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RESEARCH ARTICLE

Study of the absorption and emission spectra of polymeric films colored with laser organic dyes

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ABSTRACT

This study focuses on the absorption and emission (fluorescence) spectra of two organic dyes, Rhodamine and Fluorescein. The dyes are prepared as liquid samples dissolved in a polyvinyl alcohol (PVA) polymer solution at different concentrations (0.01, 0.02, 0.03, and 0.04 mM). Solid samples in the form of PVA polymer films doped with Rhodamine and Fluorescein are also prepared using the casting method, in which the dyes are directly mixed with the polymer solution at different concentrations (0.01, 0.02, 0.03, and 0.04 mM), while maintaining a constant film thickness of 120 μm.

The absorbance values of all prepared samples are measured using a UV–Vis spectrophotometer. The results indicate that increasing dye concentration affects the linear optical properties of the prepared samples, resulting in increased absorbance and decreased transmittance, consistent with the Beer–Lambert law. Increasing the dye concentration also results in higher calculated linear optical coefficients, including the linear refractive index and linear absorption coefficient, for all samples.

Fluorescence spectra are measured using a fluorescence spectrometer, and the fluorescence lifetime and quantum efficiency are calculated to evaluate the emission properties of the studied dyes. The results indicate that the Rhodamine- and Fluorescein-doped PVA films possess promising optical properties, demonstrating their potential for advanced photonic and laser applications.

Keywords: absorption and fluorescenc, pva polymer (polyvinyl alcohol), organic dyes, quantitative efficiency of fluorescence, linear optical properties

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1. Introduction

Organic dyes are hydrocarbon-based compounds composed of large, structurally complex molecules. They are characterized by broad absorption and fluorescence spectra that span the visible and ultraviolet regions of the electromagnetic spectrum, in addition to possessing high molecular weights. This behavior is attributed to the presence of conjugated chains formed by carbon atoms linked through alternating single and double bonds, commonly referred to as the chromophore system [1].

The chromophore is the primary structural unit responsible for light absorption in the ultraviolet and visible regions, which imparts color to the dye. This occurs because the absorption transitions from the ground state (S_0) to the first excited state (S_1) take place within the visible range [2].

Organic dyes have attracted significant attention in both academic and industrial fields due to their distinct advantages, including low cost, high flexibility, tunable properties, and unique optical characteristics [3].

Fluorescent dyes, which constitute a fundamental component of this study, are advanced aromatic organic compounds distinguished by conjugated ring systems containing delocalized π-electrons, thereby exhibiting an exceptional ability to absorb photons and undergo highly efficient photoexcitation processes [4].

Fluorescent dyes have highly distinctive and precisely defined absorption and emission spectra, making them extremely valuable for the design and enhancement of advanced optical systems aimed at precise spectral analysis and the study of their advanced photophysical properties [5].

In the past, the global production of dyes was mainly concentrated in Europe; however, the production landscape has changed in recent times, with China and India now leading the list of the largest dye-producing countries. Dyes are involved in a wide range of industrial and daily-life applications, as they are primarily used in textile and dyeing industries, inks and digital printing, color imaging, as well as in pharmaceutical and food industries, in addition to cosmetics and skin care products [6].

The raw materials used in the production of these dyes are often classified as toxic compounds, and they have been associated with carcinogenic effects. Examples include aniline, benzidine, and other amino and toluene-based compounds. Moreover, these substances may be formed or reconstituted as a result of dye degradation during certain biological processes, which increases their potential health and environmental risks [7,8].

The combination of polymers and dyes, within the framework of functional macromolecules, represents a leading research area for the development of hybrid materials with high performance and enhanced photophysical and chemical properties. This integration has elevated colored polymers as strategic components in modern technological applications, alongside their growing role in various aspects of daily life. Their applications span advanced coatings, biomedical devices, and gas separation technologies, reflecting their exceptional ability to combine structural stability with high functional efficiency and highlighting their significant potential in advancing innovation in the design of functional materials and industrial technologies [9].

