Electrical and optical properties modification of polystyrene by Vanadium (V) ion-pair organometallic complex

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ABSTRACT
The present study focused on the modification of the electrical and optical properties of polystyrene films with salt additive, namely, (n-butylammonium-oxobis (8-quinolyloxo) Vanadium(V)[VO\textsubscript{2}O\textsubscript{2}]\textsuperscript{2+} [(n.BuNH\textsubscript{2})\textsubscript{2}]\textsuperscript{-}, by preparing the composites with different percentage (2,3,4,5,6) wt% of this ion-pair additive. The experimental results show that the DC electrical conductivity for all composites is increased by several orders of magnitude with increasing filler contact. The activation energy is also determined and found to decrease with increasing filler concentration. The optical data were analyzed and interpreted in term of electronic transitions.

Key words: polystyrene, DC electrical conductivity, The activation energy.

INTRODUCTION
In general polymers are good electrical insulators, having resistivities which are about(10\textsuperscript{18}) times greater than those of metals. Although the main interest in the electrical properties of polymers was effectively limited to their electrical insulating properties, considerable scientific research projects have been devoted to modify some of these properties.[1]

These conductive composites have general emerged as a new group of engineering materials. Lately, possible application include (a) discharging static electricity, (b) heat conduction, (c) electrical shielding, (d) electrical heating, (e) converting mechanical to electrical signals, (f) absorbing electromagnetic waves, and (g) friction- anti friction materials. The materials are likely to have the following advantage comparison with metals: high corrosion resistance, low specific weight, ease of workability, when manufacturing products of complex shapes, are desired low cost, and great accessibility.[2]

Electrical properties and polymer aging are both related to molecular weight and its distribution. Thus generation of materials with desired electrical properties and optimum long term properties are very much dependent upon the knowledge of molecular weight characteristics.[3]

In an attempt to improve conductivity in solid polymers, we have examined several approaches. These include the preparation of new polymer-salt complexes, the use of soluble additives that would provide conduction pathway and the use of certain insoluble additives that might also tend to improve electrical properties.[4]

No reports have been detected in literature for using a double-salt of transition metal chelate complexes as electrical conductivity modification of polymers. Therefore in the present study, attempt were carried out to use Vanadium(V) chelate-amine ion-pair complexes as ionic additive for the modification of DC electrical and optical properties of polymers thermoplastic.
MATERIALS AND METHODS

The studied polymer-ion-pair composites were prepared by the following casting method: polystyrene (ps) grains, (commercial, type) was first purified from antioxidant additive by reprecipitations three times from chloroform solution in ethanol. The purified (ps) was dried under reduced pressure at 40°C for 48 hours, then it was dissolved in benzene. The desired salt additive \([\text{VO}_2\text{O}_2]^+ [(\text{n.BuNH}_2)_2]^−\) was added and the mixture was cast into a glass dish of dimensions 5x5 cm² and kept in a dry atmosphere at 40°C for 24h. Thickness of produced samples was 110 pm measured by digital micrometer (type Mitutoyo)0-25nm.

The ion-pair salt: (n-butylammonium-oxobis (8-quinolyloxo) Vanadium(V) was synthesized as described by Blair and Coworkers.[5]

Three- electrodes cell or (guard ring electrode method) was used to study the effect of weight % of filler additives and temperature on volume conductivity of polymer composite[6]. The complete system is schematically shown in Figure(1). The electrical input was provided by means of stabilized D.C. power supply (Phillips Harris Limited) which provided an output voltage from (0-6 kV). In this work the maximum voltage used was (1500) Volt. The output current was measured by keithly instrument (616) digital solid state electrometer which provides direct ready current ranges up to \(10^{-15}\) ampere full scale. The measurement of volume resistivity were performed in the temperature range between (30-100°C) by using a temperature controlled oven (Hereaus-Electronic).

The absorption spectrum of films was recorded at room temperature using Ultraviolet- Visible spectrophotometer type Hitachi U-2000 in the wavelength range (200-900)nm.

