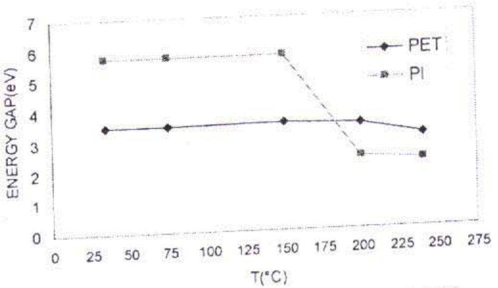


Fig.(3);The relation between energy gap (eV) & temperature (°C) for PET &PI.

Conclusion

1. The experimental results for determine the value of (r) for PET and PI represent a transition of a direct type (r=0.5) for both annealed and un annealed sample.
2. The extra bonds provided by the ring structure make the polymer more resistant to thermal degradation and in the case of PI.
3. The energy gap of PET are approximately constant at different temperature.

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