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Absorption Characteristics of Magnesium Oxide and Aluminium Oxide NPs/ Rhodamine 6G/ Polyvinyl Alcohol Films

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ABSTRACT

Pure Polyvinyl Alcohol (PVA) film and PVA polymer film/ Rhodamine 6G(Rh6G) dye film in different volume ratios of (6, 12,18, 24 and 30) ml of Rh6G were prepared via casting method. The addition of Magnesium Oxide (MgO) and Aluminium Oxide (Al_2O_3) nanoparticles as a filler to the polymer matrix. The results demonstrated that there was a 10 nm red shift in the absorption spectra of Rh6G in PVA/ Rh6G polymer matrix due to add doping ratio of Rh6G dye solution to the transparent PVA matrix. Also, there was a 5 nm red shift in polymer matrix filled with Al_2O_3 NPs; this means that Al_2O_3 NPs absorb the water and that consequently enhance the optical properties of polymer matrix. The intensity of Rh6G doped PVA polymer film was seen to be enhanced when adding MgO NPs or Al_2O_3 NPs, noted that intensity of adding Al_2O_3 NPs more than it when adding MgO NP. The electronic transition was found to be $\pi \rightarrow \pi^*$.

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خصائص الامتصاص لأوكسيد المغنيسيوم وأوكسيد الألومنيوم النانوية/ رودامين ٦ ج/ أغشية بولي فينيل الكحول

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الـــخُــلاصـــة

تم تحضير اغشية بوليمر بولي فينيل الكحول (*PVA*) / صبغة الرودامين ٦ ج (*Rh6G*) بنسب حجمية مختلفة (٦ ، ١٢ ، ١٨ ، ٢٤ و ٣٠) مل من الرودامين بطريقة الصب. إضافة جزيئات أوكسيد المغنيسيوم (*MgO*) و أوكسيد الألومنيوم (Al_2O_3) كحشو إلى مصفوفة البوليمر. أظهرت النتائج ازاحة نحو الطول الموجي الاطول(ازاحة حمراء) بمقدار ١٠ نانومتر في أطياف امتصاص الرودامين في مصفوفة البوليمر. أيضًا ، هناك ازاحة حمراء بمقدار ٥ نانومتر في مصفوفة البوليمر مملوءة بجزيئات الالومينا النانوية، مما يعني أن

الالومينا تقوم بأمتصاص الماء وبالتالي تعزز الخصائص البصرية لمصفوفة البوليمر. تتحسن شدة الامتصاص في غشاء مصفوفة البوليمر عند تطعيمها بالمواد النانوية ، وتزداد عند إضافة الالومينا. الانتقال الإلكتروني هو من نوع $\pi \rightarrow \pi^*$..

1. Introduction

Import polymers have come a long way in the previous 20 years, with a wide range of uses. [1]. Among all properties, the impressive enhancement in optical properties of polymer composites (PCs) has opened up the new technological gateway toward the design and development of the novel materials for various applications, these include light emitting diodes (LEDs), sensors, thin-film transistors and photovoltaics[2]. Material science is interested in polymer-inorganic composites to develop efficient materials with good characteristics such as low cost, lightweight nature and flexibility [3].

Polyvinyl alcohol PVA is a semi-crystalline or linear synthetic polymer that is creamy or white, tasteless, odourless, nontoxic, biocompatible, thermostable, granular or powdered [4]. It has incredible capabilities: optical properties, a high dielectric strength, and a good dielectric strength capacity to store charge. PVA is a readily available commercial substance[5].

Rhodamine 6G (Rh6G) molecule is eco-friendly and arguably the most commonly used organic dye. In addition, it has a high fluorescence quantum yield and, in spite of its hydrophobic affinity, it is water soluble. Owing to these attributes, R6G can be applied in many areas, for example the imaging of cellular and polymer objects, and dye laser applications[6]. The Rh6G is used in numerous applications such as petroleum products dyeing, paper printing, forensic technology, colour photography, cosmetic products, laser technology, optical conversion, solar cells, diode, signal amplification in optics, optical communications , optoelectronics and as an active medium for dye lasers [7]. Ionic dyes self-associate can be utilized to varying degrees in solutions, depending on a variety of conditions such as dye concentration, dye structure, temperature, pH, and solvent, among others, resulting in a deviation from Beer's law [8]. When it comes to defining physical qualities and potential, the solvent in which the dye is dissolved is playing an important role. In moderate to high polarity solvents, the properties like Stokes' shifts, fluorescence quantum yields, fluorescence lifetimes, radiative and nonradiative rate constants follow more or less linear correlation with the solvent polarity [9].

