Characterization Study and Optical properties of (GA) Gum acacia /(MF)Melamine formaldehyde composites

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Abstract
In this research we fabricated new Thin films of (Gum acacia) polysaccharide , melamine formaldehyde and their blends were prepared using cast method .Optical absorption spectra of these thin films have been recorded in the wavelength range (200-900)nm using UV-spectrophotometer. 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 concentration in the blend films have been found from (3.75-4.15) ev

Keywords: composite materials , optical band gap , optical conductivity , absorption coefficient

1.Introduction
Polymeric materials have attracted the scientific and technological researchers, because of their wide applications [1]. This is mainly due to the light weight , good mechanical strength ,optical properties and makes them to be multifunctional materials. More ever , these polymers are traditionally considered as an excellent host material for composites [2]. Polymer gum acacia (GA) is a natural polysaccharide formed during the deactivation of gum in alkaline condition. It comprises an un branched chain consisting of β-(1, 4)-2- amino-2-deoxy-D-glucopyranose, and it is a unique basic linear polysaccharide[3] .The hydrophilicity of the polymer due to amine functionality in most repeat units makes the polymer soluble in dilute acid [4] .Acaica is widely used in food and pharmaceutical industry and in biotechnology. This polysaccharide has been extensively studied in the field of biomaterials and because of its biological properties, biodegradability, bioactivity and biocompatibility it has attracted much attention [5].Polymer blending is one of the useful ways to have new material with required properties and there have been great scientific and commercial progress in the area of polymer blends. This was driven by the realization that new molecules are not always required to meet the need for new materials and blending can usually be implemented more rapidly and economically than the development of new materials Blends of synthetic and natural polymers represent a new class of materials and have attracted much attention especially in bio application as biomaterial. The success of synthetic polymers as biomaterial relies mainly on their wide range of mechanical properties, transformation processes that allow a variety of different shapes to be easily obtained and low production costs. Melamine formaldehyde MF foam is a kind of thermosetting plastic [6], and has attracted much attention all over the world. Because of its properties as the low density, corrosion resisting, good autonomous fire-re-tardancy and high thermal stability it can be used for a long time in the environment of temperature as high as 150°C [7].

2.Theorical part
The UV absorption mainly corresponds to the electron transition from the top of the valence band to the bottom of the conduction band. In general, the direct transition occurs between top of valence band and bottom of conduction band (vertical transition) at the same wave vector Δk=0 for conservation of momentum. The allowed direct transition refers to that transition which occurs between top of the valence band and bottom of the conduction band when the wave vector is equal to zero as shown in Fig. (1-a) [8].

![Figure1. The optical transitions(a)Allowed direct, (b)Forbidden direct; (c) Allowed indirect, (d) Forbidden indirect [8]](image-url)
This transition is described by the following relation [8].
\[ \alpha h\nu = B(h\nu - E_g)^{1/2} \]  \(\cdots(1)\)
Where \(\alpha\) is absorption coefficient, \(B\) is inversely proportional to amorphousity, \((h\nu)\) is the photon energy and \((E_g)\) is the energy gap.

If the transition occurs between states of the same wave vector, (but the wave vector does not equal to zero), the transition is called forbidden direct transition as shown in Fig. (1-b). It obeys the following relation [8].
\[ \alpha h\nu = B(h\nu - E_g)^{3/2} \]  \(\cdots(2)\)

In indirect transition there is a large momentum difference between the points to which the transition takes place in valence and conduction bands. This means that the conduction band minima are not at the same value of \(k\) as the valence band maxima, then, assistance of a phonon is necessary to conserve the momentum, therefore :
\[ h\nu = E_g \pm Ep \]  \(\cdots(3)\)
Where \(Ep\) is the energy of an absorbed or emitted phonon [9]. For an allowed indirect transition, the transition occurs from the top of the valence band to the bottom of the conduction band as shown in Fig. (1-c) so that [9].
\[ \alpha h\nu = B(h\nu - E_g)^{3/2} \]  \(\cdots(4)\)
While, the forbidden indirect transitions occur from any point near the top of valence band to any point other than the bottom of the conduction band, as shown in Fig. (1-d), then we have [9].
\[ \alpha h\nu = B(h\nu - E_g)^{3/2} \]  \(\cdots(5)\)

