

# Optical Properties for Thin Film of Coumarin 334 Organic Laser Dye doped with PVA Polymer and Al<sub>2</sub>O<sub>3</sub> Nanoparticles

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## الخصائص البصرية للغشاء الرقيق لصبغة اليزرية العضوية كومارين (334) المطعمة ببوليمر (PVA) وجسيمات الألومينا النانوية

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#### **ABSTRACT**

#### Background:

In this work, the optical properties for thin film of Coumarin 334 organic laser dye doped with PVA polymer and AL<sub>2</sub>O<sub>3</sub> nanoparticles are determined at different concentrations, dissolved in ethanol solvent. Methods:

Solutions at concentration (10-4 M) from coumarin (334) dye in ethanol solvent at Different concentrations from dye (1, 3, 5, and 7)  $\times 10^{-5}$  M were prepared.

#### Results:

The AFM measurements show that the grain size, root mean square and roughness belong to the surface of the thin films rises with thickness rise for thin films . It has also increased the absorbance due to the increase in concentration.

#### Conclusion:

By using Gaussian beam from CW pulsed laser at 457 nm, we used Z-scan to study the nonlinear optical properties. The nonlinearity of thin film highly excels the pure dye solutions.

Key words: Coumarin 334 Organic Laser Dyes, Non-Linear optical properties, Linear optical properties,

#### **INTRODUCTION**

An organic dye laser uses various lasing métier. These media can be in different states, namely liquid state, gas state, and solid state. Whatever the state of the dye, they all show a characterized feature: It is the absorption range within the visible light. However, this characteristic appears in the organic dyes when they have extra conjugate units connected to the bipartite[1]. These organic molecules are active so that they can be easily dissolved in solvents or they can be integrated into a solid matrix. Furthermore, these molecules envisage their maximum power in the liquid and solid states as lasing media[2]. One of the most important classes of laser dyes is coumarin. The 7-position of coumarin laser dyes contains a potent electron-donating group, either an amino (-NR2) or hydroxyl (-OH). Thus, Coumarin dyes can be used to cover a large adjustable range of (420 to 580 nm). Some of the most effective laser sources employ coumarin dye[3-5]. These compounds are dissolved in an organic solvent and used in dye lasers. They often have a strong absorption band[6]. Depending on their chemical properties, laser dyes can be classified into various classes such as xanthenes, coumarin, and pyrromethene cases [7, 8]. A dye gets its color from the attendance of a chromophore group color[2]. Such dyes can also be used in advanced photonics, fiber optics, optical limiting and optical amplifiers. The practical application of these dyes is the protection of human eye and sensors against laser output. Hence, these polymer-doped dyes are crucial[9]. With increasing particle size, the ratio of surface atoms increases, changing the material's physical and chemical characteristics[10].

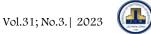
Nanotechnology is one of the best well-liked branches of polymer science and technology. This region frequently promotes novel material behavior. The mechanical, optical, electrical, and magnetic properties of nanocomposites at small nano-filler concentrations have sparked an increase in demand for nanoparticles implanted in polymer ground (1–10%)[11].

#### **MATERIALS AND METHODS**

One of the faviourte lasing dyes in the blue-green spectral region is the coumarin and related members. For instance, their quantum emission is very high which can be invested in different scientific and technological aspects. Coumarin and its derivatives also apply in coloring and non-linear optics because these molecules offer fluorescence property in the UV as well as the visible regions[12]. Molecular formula  $C_{17}H_{17}NO_3$  as shown in Figure (1). Solutions at concentration ( $10^{-4}$  M) from coumarin 334 organic laser dye in ethanol solvent are prepared. The powder is weighted by using an electronic balance type (BL 210 S, Germany), having a sensitivity of four digits. Different concentrations from each dye (1, 3, 5, and 7)× $10^{-5}$  M were prepared according to the following equation[2]:

The above equation shows the weight of the dissolved material (W in g), molecular weight ( $M_w$  in g/mol), volume of the solvent (V in ml), and concentration (C in M). Then, the newly formed solutions are made thinner according to[13]:

$$C_1 V_1 = C_2 V_2$$
 .....(2)



Where C<sub>1</sub> and C<sub>2</sub> are the primary and new concentration, respectively, V<sub>1</sub> is the volume before dilution, and V<sub>2</sub> is the volume after dilution.