PVA polymer was chosen for this study due to its exceptional properties, including high optical transparency, excellent water solubility, notable thermal stability, and resistance to corrosion, making it an ideal matrix for optoelectronic applications and a wide range of advanced technological uses [10–12].

PVA is an efficiently biodegradable polymer, as its hydroxyl groups on the carbon atoms enhance its hydrolytic degradability. Moreover, it exhibits high water solubility and a hydrophilic nature, making it an ideal material for advanced environmental and technological applications that require both performance and sustainability [13–18].

Organic polymers are often used as solid hosts because of the high yield of dyes retained in the solid host medium and the wide tunability of the visible spectrum. Therefore, they are characterized by cleanliness and low cost of active ingredients that can be radically replaced to reach different spectral regions with different dyes [19].

2. Theoretical Part

The linear absorption coefficient (α_0) was calculated using the established mathematical expression [20].

$$\alpha_0 = \frac{\ln\left(\frac{1}{T}\right)}{t} \quad (1)$$

The sample thickness is denoted by (t), transmittance by (T), and refractive index by (n_0). The equation given in reference [21] is used to accurately determine the presence of the film and evaluate its continuity based on its transmittance spectrum.

$$n_0 = \frac{1}{T} + \left(\frac{1}{T^2} - 1\right)^{1/2} \quad (2)$$

Transmittance indicates the percentage of incident light that passes through a solution. Therefore, if half of the incident light passes through, the transmittance of the solution is 50% [21].

$$T\% = \left(\frac{I}{I_0}\right) \times 100\% \quad (3)$$

Where I_0 is the intensity of the incident light beam, and I is the intensity of the light transmitted through the liquid. To demonstrate the relationship between the transmittance factor (T) and the absorption factor (A), the following mathematical expression is used [20,22].

$$A = \log_{10}\left(\frac{I_0}{I}\right) \quad (4)$$

By adopting and accurately applying the appropriate mathematical equation, both the fluorescence quantum yield (Φf) and the fluorescence lifetime can be calculated and determined based on the quantitative results obtained from the analysis of the fluorescence emission spectra [22].

$$\tau_f = \frac{a \times \tau_{fRB}}{a_{RB}} \quad (5)$$

The lifetime of the standard chemical, denoted as (τfRB), is determined with high precision and quantitatively by performing the complete integration of the fluorescence curve of the laser organic dye, based on the reliable experimental data obtained [22].

$$\phi_f = \frac{\int F(v')\,dv'}{\int \varepsilon(v')\,dv'} \quad (6)$$

The area under the curve Is denoted by∫F(v') dv', while the area under the absorption curve is denoted by ∫ε(v') dv'.

3. The Experimental Part

3.1. The materials used

Table 1. Exploring the Physicochemical Attributes of Organic Dyes in This Research

Organic Dye	The formula for a chemical	Weight of a molecule (g/mol)	Appearance	Solubility / Polymer incorporation
Rhodamine B	C28H31ClN2O3	479.01	Red powder	Soluble in water and incorporated into the PVA matrix.
Fluorescein	C20H12O5	332.31	Yellow powder	Soluble in water and incorporated into the PVA matrix.

3.2. Solutions preparation

Using the casting method, PVA (polyvinyl alcohol) polymer films doped with organic dyes, namely Rhodamine B, Fluorescein, were prepared. To prepare the polymer solution, 1 g of PVA was dissolved in 30 mL of distilled water at 50 °C under continuous magnetic stirring for 40 min until a homogeneous solution was obtained. Subsequently, specific amounts of the dyes were added to the PVA solution and stirred using a magnetic stirrer to ensure a homogeneous mixture.