Metal oxide nanoparticles attracted an attention due to their increased use in various fields such as cosmetics, electronics, material sciences, catalysis, environment, energy and Biomedicine[10]. Magnesium Oxide(MgO) nanoparticles have interesting applications in microelectronics, diagnostics, and biomolecular detection [11]. In the field of catalysis, the unique structure of Aluminium Oxide (Al_2O_3) is employed as a foundation for active phases coated with other materials. [12]. Presence of the metallic structures in the vicinity of the fluorophore can alter the optical properties of the fluorophore. There have been some attempts to show both quenching and enhancement of the fluorescence intensity of fluorophore can be introduced by NPs[13]. Kumar et al. (2014)[14] studied both quenching and enhancement of the fluorescence intensity of the Rh6G with different dye concentrations, ranging from 3 to 300 μM, in presence of 15 nm diameter Au NPs. For lower dye concentrations, fluorescence quenching and for higher concentrations, fluorescence enhancement was occurred. As a result, the fluorophore's fluorescence intensity in the presence of metal NPs is non-monotonic. Fluorescence quenching of Rh6G in Au nanocomposite polymers was investigated by Karthikeyan (2010), and found that the fluorescence decay rate of Rh6G changes because of the presence of AuNPs, and this change depends on the particle size[15]. F.F. Kareem et al showed that adding MgO NPs, Al_2O_3 NPs led to enhance the absorption spectra of Rhodamine 6G (Rh6G) dye solution[16].

The aim of this study is to characterize the absorption properties of PVA/ Rhodamine6G (Rh6G) polymer composite filled with nanoparticles. Furthermore, investigation of adding Metal Oxide Nanoparticles to polymer composite.

2. Experimental Work

2.1. Materials

Polyvinyl Alcohol (PVA) $(C_2H_4O)_n$, with a molecular weight of 14 000 g/mol obtained from DBH Chemical LTD Pooled England. Rhodamine6G ($C_{28}H_{31}N_2O_3Cl$, molecular weight 479.02 $g\cdot mol^{-1}$) obtained from Sigma-Aldrich. The Rhodamine6G was dissolved in Distilled Water (H_2O), polarity (10.2) [17], Magnesium Oxide (MgO with an average diameter of 40 nm, and purity of 99.9%) from Intelligent Materials Pvt.Ltd. While, Alumina Oxide (Al_2O_3, with an average diameter of (20-30 nm), with a purity of 99.9%) obtained from China.

2.2 Preparation of Samples

2.2.1 Preparation of Samples and Equipment's measurements

The Rhodamine6G dye solution of primary concentration (1×10^{-2}) M was prepared by dissolving the appropriate amount of this dye (weighted by Mattler balance of 0.1mg sensitivity) in Distilled Water. The amount of dye, m, (in g) was calculated using the following equation (1) [18].

$$m = \frac{M_W V C}{1000} \qquad (1)$$

Where M_w is the molecular weight of dye (g/mole), V is the volume of the solvent (ml), and C is dye concentration (M). The concentration of dye was then diluted to reach a concentrations in the range of (1×10^{-2}) M to (1×10^{-6}) M according to eq. (2)[19].

$$C_1 V_1 = C_2 V_2 \qquad (2)$$

where, C_1 is the high concentration, V_1 is the volume before dilution, C_2 is the low concentration, and V_2 is the total volume after dilution. It was noticed that the prepared solutions had a good homogeneity. The absorption spectra of all samples were recorded using a UV-Visible spectrophotometer (T70/T80). All the figures done with Origin Pro 2019b.

2.2.2. Preparation of Rh6G /PVA Polymer Film

The casting method is chosen to prepare dye doped polymer film[7]. Known amount of PVA polymer was dissolved in constant volume of Distilled water. The prepared solution was stirred very well via magnetic stirrer for (3 hours) until homogeneous solution was obtained. Then, the solution was put onto a glass petri dish and leave at room temperature to obtain homogenous and pure PVA film. The concentration of Rh6G in Distilled Water is ($1x10^{-5}$) M. Films of different volume ratios of solution were chosen: (6, 12, 18, 24 and 30) ml which added to the PVA. The as-prepared precursors were stirred very well via magnetic stirrer until the (Rh6G /PVA) solution become homogeneous, it was then cast into a glass petri dish and allowed to cool to form a homogeneous film.

