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Absorption Properties of Polyvinyl Alcohol Films Filled with Nanoparticles Doped with Acridine Orange Dye

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ABSTRACT

Polyvinyl Alcohol (PVA) polymer/ Acridine Orange (AO) dye films prepared via casting technique at room temperature. The effect of adding (Acridine Orange (AO) dye solution, Magnesium Oxide (MgO), and Aluminum Oxide (Al_2O_3) NPs) to the PVA polymer matrix were studied on the absorption spectra. The effect of AO addition on the absorption spectrum of PVA film is occurrence blue shift (5nm) from 280nm to 275 nm in the PVA and red shift (10nm) from 490nm to be 500 nm for AO maximum absorbance wavelength. The absorbance of AO dye decreases when adding PVA, but increases When the volume ratio of AO dye solution is increased to 0.49 for 18ml, the volume ratio of AO dye solution decreases for 24- and 30-ml volume ratios. Adding NPs led to enhancing the photophysical properties of polymer composite, noted that absorbance of adding alumina nanoparticles more than it is in the case of adding magnesia nanoparticles. Also, there is a 10 nm red shift in AO and a 5 nm blue shift in AO when they are added to the polymer matrix filled with MgO and Al_2O_3 NPs.

KEYWORDS: Acridine Orange; PVA Polymer; Absorption Spectrum; MgO NPs; Al_2O_3 NPs.

الخلاصة

تم تحضير أغشية بوليمر بولي فينيل الكحول (PVA) / صبغة ألاكريدين البرتقالي (AO) بتقنية الصب في درجة حرارة الغرفة. تمت دراسة تأثير إضافة (محلول صبغة الاكردين البرتقالي (AO) وأوكسيد المغنيسيوم (MgO) وأكسيد الألومنيوم (Al_2O_3) الى مصفوفةPVA على طيف الامتصاص. تأثير اضافة **AO** على طيف الامتصاص لمصفوفة البوليمرهو حدوث ازاحة زرقاء (5 نانومتر) من 280 نانومتر الى 275 نانومتر في البوليمر وازاحة حمراء (10 نانومتر) من 490 نانومتر الى 500 نانومتر لطول موجة الامتصاص الأقصى لـ AO. تنخفض امتصاصية صبغة AO عند إضافة PVA ، ولكنها تزداد مع زيادة نسبة حجم محلول صبغ AO إلى 0.49 لـ 18 مل وتنخفض لنسب حجم 24 و 30 مل. أدت إضافة الجسيمات النانوية إلى تحسين الخواص الفيزيائية الضوئية للمتراكب البوليمري ، ولوحظ أن الامتصاصية تزداد بإضافة جزيئات الألومينا النانوية أكثر منها في حالة إضافة جزيئات المغنيسيا النانوية. كذلك، هناك ازاحة نحو الطول الموجي الاحمر بمقدار 10 نانومتر في AO و 5 نانومتر إزاحة زرقاء في AO عند إضافتهما إلى مصفوفة البوليمر المملوءة بـجزيئات المغنيسيا والالومينا النانوية.

INTRODUCTION

Import polymers have come a long way in the previous 20 years, and they now have a wide range of applications [1]. The remarkable improvement in optical characteristics of polymer composites (PCs) has opened up a new technical doorway toward the design and development of innovative materials for a variety of applications, including 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].

Acridine orange (AO) is a cationic dye, nucleic acid selective fluorescent[6]. Acridine has various applications in fluorescence microscopy, endomicroscopy, intraoperative, fluorescence guidance, photodynamic therapy, so no dynamic therapy, radio dynamic therapy [7].

Acridine derivatives form an important class of heterocycles containing nitrogen due to their broad range of pharmaceutical properties. In the nineteenth century, acridine derivative was already used industrially as pigment and dye. More critical to the pharmaceutical industry, furthermore, acridine is used as a dye, fluorescent material for visualization of the biomolecule, and in laser technology. These properties of Acridine are attributed to its semi-planar heterocyclic structure, which appreciably interacts with the different biomolecular targets. Acridine/Acridone derivative is found in natural plants and various marine organisms [8].

Nanomaterials, particularly metal and metal oxide nanoparticles, are a special class of materials with unique physical and chemical properties that have a wide range of applications. Magnesium Oxide nanoparticles (MgO)NPs have been used in electronics, catalysis, additives, ceramics, photochemical products, paints, and medicine [9]. Engineered aluminum oxide nanoparticles (Al_2O_3) NPs have commercial potential in catalysis, polymer modification, and heat transfer fluids [10]. Vineet Kumar and et al [11] investigated that MgO is used as the adsorbent for Methylene Blue (MB) removal. Also, Using Nano Porous Aluminum Oxide, spectrum information on adsorbed substances may be extracted as demonstrated by Hotta et al., [12]. F.F. Kareem and et al investigated that adding MgO NPs, Al_2O_3 NPs led to enhancing the absorption spectra of Rhodamine 6G (Rh6G) dye solution[13].