The resulting solution was then poured into Petri dishes and left to dry for one week to form dye-doped PVA polymer films. This procedure was repeated for each dye concentration (0.01, 0.02, 0.03, and 0.04 mM) in the precursor solution to obtain several dye-doped PVA films with an approximate thickness of 120 μm. Figure 1 shows PVA polymer films doped with organic dyes at different concentrations.

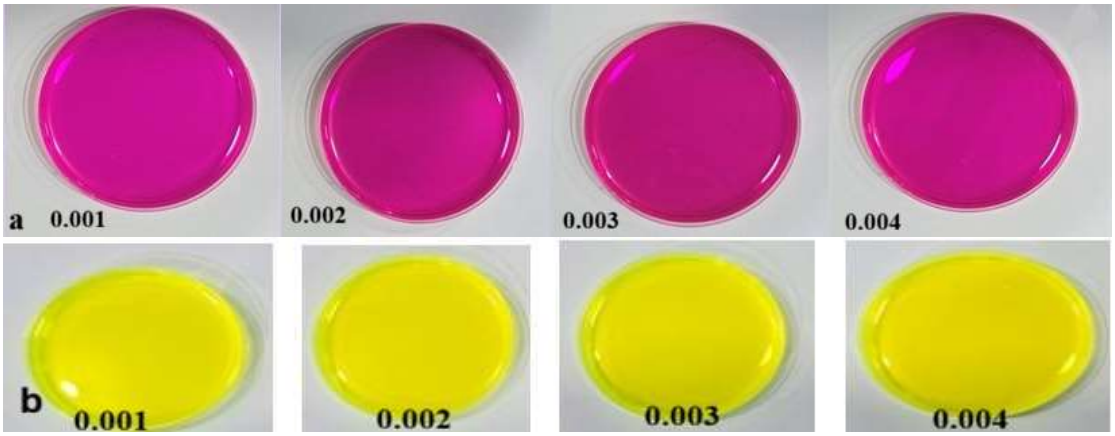


Figure 1. The figure shows Samples of PVA polymer film with organic dyes added at different levels:
(a) Rhodamine dye
(b) Fluorescein dye

3.3. UV-Visible Spectrophotometer

A UV–Visible Shimadzu 1800 spectrophotometer was used to determine the linear optical properties of all prepared samples, such as transmittance, absorption coefficient, and refractive index. The spectrophotometer has two light sources: a deuterium lamp operating in the range of 190–390 nm and a tungsten lamp operating in the range of 390–1100 nm.

A computer program was used to analyze the output data, including wavelength, absorbance, and transmittance, in order to calculate the optical constants. A silicon photodiode detector was used to receive the optical signal.

3.4. FluorescenceSpectrophotometer

The fluorescence spectra of the prepared dyes were measured using a PRO 150F96 fluorescence spectrometer. The instrument consists of a xenon arc lamp as the light source, covering an excitation and emission wavelength range of 200–700 nm. The scanning rates were 200, 400, and 600 nm/min, and detection was carried out using a high-sensitivity photomultiplier tube (PMT) connected to a computer for data acquisition.

4. Results and Discussion.

UV–visible spectrophotometry (UV–Vis) was used to investigate the absorption and transmittance spectra of the organic dyes Fluorescein and Rhodamine incorporated into polyvinyl alcohol (PVA) polymer films at different concentrations. The results showed that increasing the dye concentration significantly increased the absorbance and decreased the transmittance, in accordance with the Beer–Lambert law. The studied dyes exhibited different absorption behaviors due to differences in their molecular structures, demonstrating the influence of chemical composition on their spectral properties. The results also showed that increased absorption at higher dye concentrations enhanced the linear optical properties of the materials at specific wavelengths.

