Study Optical Properties of (GA) Polysaccharide/Polyvinyl alcohol thin films

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Abstract
In this research a new Thin films from mixing together natural polymer (Gum acacia) polysaccharide with artificial polymer (polyvinyl alcohol) have been prepared using cast method. Optical absorption spectra of these thin films have been recorded in the wavelength range (200-900) nm using UV-spectrophotometer. With thickness (3μm) the Optical band gap of the films has been calculated by using Taucs relation and variations in the values of optical band gap with the variation of concentrations in the blend films have been found from (3.75 -4.1) eV.

Keywords: Natural polymers, Optical band gap, Optical conductivity, Absorption coefficient

1. Introduction
A polymer of particular group is characterized by the molecular weight of the monomer unit. In recent years, polymers with different optical properties have been attracted much attention due to their application in the sensors [1], light emitting diodes [2]. The doped polymers have been the subjects of interest for both theoretical and experimental studies, because of the physical and chemical properties needed for specific application may be obtained by adding or doping with some dopant. Poly (vinyl alcohol) (PVA) is a polymer that has been studied intensively due to its several interesting physical properties, which are useful in technical applications including biochemical and medical [3], and is of relatively low cost in manufacture [4]. Gum acacia is a natural polysaccharide formed by alkaline deactivation of the second most abundant naturally occurring chitin of crab and shrimp shells. Due to the amino groups that (GA) possesses in its chain, it can be dissolved in dilute aqueous acid solutions, such as hydrochloric acid and propionic acid. Since it is inexpensive, non-toxic and possesses potentially reactive amino functional groups, gum acacia has been evaluated for numerous applications, including medicine, food, cosmetics and wastewater treatment [5]. The purpose of the current investigation was to study the effect variation of percentages of Gum acacia (GA) on the optical properties of PVA films.

2. Experimental work
2.1. Sample preparation:

The PVA polymer obtained in powder form (BDH chemicals) has approximately molecular weight (10000 g/mol) and GA polymer supplied by (Aldrich) were used in this study. The thickness of the prepared films was measured by a compound microscope (Nikon) in conjunction with an acculometer which gives least count 10 and 2 μm at the magnification 1:10 and 1:200, respectively was used. Small section of the sample was taken and mounted vertically to get a clear section view of the thickness. The film used for the present study is of the thickness (3 μm).

The polymers were dissolved in HCL by using magnetic stirrer in mixing process to get homogeneous solution at 75°C for about 2 hours, then the solution was cooled at room temperature. Different concentrations (0:100, 25:75, 50:50, 75:25, 100:0) of two polymers are poured in to clean glass Petri dish for 3 days to obtain homogeneous films. Ultraviolet-visible absorption spectra were measured in the wavelength region of (200-900) nm using single beam (Jenway 7315) UV/VIS spectrophotometer.

2.2. Optical measurements:
The UV-vis absorption spectra of blend GA/PVA films are recorded at room temperature in the wavelength range (200-900) nm as shown in Fig.1. The optical absorption of the polymer films in the UV region is high, and this aspect highlights the possibilities of uses of these films in the fields related to the UV protecting.
The fundamental absorption edge is one of the most important features of the absorption spectra, which provides the most valuable optical information available for material identification. The nature of optical transition involved in the blends can be determined on the basis of the dependence of the absorption coefficient (\(\alpha\)) on photon energy (\(hv\)). The absorption coefficient (\(\alpha\)) was calculated from the absorbance (\(A\)) using Lambert Beer's law:

\[ I = I_0 \exp(-\alpha d) \quad \ldots \ldots (1) \]

\[ \alpha = \frac{2.303A}{d} \quad \ldots \ldots (2) \]

where \(I_0\) and \(I\) are the intensities of incident and transmitted radiation respectively, \(d\) is the thickness of the sample in cm.

Fig.2 shows the plot of absorption coefficient versus photon energy for different concentrations of GA/PVA blend films. The values of the absorption edge were calculated by extrapolating the linear portion of the curves to zero absorption value. The values of the absorption edge are listed in Table 1. It was observed clearly that the values of the absorption edge for GA/PVA polymer increased as GA concentrations decreases. This indicates the creation of localized states in the band gap as a result of the compositional disorder [6].

According to Tauc relation [7], the absorption coefficient (\(\alpha\)) of band gap material is given by:

\[ ahv = \beta(hv - E_g)^\gamma \quad \ldots \ldots (3) \]

where \(E_g\) is the energy band gap, constant \(\beta\) is inversely proportional to amorphousity, also is a useful diagnostic of the material. \(hv\) is photon energy, and \(\gamma\) is an index used to be assumed the values 1/2, 3/2, 2 or 3 depending on the nature of the electronic transition, corresponding to allowed direct, forbidden direct, allowed indirect and forbidden indirect transitions, respectively.