The aim is to characterize the absorption properties of PVA/ Acridine Orange (AO) polymer composite filled with nanoparticles. Furthermore, adding Metal Oxide Nanoparticles to polymer composite and study the effect of adding these nanoparticles.

EXPERIMENTAL WORK

Materials

Polyvinyl Alcohol (PVA) $(C_2H_4O)_n$, molecular weight 14 000 g/mol from DBH Chemical LTD Pooled England. Acridine Orange ($C_{17}H_{19}N_3.1/2ZnCl_2.HCl$, molecular weight 369.94 g/mol) from Qualikems Fine Chem Pvt. Ltd. Acridine was dissolved in Distilled Water (H_2O), polarity (10.2) [14], 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), purity of 99.9%) from China.

Preparation of Samples

Preparation of Samples and Equipment's measurements

Acridine Orange dye solution of primary concentration of (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) [15].

$$m = \frac{M_W VC}{1000} \quad (1)$$

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 get concentrations in the range of (1×10^{-2}) M to (1×10^{-6}) M according to eq. (2) [16].

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

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

Preparation of AO /PVA Polymer Film

The casting method is chosen to prepare dye-doped polymer film[17]. Knowing the amount of PVA polymer is dissolved in a constant volume of Distilled water. The preparation solution is stirred very well via magnetic stirrer for (3 hours) until getting a homogeneous solution. Then put onto a glass petri dish and leave at room temperature to obtain homogenous pure PVA film. The concentration of AO in Distilled Water is (3×10^{-5}) M. Films for different volume ratios of solution are chosen: (6, 12, 18, 24, and 30) ml which added to the PVA. The as-prepared precursors are stirred very well via a magnetic stirrer until the (AO/PVA) solution has become homogeneous, it is cast into a glass petri dish and allowed to cool to form a homogeneous film.

Preparation of AO/NPs/PVA Films

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

RESULTS AND DISCUSSIONS

The concentration of Acridine Orange dissolved in Distilled water was ($3×10^{-5}$) M that obeys Beer-Lambert law as shown in Figure 1. The maximum absorption wavelength (λ_{abs}) was 490 nm with shoulder beak at 470 nm and the absorbance 0.80 as shown in Table 1. The transition is $\pi\rightarrow\pi^*$ [18,19].

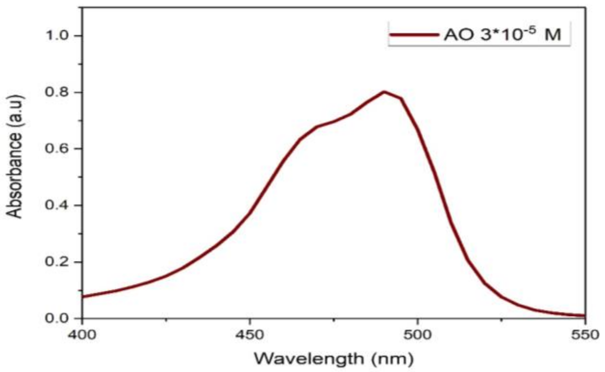

Figure 1. Absorption spectra of Acridine Orange dissolved in distilled water.

The absorption spectra of pure PVA has a wide peak with a maximum wavelength of about 280 nm with an absorbance of 0.21, this result has a good agreement with the research[20].

Table 1. Absorption information of pure PVA and AO/ PVA films with different volumes of AO solution

Samples	PVA Polymer		AO Dye	
	λ_{absmax} (nm)	Abs.	λ_{absmax} (nm)	Abs.
Pure PVA	280	0.21	……..	………
AO ($3×10^{-5}$) M Solution	……..	……	490	0.80
PVA+ 6ml ($3×10^{-5}$) M AO	275	0.19	500	0.10
PVA+ 12ml ($3×10^{-5}$) M AO	275	0.42	500	0.24
PVA+ 18ml ($3×10^{-5}$) M AO	275	0.66	500	0.49
PVA+ 24ml ($3×10^{-5}$) M AO	275	0.44	500	0.35
PVA+ 30ml ($3×10^{-5}$) M AO	275	0.41	500	0.33

The absorption spectra of pure PVA and AO / PVA film with different volume ratios of dye solution (6,12,18,24 and 30) ml at concentration ($3×10^{-5}$) M AO aqueous solution are displayed in Figure 2. Table 1 demonstrates all results. The effect of AO addition on absorption spectra of PVA film is occurrence blue shift (5nm) in the PVA polymer matrix and red shift (10nm) for AO maximum absorption wavelength (Explain the shift of the peak). The small violet shift of approximately 10 nm is due to the weak interaction between the dye molecule and polymer matrix. The difference in the effect of water molecules surrounding the solvent and the solid polymer matrix also contributes to the violet shift in the absorption spectrum corresponding to the polymer matrix[21].

