Optical Properties of Prepared Polyaniline and polymethylmethacrylate blends

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Abstract

The optical transmission and UV-VIS absorption spectra have been recorded in the wavelength range (200-850nm) for different composition of polyaniline and polymethylmethacrylate (PMMA) blends thin films. The optical energy gap ($E_{opt}$) refractive index and optical dielectric constant real and imaginary part have been evaluated. The effects of doping percentage of prepared polyaniline on these parameters have been discussed and the non-linear behavior for all the parameters are investigated.

Keywords: optical properties, PANI-PMMA blends, prepared polyaniline, Non-linear behavior

1. Introduction

During the last decade there has widespread interest in conducting polymer, polyaniline (PANI) is one of the most useful conducting polymers due to their simple synthesis, good environmental stability. It also has a wide range of electrical properties which can be easily controlled by changing its oxidation and protonation states [1], [2]. However, major problems relating to successful utilization of the PANI are poor mechanical property and low solubility in aqueous and organic solvents. Improvement of polyaniline properties can be achieved either by forming composites and nanocomposites of aniline, or blending with commercially available polymers or inorganic material which offer better mechanical and optical properties, stability and process ability of the PANI [3],[4]. The PMMA is chosen as dielectric matrix due to its high transparent ability in visible spectral range which is important for optoelectronics, sensors and “smart window” applications [5].

Therefore, we have studied, in this work, the optical properties and the energy gap as a function of preparation conditions and doping concentration but this study needs more attention in the nearest future

2. Basic relations

The complex refractive index N is given by [6].

$$ N = n - ik $$  

where, (n) is the real refractive index, and extinction coefficient (k) which is the imaginary part of N and can be obtained from the relation

$$ k = \frac{\alpha \lambda}{4\pi} $$  

where, $\alpha$ is the absorption coefficient which is the decrement ratio of incident radiation relative to unit length in the direction of wave propagation inside the medium. $\lambda$ is the wavelength. The reflectance part (R) of incident electromagnetic plane wave can be obtained when the transmittance (T) and the absorbance (A) part are known since

$$ R = 1 - (A + T) $$

For normal incident of plane electromagnetic wave the reflectance is given by the equation (4)

$$ R = \frac{(1+n)^2 + k^2}{(1-n)^2 + k^2} $$

which leads to

$$ n = \sqrt{\frac{4R}{(2-R)(2+R) - 1}} $$

thus n can be calculated when the reflectance R and k values are known.

The transmittance part of incident light is depending on $\alpha$ through the following equation [6].

$$ I = I_0 e^{-\alpha d} $$

where d is the thickness of the sample. Thus the absorption coefficient $\alpha$ that is corresponding to any wavelength $\lambda$, can be calculated by applying the relation:

$$ \alpha = \frac{1}{d} \ln \frac{I_0}{I} $$

The dielectric constant $\varepsilon$ which represents the responsively of electron in matter to be the incident electromagnetic field, depends on frequency. Its real part is $\varepsilon_1$ which represents the polarization term and its imaginary part $\varepsilon_2$ can be calculated from equation [7].
\[ \alpha h \nu = A(h \nu - E_g)^{r} \]

where \( A \) is a constant, \( h \nu \) is the energy of incident photon, which can be calculated using the equation

\[ \nu = \frac{1240}{\lambda (\text{nm})} \]

And \( r \) is the order of the optical transition depending on the nature of electronic transition.

3. EXPERIMENTAL

The preparation of (PANI) is based on the oxidation of 0.2 M aniline hydrochloride with 0.25 M ammonium peroxy disulfate in aqueous medium which is dissolved in 1 M HCl aqueous solution in a volumetric flask ending with a 50 ml of solution. On the other hand, ammonium peroxy disulfate is similarly dissolved in 1 M HCl, yielding also a 50 ml solution. Both of these solutions are mixed at room temperature in a rounder and gentle stirring to polymerize the mixture is left to rest to the next day. The (PANI) precipitate is collected on a filter and washed with three 100 ml of 0.2 M HCL and 150 ml of acetone. Polyaniline (emeraldin) hydrochloride powder is dried in air for about one hour and then in vacuum oven set at 80 \(^\circ\)C for 6 hours the average yield is 1.95 g.