The absorbance and emission spectra were used to determine the linear absorption coefficient, refractive index, fluorescence lifetime, and fluorescence quantum efficiency. The findings indicated that reducing the dye concentration enhanced the fluorescence quantum efficiency, thereby improving the fluorescence emission efficiency. This behavior can be attributed mainly to concentration quenching and increased interactions between neighboring dye molecules at higher concentrations. As the dye concentration increases, the probability of molecular aggregation and non-radiative energy transfer increases, providing additional non-radiative relaxation pathways and consequently reducing the fluorescence efficiency. These molecular interactions can also affect the fluorescence lifetime by increasing the non-radiative decay rate. Therefore, the

observed changes in fluorescence lifetime and quantum efficiency with increasing dye concentration can be associated with concentration-dependent molecular interactions and aggregation within the PVA matrix.

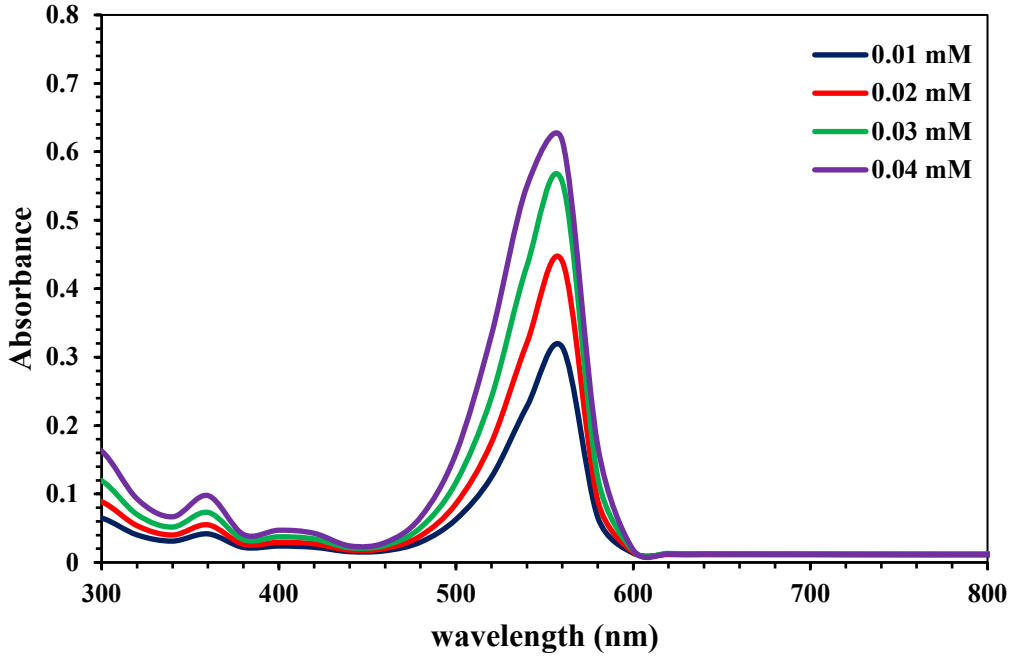


Figure 2. Absorbance spectra as a function of wavelength for (RB-PVA) films at different values of dye concentrations