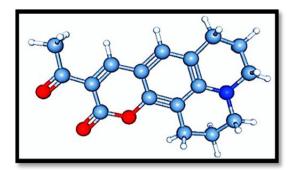


Figure (1): Molecular structure of Coumarin 334 and organic dye.

#### **RESULTS AND DISCUSSION**

Figures (2and 3) show 2-D and 3-D images of AFM for thin films coumarin (334) doped with (PVA )polymer and (Al<sub>2</sub>O<sub>3</sub>) nanoparticles at (10<sup>-3</sup>) M respectively. Table (1) states the average grain size that form the thin films. We have found that the root mean square and size grain and roughness belong to the surface of the thin films rises with thickness rise for thin films coumarin (334) doped with PVA polymer and (Al<sub>2</sub>O<sub>3</sub>) nanoparticles[14]. Absorbance spectra of coumarin organic laser dye at different concentrations (1, 3, 5, and 7) ×10<sup>-5</sup> M in ethanol solvent are observed in wavelengths starting from 190 nm to 1100 nm. We have used UV-visible spectrometer with the following detail. It is Japanese Aquarius 7000 spectrometer from Optima company. Further, the measurements are performed at room temperature. These finding were illustrated in figure (4). From these Figures we can observed that absorption spectrum of coumarin (334) solution has a wide peak over wavelengths from 328 nm to 530 nm. It has also increased the absorbance due to the increase in concentration which produces a high number of moieties pre volumetric part. This is affect the energy state, as well as increasing of linear absorbance index and refractive index and .The results are in consistent behavoiur compared to Beer-Lambert law speculations[15].

The linear absorbance spectra of coumarin (334) dye nano films along different concentrations that also doped with PVA and (Al2O3) nanoparticles are shown in Figure (5).

The absorption peaks obtained here had moved to the red region when we added PVA and Al<sub>2</sub>O<sub>3</sub>. This shift obtain due to electronic and vibrational states of interfacial molecules, which is lead to increasing absorption for all samples of nanocomposites, this is suggested to take place because of the excitations of high occupation molecular orbital (HOMO) electrons to the lowest inoccupation molecular orbital (LUMO). We also use closed- and opened-aperture to measure the Z-scan for nonlinear refractive and absorption coefficients (n2) and ( $\beta$ ), respectively. The experiment is performed under 457 nm and 84 mW power. The obtained results of Z-scan are shown in figure 6 and 7. These normalized transmittances are measure as a function of distance of coumarin 344 dye doped with PVA polymer and (Al<sub>2</sub>O<sub>3</sub>) NPs dissolved in ethanol

solvent. The experiment was also conducted in four concentrations (1, 3, 5, and  $7\times10-5$  M). It should be mentioned that the region of the nonlinear effect was (-2) to (+2) mm. The negative slope of the transmittance of the closed Z-Scan refers to positive refraction nonlinearity (n2 > 0 ), and hence it shows a self-focusing feature are shown in Figure (8). Figure (9) illustrates saturable absorption phenomenon that is got from the open-Z-Scan). The nonlinear parameters are calculated ,as tabulated in Table (2) from this Table we show that the values of nonlinear parameters (n2 and β) are increased with increasing the concentrations, as omit due to its repetition the values of linear parameters (ao and no). This is due to increasing number of molecules per volume unit at high concentrations.

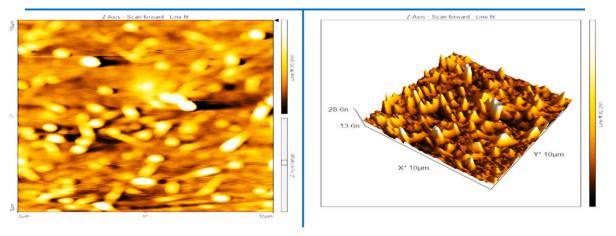


Figure (2): 2-D and 3-D AFM images for thin films of Coumarin (334) doped with PVA polymer.