2.2.3. Preparation of Rh6G /NPs/PVA Films

Certain amount of PVA polymer was dissolved in Distilled Water with Rh6G, then MgO NPs or Al_2O_3 NPs was added to prepare the solution via magnetic stirrer since the nanoparticles were diffused homogeneously through dye solution, then pour into glass petri dish and leave to dry to get homogeneous films.

3. Results and Discussions

The concentration of Rh6G dissolved in Distilled water was (1×10^{-5}) M that obey Beer-Lambert law as shown in fig. (1). The maximum absorption wavelength (λ_{max}) at (525nm), that is a good agreement with [20,21], with shoulder peak at (495 nm) and the intensity 0.75 as show in table (1).The transition is $\pi\rightarrow\pi^*$ and this transition is typical for basic Rhodamine 6G dye [22].

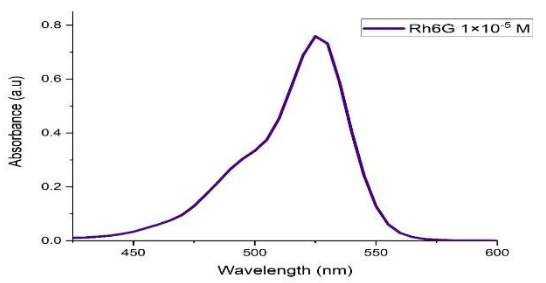

Figure (1) Absorption Spectra of Rhodamine 6G Dissolved in Distilled Water

The absorption spectra of pure PVA had a wide peak with a maximum wavelength at about 280 nm with intensity of 0.19, this result has a good agreement with the research[7].

The absorption spectra of the Rh6G doped PVA film with different volume ratio of dye solution (6, 12, 18, 24 and 30) ml at best concentration (1×10^{-5}) M. The absorption spectrum of pure PVA had a wide peak with a maximum wavelength about of 280 nm with intensity 0.19, this finding agreed well with the research[7]. The wavelength of PVA peak didn't affect by Rh6G solution addition. However, the wavelength of the absorption spectrum of Rh6G dye was clearly altered from 525 nm for Rh6G solution to peak 535 nm for Rh6G/PVA films. The change in conjugation or auxo- chromic groups of organic dye atoms could explain the red shift toward long wavelength (10 nm) that caused by increased doping ratio. Furthermore, higher Rh6G dye doping ratios result in increased absorbance for PVA peak. The intensity at first increases, becomes maximum at 0.3 for doping ratio 25 ml because the dye molecules in the energy ground state have the maximum value and are able to absorb sufficient light photons[23]. The intensity of Rh6G peak decreased as in Rh6G only without polymer, but it increases as the volume ratio increased to be 0.56 for 30ml. The reason for these changes in absorbance may be due to aggregates formation. This finding may be discussed as increasing the number of dye molecules as mentioned by J. B. Birks and Berlman,[24,25] .An important point is that an attractive dissolution of Rh6G in PVA matrix, which abolishes the Rayleigh scattering, falls exclusively in the visible range, thereby holding on to the optical purity [2]. All the result illustrated in fig. (2) and table (1).

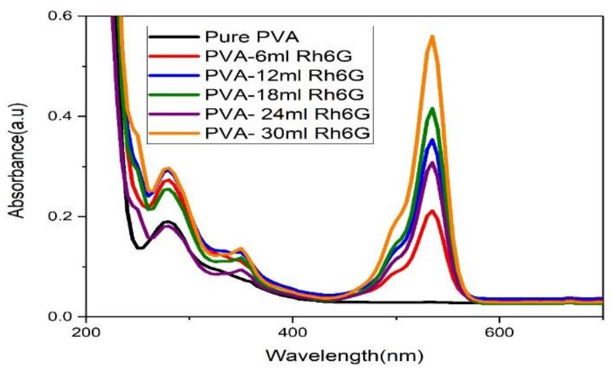

Figure (2) Absorption Spectra of Pure PVA and Rh6G/ PVA Films with Different Volume of Rh6G Solutions

Table (1) Absorption Information of Pure PVA and Rh6G / PVA Films with Different Volume of Rh6G Solution.