Experimentally, it is possible to differentiate between direct and indirect processes by the level of the absorption coefficient \(\alpha\); \(\alpha\) takes values from \((10^0\) to \(10^5\) \(\text{cm}^{-1}\) for direct transitions and \((10 \text{ to } 10^6)\) \(\text{cm}^{-1}\) for indirect transitions at the absorption edge [10]. From the equation related to the absorption of ray, the relation between the incident light intensity \((I_0)\) and the penetrating light intensity \((I)\) is described in the following equation [10]:
\[ I = I_0 e^{-\alpha t} \]  \(\cdots(6)\)
where \((t)\) is the thickness of the matter and \((\alpha)\) is the absorption coefficient, it is measured by \(\text{cm}^{-1}\) [9].
\[ \alpha t = 2.303 \log(I/I_0) \]  \(\cdots(7)\)
here the amount of \((\log(I/I_0))\) represents the absorbance \((A)\). The absorption coefficient can be calculated as follows:
\[ \alpha = 2.303(A/\ell) \]  \(\cdots(8)\)
The absorbance \((A)\) and transmittance \((T)\) can also be calculated as in the following equation [9]:
\[ R + A + T = 1 \]  \(\cdots(9)\)
The fast increase in absorption of the ray energy is proportional to the energy gap of the absorbing material. The fundamental absorption edge represents the lowest difference in energy between the highest point in the valence band and lowest point in the conduction band [11].

The extinction coefficient \((K)\) was calculated using the following equation [8]:
\[ K = \alpha \lambda/4\pi \]  \(\cdots(10)\)
The relation between reflectance and transmittance \((R)\) is given in the following equation [12]:
\[ R = (n - 1)^2 + K^2/(n+1)^2 + K \]  \(\cdots(11)\)
where \((n)\) is the refractive index, \((K)\) is the Extinction Coefficient. \(R\) is the reflectance. Refractive index can be expressed by the following equation [12]:
\[ n = 4R/(R-1)^2-K^2/2-(R+1)/(R-1) \]  \(\cdots(12)\)
The values of optical band gap \((E_{opt})\) \(E_g\) can be correlated to the number of carbon atoms per molecule through the expression given by eq.(10) [13].
\[ E_{opt} = 34.3/M^{1/2} \]  \(\cdots(13)\)
Where \(M\) is the number of carbon atoms in carbonaceous cluster.

The absorption coefficient \(\alpha\), and the refractive index \(n\) from eq.(12), were used to obtain the optical conductivity \((\sigma)\), using the relation [10].
\[ \sigma = \alpha c/(4\pi) \]  \(\cdots(14)\)
where \(c\) is the velocity of light in the space.

3. Sample preparation:

The materials used in this work was a powder of commercial GA polymer supplied by (Aldrich), Melamine were provided from AMI Agrolinz Melamine international GMBH, HCL(37%), THF and formaldehyde solution (40%) in water, NAOH, used in this study. The synthesis GA/MF polymer was processed in two steps based on previous work. First GA polymer were dissolved in HCL by using magnetic stirrer in mixing process to get homogeneous solution at 75°C for about 2 hours, second step is prepared melamine solution by dissolve melamine in HCL with some drops of THF and 10 ml formaldehyde solution (40%) (adjusted with sodium hydroxide to ph=8) by using magnetic stirrer in mixing process to get homogeneous solution at 65°C. After the melamine was completely dissolved let the white gray solution cooled at room temperature. Then mixing together in different concentrations (100:0 , 75:25 , 50:50 , 25:75 , 0:100) polymers. After which solution was transferred to clean glass Petri dish of (5.5cm) in diameter placed on plate form. for 3 days to obtain homogeneous films. The dried film was then removed easily by using tweezers clamp. Small section of the sample was taken and mounted vertically to get a clear section view of the thickness of the prepared films used for the present study is of the thickness \((3\mu m)\) (measured by a compound microscope (Nikon) equipped with a computer program to measure the thickness in pixels least count \((10-2)\mu m\) at the magnification 1:10 and 1:200,respectively) The polymer systems were evaluated spectra photo metrically. Ultraviolet-visible absorption spectra were measured in the wavelength region of \((200-900)\) nm using single beam (Jenway 7315) UV/VIS spectrophotometer.