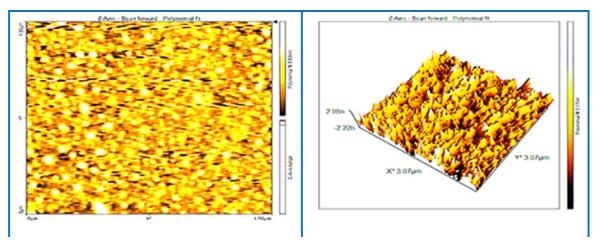


Figure (3): 2-D and 3-D AFM images for thin films of Coumarin (334) doped with PVA polymer and Al<sub>2</sub>O<sub>3</sub> NPs.



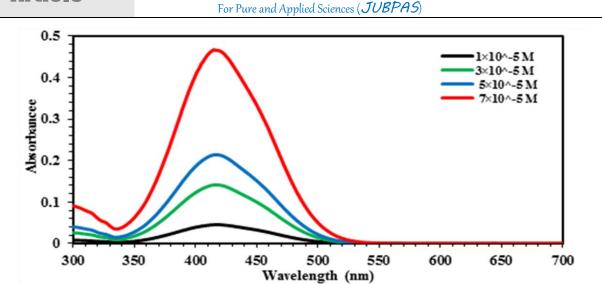


Figure (4):The absorbance spectra for Coumarin (334) organic laser dye at different concentrations.

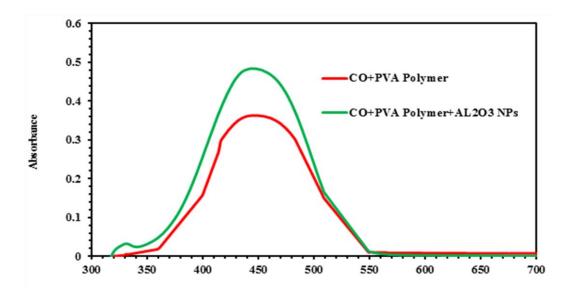


Figure (5): The Absorbance Spectrum For Thin Films of Coumarin (334) Organic Laser Dye Doped With PVA Polymer And Al<sub>2</sub>O<sub>3</sub> Nps.

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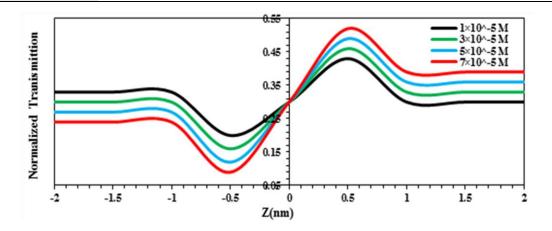


Figure (6): Closed-aperture Z-Scan data for different concentrations of (Coumarin (334)) organic laser dye in (Ethanol) solvent.

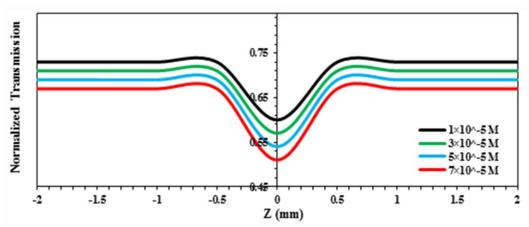


Figure (7): Open-aperture Z-Scan data for different concentrations of (Coumarin (334)) organic laser dye in ethanol solvent.

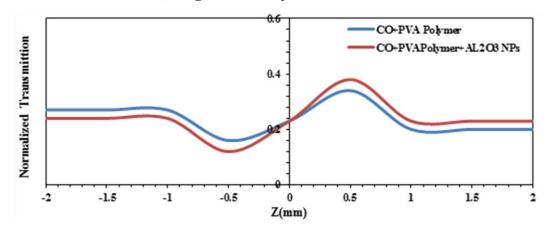


Figure (8): Closed-aperture Z-Scan data for thin films of (Coumarin (334)) organic laser dye doped with PVA polymer and (Al<sub>2</sub>O<sub>3</sub>) NPs.