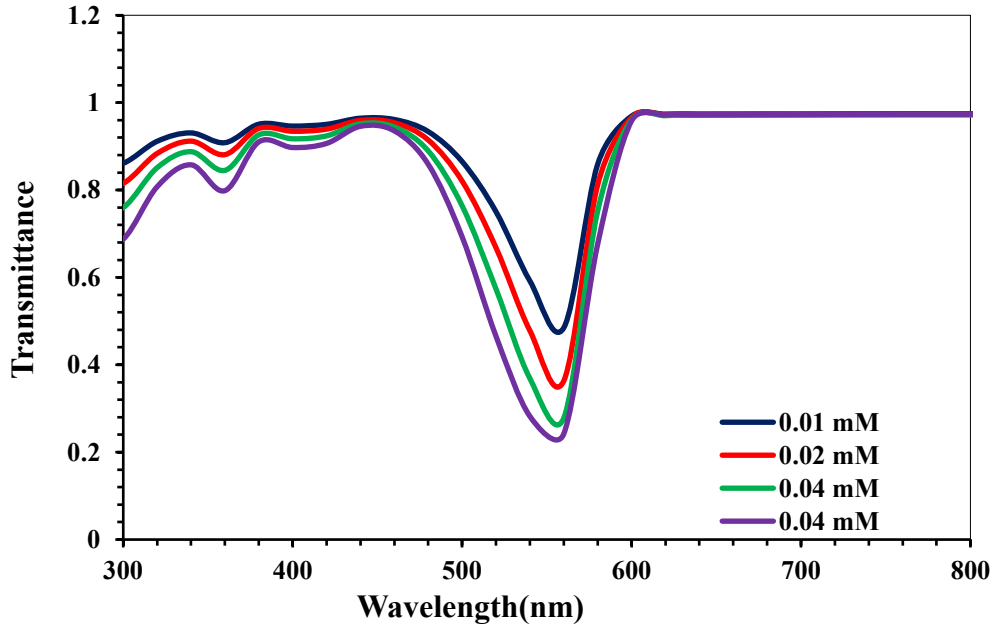


Figure 3. Transmittance spectra as a function of wavelength for (RB-PVA) films at different values of dye concentration

Table 2. Optical characteristics of RB-PVA films exhibiting varying dye concentrations at the peak wavelength (λmax = 560 nm).

Samples	Dye Concentration (mM)	A	T	α	n	K × 10^{-4}	1Ɛ	2Ɛ × 10^{-4}
RB+PVA	0.01	0.31	0.49	60.35	2.21	2.69	4.88	14.12
	0.02	0.44	0.36	84.41	2.38	3.76	5.65	19.54
	0.03	0.55	0.28	106.65	2.59	4.76	6.74	22.60
	0.04	0.62	0.24	118.24	2.61	5.27	6.89	23.28

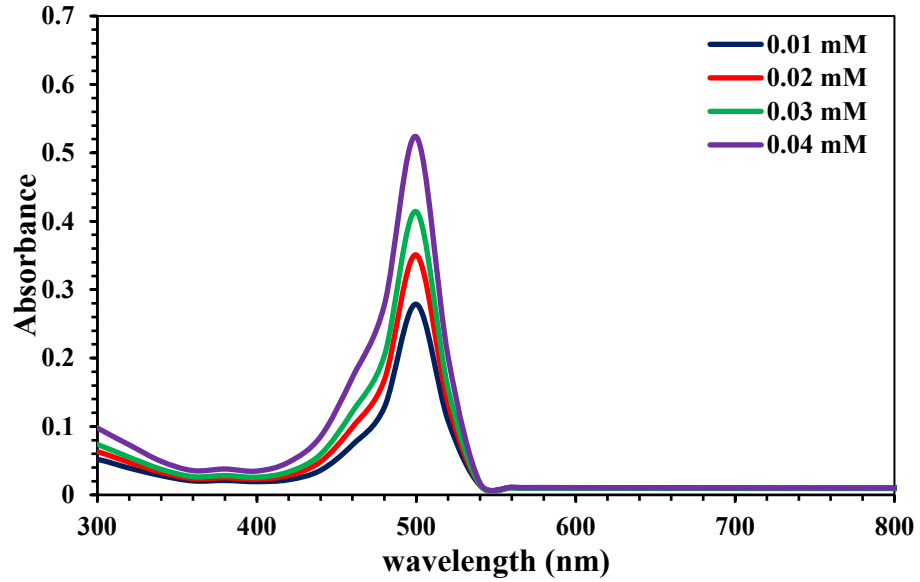


Figure 4. The absorbance spectra for FL-PVA films at different dye concentration levels as a function of wavelength.