4. Results and Discussions:

4.1. The absorbance of composite
The UV-vis absorption spectra of blend GA/MF films are recorded at room temperature in the wavelength range (200-900)nm shows the relationship between absorbance of GA/MF composite and wave length, from the figure, it was appeared that the absorbance tends to decrease with increasing the wavelength in UV region, this behavior attributed to the absorbance of polymer in high energies. 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.[14]

### 4.2. The absorption coefficient

Fig.(3) shows the variation of absorption coefficient of composites for different concentrations of impurities. The composites have a low absorption coefficient at a small energy, also, the absorption coefficient is increased with increasing the concentrations of GA, this due to increase the absorbance of composites with increasing the percentages of GA [14].

### 4.3. The direct and indirect transitions

Fig. (4) and Fig. (5) represented the direct and indirect transition were calculated by using Eq.9, the energy gap values dependence in general on the crystal structure of the composites and the arrangement and distribution way of atoms in the crystal lattice. From these figures we can see that the energy band gap is decreased with increasing the GA concentrations, the behavior of energy band gap with GA concentration attributed to decrease the distance between valance band and conduction band [13].

![Figure 2](image2.png)

**Figure 2.** The relationship between absorbance and the wave length of variation GA/MF polymer

![Figure 3](image3.png)

**Figure 3.** Relation between absorbance coefficient ($\alpha$) versus ($h\nu$) for variation GA/MF polymer
4.4. The Urbach edges

Fig. (6) shows the variation of the \( \Delta E \) is the energy width of the tail of localized states in the band gap was evaluated using the Urbach-edges method. From the figure shown below we found that pure GA is better than adopted with MF of band gap.

4.5. The extinction coefficient \( K \)

Fig. (7) shows the variation of the extinction coefficient \( K \) with the photon energy. This figure shows the high value of extinction coefficient at high energies of photon, also the extinction coefficient \( k \) is increased with increasing the GA concentration. The behavior of extinction coefficient related to absorption coefficient according to Eq.10 [13].
4.6. The number of carbon atoms per molecule.
The values of optical band gap ($E_{\text{opt}}$) $E_g$ can be correlated to the number of carbon atoms per molecule through the expression given by eq13 [14]. The calculated values of $M$ for GA, MF and their blends are presented in table (1).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Absorption edge (ev)</th>
<th>Direct band gap (ev) ($E_{\text{opt}}$)</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% MF</td>
<td>3.7</td>
<td>3.9</td>
<td>3.3</td>
<td>77</td>
</tr>
<tr>
<td>50% GA+50% MF</td>
<td>3.8</td>
<td>4</td>
<td>3.4</td>
<td>74</td>
</tr>
<tr>
<td>25% GA+75% MF</td>
<td>4</td>
<td>4.15</td>
<td>3.9</td>
<td>68</td>
</tr>
<tr>
<td>Pure MF</td>
<td>3.9</td>
<td>4.1</td>
<td>3.7</td>
<td>70</td>
</tr>
</tbody>
</table>

4.7. The Optical conductivity

Fig. 8 shows the variation of optical conductivity $\sigma$ with the incident photon energy $\hbar \nu$. 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[15].

5. Conclusions
The absorbance of (GA/MF) is increased with increasing the GA concentrations.
- The composites have indirect energy band gap which decrease with increasing the GA concentrations.
- The optical constants (absorption coefficient, direct and indirect transitions' energy, urbach energy, Extinction coefficient) are changed with increasing percentages of GA.
6. References


دراسة خصائص و الخواص البصرية للمتراكب

(GA)Gum acacia/(MF)Melamine formaldehyde

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الملخص
في هذا البحث تم دراسة خواص المتراكب الجديد كم أكاسيه, ميلامين فورمالديهايد وتم تصنيعها بطريقة الصب. طيف الامتصاص الضوئي لهذه الأغشية الرقيقة تم تسجيلها بين مدى الطيف (200-900) نانوميتر بواسطة جهاز مطياف الأشعة فوق البنفسجية وفجوة الطاقة البصرية للاغشية تم حسابها بواسطة علاقة (Tauc) وقد وجد أن فجوة الطاقة لهذه الأفلام المختلفة باختلاف التراكيز تتراوح بين (3.75 إلى 4.15) إلكترون فولت

كلمات مفتاحية: مواد متراكبة , فجوة الطاقة البصرية , التوصيلية البصرية , معامل الامتصاص