RESULTS AND DISCUSSION

1. DC-electrical properties:

The temperature dependence of electrical conductivity is shown in Fig(2) for different weight percentage of the salt additive. The figure show that the conductivity is increasing with increasing temperature, this behavior can be explained by the increasing of ionic charge carrier as well as increasing of polymer segmental motion as a result of temperature increase[7]. Similar behavior was reported by Frand, et, for PMMA-LiClO₄ system[8] and by Ander for polythiophene-BF₄ system[9].
The relationship between \( \ln \sigma \) and \( 1/T \) gives two straight lines as shown in figure(2). The presence of two activation energies suggests two different activation processes. These are the band conduction and conduction by hopping phenomena. The same conclusion has been reported by Matsushita and Coworkers for PS-silver composite[10] and by Kaplan for PEO (polyethylene oxide)- LiCF3SO3 complexes[4] and by Swapan for PVC (poly vinylchloride)-copper composites[11] and by Angelos for polyethane-Nickel composites[12].
Activation energy values are tabulated in Table (1). The high activation energy values for polymer sample without additive (control) can be attributed to the thermal movement of the ions and molecules. Whereas the electronic conduction mechanism which is related to the decreasing of the distance between filler particles. It has been reported that for these kinds of composites, ionic, electronic, or even mixed conducting processes are possible [13, 14].

Table 1. The values of activation energies for the dc electrical conduction in ps-[VO₂O₂]⁺[(n.BuNH₂)₂]- salt composites

<table>
<thead>
<tr>
<th>Wt %</th>
<th>E_g1 (eV)</th>
<th>E_p1 (eV)</th>
<th>E_g2 (eV)</th>
<th>E_p2 (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure ps (control)</td>
<td>0.80750</td>
<td>0.25500</td>
<td>3.850</td>
<td>0.250</td>
</tr>
<tr>
<td>2%</td>
<td>1.925</td>
<td>0.325</td>
<td>3.100</td>
<td>0.100</td>
</tr>
<tr>
<td>3%</td>
<td>1.825</td>
<td>0.375</td>
<td>2.980</td>
<td>0.120</td>
</tr>
<tr>
<td>4%</td>
<td>1.625</td>
<td>0.275</td>
<td>2.650</td>
<td>0.150</td>
</tr>
<tr>
<td>5%</td>
<td>1.550</td>
<td>0.350</td>
<td>1.950</td>
<td>0.550</td>
</tr>
<tr>
<td>6%</td>
<td>1.500</td>
<td>0.650</td>
<td>1.900</td>
<td>0.500</td>
</tr>
</tbody>
</table>

The variation of electrical conductivity as a function of filler content at temperatures (30, 100°C) is shown in figure (3). The conductivity increases as a result of increasing of ionic charge carries [15].

II. Optical properties:

The absorption coefficient $\alpha$ is calculated using the following relation [16].

$$\alpha = \frac{2.303}{d} A$$

Where $A$ is the absorbance and $d$ is the thickness of the film.

At a low absorption coefficient $\alpha \leq 10^4$ cm$^{-1}$, the absorption data were analyzed in terms of the theory of phonon assisted indirect electronic transition.

According to this theory the absorption coefficient depends on the photon energy $hv$ [17].

$$\alpha = \alpha_o (hv - E_g \pm E_p)^r / hv$$

Where $E_g$ is the minimum energy gap, $E_p$ is the phonon energy, (+) absorbed and (-) emitted, $r$ takes the value of 2 for allowed indirect transition and 3 is for forbidden indirect transition [17].

The spectrum for the undoped ps sample shown in figure (4) exhibits one absorption band and this band corresponds to the known electronic transition of the delocalized electrons of the aromatic rings hanging on the main polymer chain [18].

For doped samples, two new bands are apparent in the absorption spectrum fig (5 (a,b)) that was attributed to the formation of polarons and biopolarons in the doped films [19].
The evidence of polaron formation is made the reaction in band to band transition due to shift the band density of state towards the gap. This observation is not similar to the doping in conventional semiconductor when the band to band absorption strength does not affected by the formation of dopant state in the gap.[20].

The present results indicate the existence of two bipolaron bands in the energy gap. The first one which represents the transition from valance band to bonding bipolaron band. The second band represents the transition from valance band to anti-bonding bipolaron band which is in a good agreement with results found by Ziadan for polypyrrole/PVC conducting polymers films[21].

Finally one might conclude that n-butylammonium-oxobis(8-quinolyloxo) Vanadium(V) ion-pair complex is effectively modify the DC electrical and optical properties of polystyrene thermoplastic. The activation energy of the conductivity process is found to be decreased as the percent weight ratio of the ion-pair complex is increased.
The two new bands apparent in the optical spectrum of the polystyrene ion-pair vanadium(V) complex blend is attributed to the formation of polarons and bipolarons in the doped polystyrene films.

REFERENCES