Investigate Physical Properties and Intensity of Sun Light Transmitted through Safranin/PMMA Films

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ABSTRACT
To investigate the effect of safranin additions on the optical properties of PMMA hosts, films of pure and doped polymethylmethacrylate (PMMA) with various volumes of safranin (S) dye solution (6, 12, 18, 24, 30, and 35 ml) were equipped via the solution-casting method at room temperature. For an aim of assessing the kind of transition that was established to be indirect transition, these films were described using the method of UV/VIS. It showed absorption characteristic peak at 530 nm which increased with dye concentration until 24ml after that absorbance will decrease for (30 and 36) ml. The optical energy gap of polymethylmethacrylate (PMMA) was (5.0 eV) and after doping PMMA polymer with safranin dye, the energy gap value of the PMMA films raised as the volume ratio of Safranin solution raised but for volume doping 24ml of safranin solution, the energy gap reduced. The intensity of solar radiation was measured for pure PMMA and safranin/PMMA films, for four consecutive days from 7 A.M. to 5 P.M. (17 hr.), at a rate one hour. It can be concluded that the ratio of the transmitted radiation intensity to the intensity of the sun's radiation for all films is equal for every hour and for all days.

KEYWORDS: Safranin Dye; Polymethylmethacrylate; Physical Properties; Sun Light.

INTRODUCTION
Scientists have recently become interested in polymer composites because of their diverse and remarkable properties, such as simplicity of manufacture, weathering flexibility, light weight, and strong optical and mechanical properties [1]. Organic solar cells, thermal and photo solar collectors, and greenhouses are only a several of the modern applications for polymer composites. To establish a good environment for greenhouse applications including planting, drying vegetables and fruits, and desalination, a suitable polymeric film for covering the greenhouse is needed [2]. One of these polymers is Polymethylmethacrylate (PMMA) are used because of its low cost, perfect optical properties and good mechanical properties [3]. PMMA polymeric composites are well-known for their utility in technical applications. PMMA is inherently translucent and colorless, with a high transmission of visible light. [4].

Safranin-O (similarly identified as Basic Red 2 (BR2)) is an organic dye that be appropriate to the Quinone–Imine class. Organic dyes are produced from natural plant pigments. This indicates that they are made from organic materials such as seeds, herbs, or other organic materials. This dye is used in histology and cytology. It's usually used to distinguish microorganisms and make them more apparent. It's commonly used as a metachromatic tool for yellow-staining cartilages, for example. Even traces of this dye in wastewater will affect marine life [5, 6].

UV light is a form of electromagnetic radiation. It has a higher energy than visible light and is accompanied by X-rays and Gamma rays. UVA (320-400nm), UVB (280-320nm), and UVC (320-400nm) are the three forms of UV radiation (100-280nm). One of the most difficult aspects of studying the effects of UV rays on polymers is determining the intensity of UV rays in relation to: stratospheric ozone, clouds, altitude, and sun height (time of day and year), and reflection. The effects' complexity can be very high. All kinds of UV can generate a photochemical reaction within the polymer structure, which can be beneficial or lead to material degradation [7]. Direct sunlight has a very high intensity and is constantly moving. The luminance formed on the
earth’s surface may be in excess of 100 000 lux. Season, time of day, place, and sky conditions all influence on the brightness of direct sunlight. A thoughtful architectural design, with careful management of allowance, diffusing, shading, and reflecting, is needed in a sunny environment. In the winter, an overcast sky can produce up to 10 000 lux, and on a clear overcast day in the summer, it can produce up to 30 000 lux. The diffuse sky is often the only source of usable daylight in a cloudy environment [8].

Many research investigated physical characteristics of PMMA film and Safranin dye doped with PMMA or with different types of polymers, and got good results and applications [9–13]. This work aims to synthesize the optical properties and measure the intensity of sun light that transmitted through pure PMMA and Safranin / PMMA films.

THEORETICAL PART

As light passes from one medium to another, some of its energy can be transferred through the medium. (for example; from air into a solid material). At the interaction between the two media, some will be absorbed and some will be mirrored.

The decreasing ratio of incident light energy in the length unit to wave propagation within the medium can be regarded as the absorption coefficient, which varies with incident photon energy. The photon is transmitted if the incident photon energy is less than the energy wavelength, and the thin film transmittance (T) is given by the relationship [14].

\[ T = 1 - A - R \]  

Wherever: R: Reflectance and A: Absorbance. The absorption coefficient (symbol; \( \alpha \) cm\(^{-1}\)) is determined via Lambert law in the fundamental absorption region [15]

\[ I = I_0e^{-\alpha x} \]  

That \( I_0 \) and \( I \) act intensity of the incident and transmitted light, respectively. Thin film thickness is \( x \).