Samples	PVA Polymer		Rh6G Dye	
	λ_{absmax} (nm)	I_{abs}	λ_{absmax} (nm)	I_{abs}
Pure PVA	280	0.19	……..	………
Rh6G Solution	……..	……	525	0.75
PVA+ 6ml Rh6G	280	0.27	535	0.21
PVA+ 12ml Rh6G	280	0.29	535	0.35
PVA+ 18ml Rh6G	280	0.25	535	0.41
PVA+ 24ml Rh6G	280	0.18	535	0.30

PVA+ 30ml Rh6G	280	0.3	535	0.56

To examine the effect of these NPs on PVA/ Rh6G polymer composite, Rh6G dissolved in Distilled Water was added to PVA polymer as host matrix with the presence of MgO or Al_2O_3 NPs as filler, as shown in fig (3).

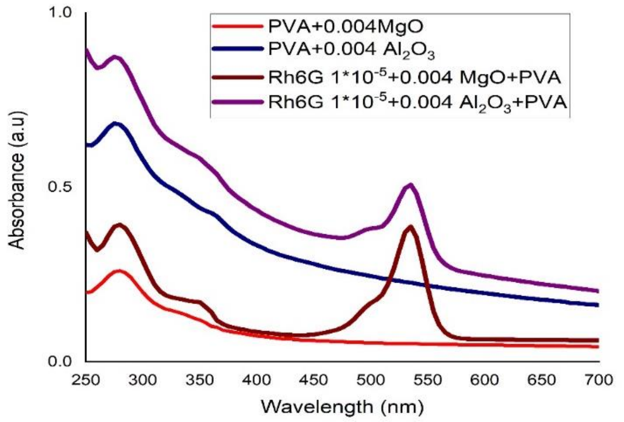

Figure (3) Absorption Spectra of PVA/Rh6G Polymer Composite Filled with 0.004 g Amount of (MgO - Al_2O_3) Nanoparticles.

It is observed that the intensity increased when adding MgO and Al_2O_3 NPs in Rh6G polymer matrix, noted that intensity of adding alumina nanoparticles more than it in the case of adding magnesia nanoparticles. This is due because Al is a metal, it may generate electrons and transform to a cation. Al_2O_3 NPs may also absorb water, making them useful as a drying agent. Due to its great stability, it is also considered an oxidizing agent[26]. Furthermore, change in peak position. Also, there is a 10 nm red shift in Rh6G when it added to the polymer matrix filled with MgO and Al_2O_3 NPs. which means that adding NPs led to enhance the photophysical properties of polymer composite. as see in table (2). The using of PVA as a good host polymer for metal oxide nanoparticles is favourable regarding with excellent physical and chemical properties because of its excellent biodegradability, solubility in water and chemical resistance[27].

Table (2) Spectral Information of Rh6G Dye Solution Doped PVA Polymer Matrix Filled with

Samples	**PVA Polymer**		**Rh6G Dye**	
	$\lambda_{abs\ max}$ (nm)	I_{abs}	$\lambda_{abs\ max}$ (nm)	I_{abs}
Rh6G (1×10^{-5})	…..	…….	525	0.75
0.004 MgO+ PVA	280	0.26	……	…….
0.004 Al_2O_3+ PVA	275	0.68	…….	…….
Rh6G (3×10^{-5}) + 0.004 MgO+ PVA	280	0.39	535	0.38
Rh6G (3×10^{-5}) + 0.004 Al_2O_3+ PVA	280	0.89	535	0.50

4. Conclusions

In this work, the effect of adding (Rh6G dye solution, MgO and Al_2O_3 NPs) to PVA polymer matrix were studied on the absorption spectra and the result found to be:

1- The Rh6G impact in PVA polymer led to red shift about 10 nm in absorption spectrum of Rh6G due to the fact that Rh6G dye solution sensitive to the solvent and concentration and that's led red shift of Rh6G dye solution inside transparent PVA matrix.

2- There was 5 nm red shift in PVA polymer composite filled with alumina nanoparticles because Al_2O_3 NPs absorb water.

3- The intensity of Rh6G doped PVA polymer film improves when adding MgO NPs or Al_2O_3 NPs, noted that intensity of adding Al_2O_3 NPs more than it when adding MgO NP.

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