3.1 Preparation of PMMA solution

The 1.00 g of PMMA was dissolved in 10 ml of chloroform solvent, the solution stirring for 2 hrs. to allow polymer to dissolve completely to yield clear solution. in the same way The PANI solution was prepared by weighted 0.1 g of PANI and dissolved in 10ml of dimethyl formide (DMF) and stirring for 3 hrs.. After allowing those to dissolve completely, the solution were mixed of PANi and PMMA were prepared separately. The solution was prepared by mixing the appropriate amount of each stock solution to a chive the desired blend composition. The final concentration of each casting solution was adjusted to the (0,10%, 30%, 50%, 70%) of PANI (100%,90%.70%,50%,and 30%) of PMMA, the blend solution was cast onto a glass plate. A glass plate of 10 cm long was washed with hot water and then cleaned with acetone to serve as a substrate. To achieve perfect leveling and uniformity in the thickness of the film the glass plate was kept freely in the air for 24 hrs. and for another 2hr in oven and the film was heating at constant temperature (50 \(^\circ\)C) to remove the traces of solvent finally, the UV/Visible spectroscopy was used to study the structure of transmission and absorption of the prepared samples. The absorbance A and transmittance T of the sample were measured in the 190 – 850 nm wavelength range.

4. RESULTS AND DISCUSSION

Figure 1 shows the variation of \((\alpha h \nu)^{2}\) with photon energy \((h \nu)\) for direct allowed transition of both pure, Figure 1 (a),

\[ \text{Figure 1 (\(\alpha h \nu)^{2}\) vs. (\(h \nu\)) for (a) PMMA pure and (b) for doped samples with different polyanilin weight percentage as a doping material.} \]

curve in figure is extrapolated to the energy axis to give the value of the optical energy band gap. The calculated values are given in table 1 and plotted in figure 2.

<table>
<thead>
<tr>
<th>PANI wt%</th>
<th>Optical energy gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA pure</td>
<td>5.4</td>
</tr>
<tr>
<td>10%</td>
<td>4.4</td>
</tr>
<tr>
<td>30%</td>
<td>3.9</td>
</tr>
<tr>
<td>50%</td>
<td>3.6</td>
</tr>
<tr>
<td>70%</td>
<td>2.85</td>
</tr>
<tr>
<td>PANI pure</td>
<td>2.7</td>
</tr>
</tbody>
</table>
From the table, the PANI doping decreases the optical band gap from 5.2 to 2.85 eV for PMMA and upon increasing the PANi concentration to 70%, the transition changed to the forbidden direct transition. The reduction in the optical band gap is probably due to the modification of the polymer structure [5].

Figure 2 shows the relation between the energy gap and the concentration weight percentage of PANI. It can be seen from this Figure that all samples have one allowed direct optical energy gap except the sample with 70% PANI which has a forbidden direct optical gap. It’s been found that energy decreases with increasing the concentration percentage of PANi. The addition PANI, above 10%, increases the degree of disorder then selective absorption of the photon energies of incident light that such energy is devoted to breaking up and hence deforming of partially crystalline structure of the polymers [9].

The dispersion curve of n (λ) is presented in figure 3 for pure and doped PMMA samples. The refractive index is as a function of light wavelength. The reflective index is decreasing in PMMA pure, and the doped sample with 70% PANI with increasing wave length, compared with (10, 30 and 50 wt. %) where in this sample the reflective index is increasing with wave length. Because the addition of PANI it deportation that is led to decreasing, in general, the reflective index increases by increasing the C – H bonds [10], [11].

The real and imaginary parts of the dielectric constant as a function of wavelength are shown in Figure 4 (a and b) for pure and blend samples at different concentration. It is clear that the variation of ε₁ mainly depends on the values of n² as a result of small values of k² in comparison with n², while ε₂ mainly depends on the k values which are related to the variation of absorption coefficient.

Figure 2: The optical energy gap as a function of PANI Wt. % for PMMA polymer.

Figure 3: The vibration of reflective index as a function of wavelength for pure and doped blend samples.

Figure 4: The real, ε₁, and imaginary, ε₂, dielectric constants vs. wavelength for PMMA and polyaniline blend polymers (a) and (b) respectively.
5. CONCLUSIONS
In this work, we have prepared the polyaniline polymer via the oxidation of 0.2 M aniline hydrochloride with 0.25 M ammonium peroxy disulfate in aqueous medium. Measurements of optical energy gap and optical parameters such as refractive index and dielectric constants are strongly depending on the light wavelength. The minimum optical energy gap value is about 5.4 eV for PMMA polymer and decreasing when the polymer is doped with polyaniline wt% in blend samples. It is found that all samples have allowed optical energy gap except the 70% polyaniline wt% which has showed forbidden direct energy gap.

References

AUTHOR

Salma M. Hassan (born in Baghdad in July, 1972). Received a B.Sc (1994) M.Sc (2001), and Ph.D. (2010) in material physics from Baghdad university. She was a lecture at the material lab of the physics Department-College of Science of Baghdad university. Her research interest in material physics field, and she has many published research in conjugated polymer and polymer blends.