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

A. K. Abdullah, H. I. Jaffer and Z. R. AL-Shamri
Department of Physics, College of Science, University of Baghdad, Baghdad-Iraq.
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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.

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 affected 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 Maesco 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 Polycarbonate, alkyds and unsaturated polyesters [5].

Theoretical Part
1. Absorption Coefficient
The fundamental absorption edge of semiconductors and insulators corresponds to electron transition between the highest nearly filled band and the lowest nearly empty band was the object of some of the earliest investigations of the optical properties [6].

The decrease of light intensity during transmission —dl/ld is proportional to the light intensity, I:

\[ \text{dl}/ld = \alpha I \]  

where \( \alpha \) is the absorption coefficient, or

\[ l = l_0 e^{-\alpha l} \]  
\[ l_1/l = e^{-\alpha l} \]  
\[ \alpha = \ln (l_0/l) \]  
\[ \alpha = 2.303 \log (l_0/l) \]  
\[ \log (l_0/l) = \alpha \]  
\[ \alpha = 2.303 A \]  

The absorption coefficient \( \alpha \) in terms of absorbance becomes

\[ \alpha = 2.303 A / l \]  

2. Optical energy gap
The developed power law which identify optical property is [7]

\[ (a + b) r = (c - d) E_g \]  

where a: is the absorption coefficient, \( r \): is the frequency (Hz) and \( E_g \): 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 were used, PET and PI polymers

<table>
<thead>
<tr>
<th>Material</th>
<th>( T_g (^\circ C) )</th>
<th>( T_m (^\circ C) )</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>80</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>PI</td>
<td>320</td>
<td>385</td>
<td></td>
</tr>
</tbody>
</table>

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

2. SPECTROSCOPIC MEASUREMENTS
The UV-VIS spectroscopy measurements were carried out using UV/160 Shimadzu spectrophotometer 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 scale 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 ⁰C 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 unannealed sample [10].

By plotting \( (a+b)r \) versus \( h\omega \), 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 valence 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 \( 240 \) ⁰C 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 of 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 diamine portion, thermal
oxidation began at temperatures as low as 230 °C
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.
3. The energy gap of PET are approximately constant at different temperature.

References

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 unannealed sample.
2. The extra bonds provided by the ring structure make the polymer more resistant to thermal degradation and in the case of PI.