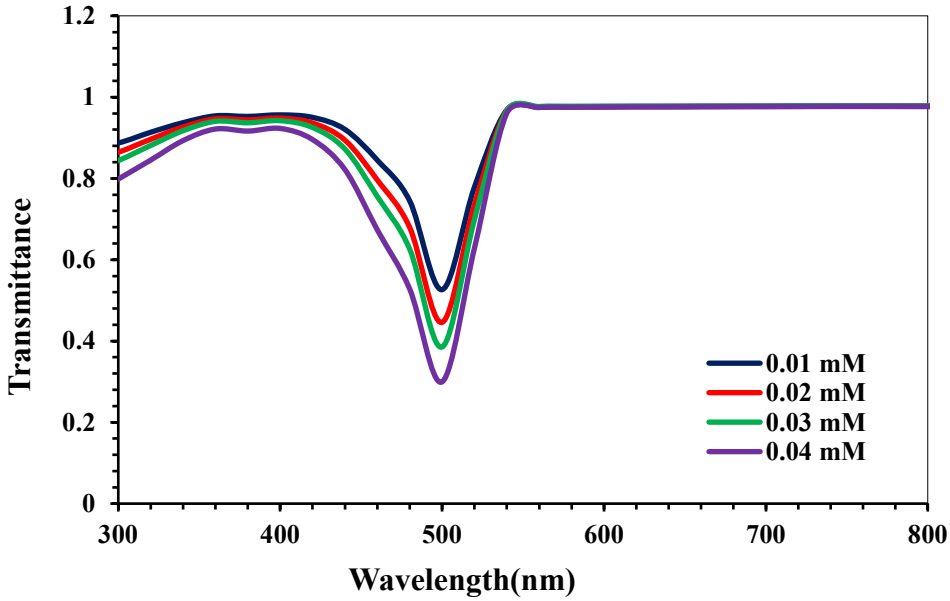


Figure 5. Transmittance spectra for FL-PVA films with different amounts of dye, plotted against wavelength.

Table 3. Optical properties of FL-PVA films with different amounts of dye at the highest wavelength (λmax = 500 nm)

Samples	Concentration of Dye(mM)	A	T	α	n	K × 10^{-4}	1Ɛ	2Ɛ × 10^{-4}
FL+PVA	0.01	0.28	0.53	53.49	2.45	2.13	6.01	10.99
	0.02	0.35	0.45	67.31	2.59	2.68	6.66	14.16
	0.03	0.41	0.39	79.49	2.62	3.16	6.87	16.59
	0.04	0.52	0.29	100.48	2.64	4.01	6.98	19.62

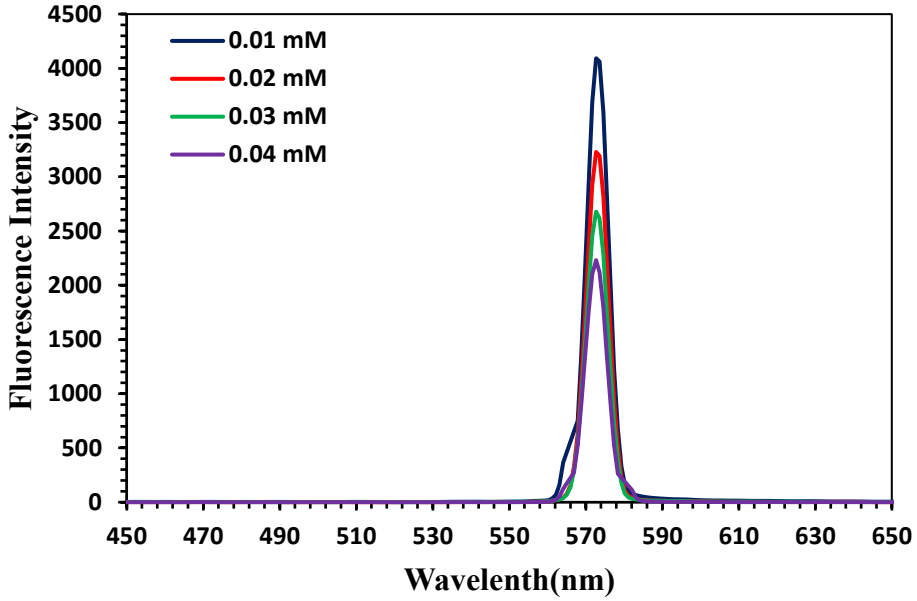


Figure 6. Fluorescence spectra for RB-PVA films with different dye concentrations as a function of wavelength