If \( \left( \frac{1}{I_0} \right) = T \) Then \( \left( \frac{1}{I} \right) = e^{\alpha x} \)

So that \( \ln \left( \frac{1}{I} \right) = \alpha x \),  
\[ 2.303 \times \log_{10} \left( \frac{1}{I} \right) = \alpha x \]  

\[ A = \log_{10} \left( \frac{1}{I} \right) \]  

So that the absorption coefficient written as [16]:

\[ \alpha = \frac{(2.303 \times A)}{x} \]  

In the study of optical properties, direct and indirect electrical transformations can be distinguished based on the lower position in the conduction band and the upper position point in the valance band. An significant relationship exists between the forbidden energy gap (\( E_g \)) and the photon energy gap (\( h\nu \)), presented in the following equation. [17, 18]:

\[ a h\nu = B(h\nu - E_g)^r \]  

Where B: Constant whose value is determined by the conduction and valance band properties, \( r \): constant whose value is determined by the transformation existence, where \( r = 1/2 \) for allowed direct transitions, \( r = 3/2 \) for forbidden direct transitions.

EXPERIMENTAL WORK

Safranin dye has chemical formula \( C_{20}H_{19}ClN_4 \) and molecular weight (Mw=350.84 g/mol) processed by the company (DC Panreac Quimica Company/ Barcelona Spain). Polyvinylmethylacrylate (PMMA) polymer has been choosing as host material for safranin owing to its brilliant optical properties. PMMA processed by the (Sabic) company, with chemical formula \( [C_3H_8O_2]_a \) and molecular weight 200,000 g/mole.

The PMMA film was performed by dissolving PMMA (0.3 g) in (10 ml) Chloroform, and pure PMMA film is formed by casting- solution process [19]. The as-prepared PMMA solution was shaken vigorously with a magnetic stirrer till the polymer was totally dissolved, then poured into a clean glass petri dish with diameter (7 cm). After one day of drying at room temperature (20–23 °C), homogeneous pure PMMA films were obtained. Safranin solution has a concentration of (1×10\(^{-4}\) mole/liter) and is obtained by dissolving a certain dye powder amount (symbol;m in g) in an identified volume (symbol; V in ml) of Chloroform according to Eq. (8) [20].

\[ m = \frac{C \times V \times M_w}{1000} \]  

Safranin dye solution (6, 12, 18, 24, 30, and 36) ml was applied to PMMA solution (0.3 g) with Chloroform to prepare S / PMMA films for a variety of volume ratios (10 ml). The mixture was then vigorously mixed with a magnetic stirrer until the S/PMMA solution was homogeneous. To get
homogeneous films, pour the solution into a petri clean glass dish and keep it at the temperature of the room (20-23) for one day. The thickness of as-prepared films was measured using a digital micrometer with a measurement precision of (0.001) mm over a spectrum of (0-150) mm (Type Tesha), with PMMA polymer films measuring around (0.049) mm and S/PMMA films measuring around (0.0576) mm. Finally, using the Lux Meter software on the Huawei mobile unit, the intensity of sunlight as well as the intensity of radiation emitted for all prepared films is calculated. The UV-Vis spectrophotometer (Type T70/T80) is a device that measures the absorption and transmission spectra in the wavelength range of 200-1100 nm.

RESULTS AND DISCUSSIONS

Figure 1 displays the Safranin absorption distribution in Chloroform at a concentration of (1x10^{-4}) mole/liter. Broadband absorption spectrum activities exist, with a maximum wavelength at (530) nm and related intensity (0.472). These data suitable with an ordinary study referred to [21]. The π-π* transition is “a type of electronic transition that is characteristic Safranin dye and associated to the charge transfer from the benzene cycle to the pianos moiety”. This transition is related to an excitation from the LUMO (the lowest unoccupied molecular orbital) HOMO (the highest occupied molecular orbital) and the HOMO orbital, respectively [14].

The behavior of the absorption coefficient (α) of Safranin (S) solution determined from Eq. (6), as seen in Figure 1, is close to that of the absorption continuum, however with a higher value (0.969). Figure 2 demonstrates optical energy gap of Safranin (S) solution, the result exposes that the energy gap is equivalent to (4.02) eV.