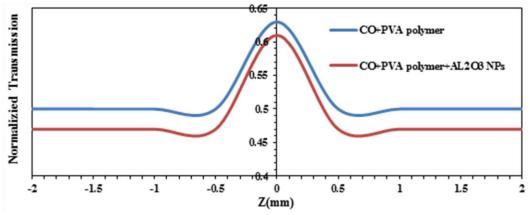


Figure (9): Open-aperture Z-Scan data for thin films of (Coumarin 344) organic laser dye doped with PVA polymer and(Al<sub>2</sub>O<sub>3</sub>) NPs.

#### Table (1): The Linear Optical Parameters for Thin Films of Coumarin 344 Dye in Ethanol Solvent.

Material	r.m.s (nm)	Roughness (nm)	Average Grain Size (nm)	Thickness (nm)	
CO+PVA polymer	1.191	0.277	18.29	110	
CO+PVA polymer +Al <sub>2</sub> O <sub>3</sub> NPs	2.338	0.667	40.72	124	

Table (2): Linear and nonlinear optical parameters for different concentrations of Coumarin (344) and its thin films at  $\lambda$ =457nm.

Material	Concentratio n (Mol/L)	T	(α°) cm <sup>-1</sup>	n°	ΔTP-V	n <sub>2</sub> (cm2/mW)	β (cm/mW)
Coumarin (344) (Solutions)	1×10 <sup>-5</sup>	0.9353	0.0667	1.1470	0.011	2.1188×10 <sup>-11</sup>	0.8392×10 <sup>-3</sup>
	3×10 <sup>-5</sup>	0.8170	0.20208	1.4296	0.024	4.2731×10 <sup>-11</sup>	1.0786×10 <sup>-3</sup>
	5×10 <sup>-5</sup>	0.7361	0.3062	1.6777	0.031	6.3839×10 <sup>-11</sup>	1.3073×10 <sup>-3</sup>
	7×10 <sup>-5</sup>	0.5086	0.6759	2.0583	0.043	6.9855×10 <sup>-11</sup>	1.4265×10 <sup>-3</sup>
CO+PVA polymer (Thin films)	1×10 <sup>-3</sup>	0.6018	5374.2	1.158	0.110	1.7310-7	1.245
CO+PVA polymer + Al <sub>2</sub> O <sub>3</sub> NPs (Thin films)	1×10 <sup>-3</sup>	0.5717	5971.44	1.1623	0.123	2.3410 <sup>-7</sup>	2.673

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#### Conflict of interests.

There are non-conflicts of interest.

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#### الخلاصة

#### مقدمة:

في هذا العمل تم تحديد الخواص البصرية للغشاء الرقيق للصبغة اليزرية العضوية كومارين (334) المطعمة ببوليمر PVA وجزيئات Al<sub>2</sub>O<sub>3</sub> النانوية في مذيب الإيثانول.

#### طرق العمل:

تم تحضير المحلول بتركيز (4-10) مولاري من صبغة الكومارين (334) الليزرية العضوية في مذيب الايثانول. بعد ذلك تم تحضير تراكيز مختلفة من صبغة الكومارين  $10^{-5} \times (7, 5, 5, 1)$ .

#### الاستنتاجات:

أظهرت قياسات AFM أن معدل الحجم الحبيبي ومتوسط الجذر التربيعي وخشونة السطح للأغشية الرقيقة تزداد مع زيادة سمك الغشاء الرقيق للكومارين (334) المطعمة ببوليمر PVA و (Al2O3) النانوية . كما نلاحظ ان الامتصاصية تزداد بزيادة التركيز .

الكلمات المفتاحية: صبغة الكومارين (334) الليزرية العضوية ، الخصائص البصرية غير الخطية ، الخواص البصرية الخطية