According to Tauc's extrapolation, the band gap of a material can be obtained from the extrapolation of the straight line portion of the \((ahv)^\gamma\) against \(hv\) to \(\alpha=0\) [8]. The direct band gap values were obtained by plotting \((ahv)^2\) versus \(hv\) curves, as shown in Fig.3. The indirect band gap values were obtained from the plot of \((ahv)^{3/2}\) versus \(hv\) (see Fig.4).
The decrease in optical band gap energy by increasing GA concentration content can be explained by the fact that the incorporation of GA polymer forms charge transfer complexes in the polymer matrix. These increases the electrical conductivity by providing additional charges in the lattice [9].

The extinction coefficient (K) was calculated using the following equation [10]:
$$K = \alpha \lambda / 4\pi$$  -----(4)

The relation between reflectance and refractive index is given in the following equation [11]:
$$R = (n-1)^2 + K^2/(n+1)^2 + K^2$$  -----(5)

Where (n) is the refractive index, (K) is the Extinction Coefficient. R is the reflectance.

Refractive index can be expressed by the following equation [11]:
$$n = [4R/(R-1)^2-K^2]^{1/2} - (R+1)/(R-1)$$  -----(6)

The values of optical band gap (E_{opt}) Eg can be correlated to the number of carbon atoms per molecule through the expression given by eq 4 [12]
$$E_{opt} = 34.3/M^{1/2}$$  -----(7)

Where M is the number of carbon atoms in carbonaceous cluster. The calculated values of M for GA,PVA and their blends are presented in table (1).

**Table 1. Optical data for GA/PVA and their blend thin films of various compositions**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Absorption edge (eV)</th>
<th>Direct band gap (eV) (E_{opt})</th>
<th>Indirect band gap (eV)</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure GA</td>
<td>3.2</td>
<td>3.75</td>
<td>3</td>
<td>84</td>
</tr>
<tr>
<td>75% GA+ 25% PVA</td>
<td>3.5</td>
<td>3.85</td>
<td>3.3</td>
<td>79</td>
</tr>
<tr>
<td>50% GA+50% PVA</td>
<td>3.7</td>
<td>3.94</td>
<td>3.5</td>
<td>76</td>
</tr>
<tr>
<td>25% GA+75% PVA</td>
<td>3.8</td>
<td>4</td>
<td>3.7</td>
<td>74</td>
</tr>
<tr>
<td>Pure PVA</td>
<td>4</td>
<td>4.1</td>
<td>4</td>
<td>70</td>
</tr>
</tbody>
</table>

The absorption coefficient \(\alpha\), and the refractive index \(n\) from eq (6), were used to obtain the optical conductivity (\(\sigma\)), using the relation [12]
$$\sigma = \alpha n c / 4\pi$$  -----(8)

where \(c\) is the velocity of light in the space.
Fig. 6 shows the variation of optical conductivity $\sigma$ with the incident photon energy $h\nu$. The optical conductivity increases with increase GA polymer concentration. The conductivity enhancement in polymer attributed to the reducing the crystalline phase which provide the conducting pathways for the mobility of ions as well as polymer segments. Thus the observed effect of GA on the optical conductivity and the conduction behavior of blend polymer films can be explained on the basis of charge transfer complex formation [13].

3. Conclusions

4. References
دراسة الخواص البصرية للغشاء الرقيق

مهند قادر كريم
قسم الفيزياء، كلية العلوم، جامعة كركوك، كركوك، العراق

الملخص

في هذا البحث تم تحضير غشاء جديد رقيق من مزج بوليمر طبيعي (كم اكاسيه) وبوليمر صناعي (بولي فانيل الكحول) بطريقة الصب. طيف الامتصاص الضوئي لهذه الأفلام الرقيقة تم تسجيلها بين مدى الطيف (200-900) نانومتر بواسطة جهاز مطياف الأشعة فوق البنفسجية بسمك (μm). تم دراسة فجوة الطاقة البصرية للأغشية وحسابها بواسطة علاقة (Tauc) وتم استنتاج ان فجوة الطاقة المسموحة المباشرة لهذه الأغشية المختلفة باختلاف التراكيز تتراوح بين (3.75 - 4.1) إلكترون فولت.

كلمات مفتاحية: بوليمر طبيعي، فجوة الطاقة البصرية، التوصيلية البصرية، معامل الامتصاص.