Figure 3 shows the absorption variety of pure PMMA and S/PMMA films with various volumes of safranin (S) dye solution (6, 12, 18, 24, 30, and 36) ml at a concentration of (1x10^{-4}) mole/liter (3). In addition, Table 1 shows the absorption information (1). When Safranin dye is doped with PMMA polymer, the maximum absorption wavelength for safranin (S) dye still constant at (530) nm. While absorbance increased with increase of volume of safranin solution until 24ml after that absorbance will decreased for (30 and 36) ml. This may be interpreted as increasing the number of safranin dye which causes aggregates that will inhibit the intensity of absorption spectrum. This discussion matched with Birks and Berlman in previous studies [23, 24].
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The absorption coefficient for pure PMMA and S/PMMA was calculated from eq. (6) and plotted in Figure 4. As seen in Figure 4 and Eq. (1), a value of diffusion coefficient > $10^4$ cm$^{-1}$ means that the occurrence of a vertical transformation at the fundamental absorption edge and is indicative of an indirect transition (3). Figure 5 shows the difference in energy gap for pure PMMA and S/PMMA films (5), the size of the energy difference of the PMMA films seemed to rise as the volume ratio of Safranin solution was improved. Because of the construction of a new band gap, this enlargement supports the transfer of electrons mostly from valance band to these limited levels and into the conduction band. Only for volume doping 24ml of safranin solution, the energy gap reduced. This may be referred to high absorption. The optical band gap values for S solution, pure PMMA, and S/PMMA films is described in Table 1.

### Table 1. The information of absorption for pure PMMA and S/PMMA films with various volume of S solution

<table>
<thead>
<tr>
<th>Samples</th>
<th>λ (nm)</th>
<th>Abs.</th>
<th>$E_g$ (eV)</th>
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<tbody>
<tr>
<td>Pure PMMA</td>
<td>-------</td>
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<tr>
<td>PMMA + S (6ml)</td>
<td>530</td>
<td>0.472</td>
<td>4.02</td>
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<tr>
<td>PMMA + S (12ml)</td>
<td>530</td>
<td>0.181</td>
<td>5.06</td>
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<tr>
<td>PMMA + S (18ml)</td>
<td>530</td>
<td>0.201</td>
<td>5.08</td>
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<tr>
<td>PMMA + S (24ml)</td>
<td>530</td>
<td>0.275</td>
<td>5.02</td>
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<tr>
<td>PMMA + S (30ml)</td>
<td>530</td>
<td>0.367</td>
<td>4.96</td>
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<tr>
<td>PMMA + S (36ml)</td>
<td>530</td>
<td>0.235</td>
<td>5.01</td>
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### Table 2. Information about temperatures for four consecutive days

<table>
<thead>
<tr>
<th>Day Time (O’clock)</th>
<th>Monday 8/2/2021</th>
<th>Tuesday 9/2/2021</th>
<th>Wednesday 10/2/2021</th>
<th>Thursday 11/2/2021</th>
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</table>

The intensity of solar radiation was measured for four consecutive days at the beginning of February 2021, with and without pure PMMA and S/PMMA films, and Table 2 shows the temperatures for these days from 7 A.M. to 5 P.M. (17 hr.), at a rate one hour. The temperatures have been taken in Wasit Governorate, the city of Kut. The ratio of the intensity of solar radiation with the presence of the films (symbol $I$) to the intensity of the normal solar radiation (symbol $I_0$) was calculated for all films and plotted in the Figures (6-A, B, C, D, E, F, G).
Figure 6. The ratio $I/I_0$ for A- Pure PMMA, B- S(6ml)+PMMA, C- S(12ml)+PMMA, D- S(18ml)+PMMA, E- S(24ml)+PMMA, F- S(30ml)+PMMA, G- S(36ml)+PMMA for four days.
From all these columns mentioned in Figure 6, it can be concluded that the ratio of the transmitted radiation intensity to the intensity of the sun’s radiation for all films is equal for every hour and for all days. The intensity of the transmitted radiation is the highest possible at eleven o’clock in the morning for the pure PMMA and S/PMMA with variant volume ratio of Safranin solution except for S(18ml) that starts to rise in the twelve and one o’clock hours, as in Figure 7. This may be explained as:

![Graph]

Figure 7. The ratio I/Io against prepared samples at eleven o’clock.

CONCLUSIONS

Based on the findings and discussion, the following conclusions can be drawn about Safranin dye and Safranin/PMMA films: At 530 nm, the maximum absorption wavelength is plainly visible. The optical energy gap of the Safranine/PMMA composite is (4.96–5.08) eV, and the transition is indirect, according to the UV-Vis measurements. As a result, safranin/PMMA polymer films with a low degradation rate can be used to make clear ultraviolet-shielding applications. The addition of safranin to PMMA improves its performance significantly, resulting in low-cost, high-thermicity transparent films.

REFERENCES


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