When 18ml of AO dye solution is added, the absorbance of the PVA peak increases to 0.66. The absorbance of AO dye reduces when PVA is added from 0.80 at AO dye solution to be 0.1 and 0.24 at 6 ml and 12 ml respectively, but it increases when the volume ratio of AO dye solution is increased to 0.49 for 18ml and declines for 24- and 30-ml volume ratios owing to form dye aggregation, which inhibits the intensity of the absorption spectra (0.35, 0.33). The transitions are $\pi\rightarrow\pi^*$ due to chromophore groups (the extended conjugated double bond[17,18]. The increase in the volume ratio of AO inside the polymer matrix increases the radiation absorbing species, increasing in absorbance. A key thing to remember is that an attractive dissolving of AO in the PVA matrix, which eliminates Rayleigh scattering, occurs solely in the visible region, maintaining optical purity.[22].

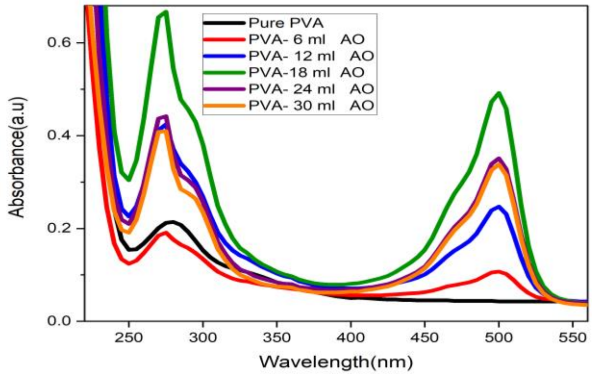

Figure 2. Absorption spectra of pure PVA and AO/ PVA films with different volumes of AO solutions.

To examine the effect of these NPs on PVA/AO polymer composite, Acridine Orange 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 Figure 3.

It is observed that the absorbance increased when adding MgO and Al_2O_3 NPs in the AO polymer matrix, noted the absorbance of adding alumina nanoparticles is more than it is 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[23].

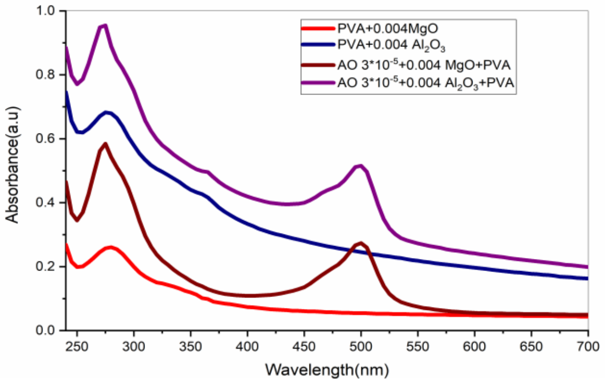

Figure 3. Absorption spectra of PVA/AO polymer composite filled with 0.004 g amount of (MgO - Al_2O_3) nanoparticles.

Furthermore, change in peak position. Also, there is a 10 nm red shift in AO and a 5 nm blue shift in AO when they are added to the polymer matrix filled with MgO and Al_2O_3 NPs which means that adding NPs led to enhancing the photophysical properties of polymer composite as seen in Table 2. Because of its great biodegradability, water solubility, and chemical resistance, using PVA as a suitable host polymer for metal oxide nanoparticles is advantageous in terms of physical and chemical properties.[24].

Table 2. Spectral information of AO dye solution doped PVA polymer matrix filled with

Samples	PVA Polymer		AO Dye	
	λ_{abs} max (nm)	Abs.	λ_{abs} max (nm)	Abs.
AO (3×10^{-5})	…..	…….	490	0.80
0.004 MgO+ PVA	280	0.26	……	…….
0.004 Al_2O_3+ PVA	275	0.68	…….	…….
AO (3×10^{-5}) + 0.004 MgO+ PVA	275	0.58	500	0.27
AO (3×10^{-5}) + 0.004 Al_2O_3+ PVA	275	0.95	500	0.51

CONCLUSIONS

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

1. Impact AO in PVA polymer led to red shift about 10 nm in the absorption spectrum of AO and 5 nm blue shift in PVA polymer composite.
2. The absorbance of AO 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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