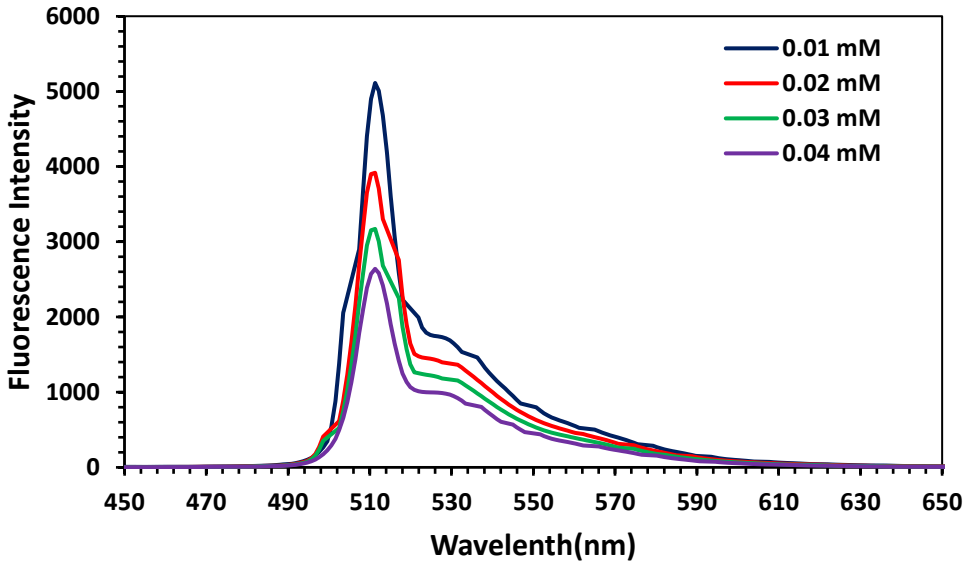


Figure 7. Fluorescence spectra as a function of wavelength for (FL-PVA) films at different values of dye concentrations

Table 4. Fluorescence Properties of Rhodamine B and Fluorescein in a PVA Polymer Matrix with Different Dyes

Samples	Dye Concentrations (mM)	Fluorescence Intensity	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift $\lambda_{em}-\lambda_{abs}$ nm)(	$_{fm}\tau$ (nsec)	Φ_{fm}	q_{fm} %
(PVA+Rh B)	0.01	4092	560	572	12	1.31	0.52	52
	0.02	3228	560	572	12	2.12	0.29	29
	0.03	2678	560	572	12	3.15	0.18	18
	0.04	2231	560	572	12	3.77	0.12	12
(PVA+FL)	0.01	5112.07	500	511	11	0.98	0.59	59
	0.02	3917.11	500	511	11	1.56	0.37	37
	0.03	3170.44	500	511	11	2.33	0.26	26
	0.04	2639.79	560	511	11	2.96	0.09	9

5. Conclusions

As stated above, increasing the concentration of organic dyes used in this study leads to higher absorbance values and lower transmittance, which is consistent with the Beer–Lambert law, thereby resulting in an increase in the linear optical properties (linear absorption coefficient and refractive index). It was observed that the highest absorbance values and optical properties were found in the Rhodamine-doped PVA films.

The results showed a clear increase in the values with increasing concentration. The fluorescence spectra also demonstrated a direct relationship with concentration, where the fluorescence intensity increased as the concentration increased. Conversely, the increase in radiative lifetime and fluorescence lifetime led to a decrease in quantum efficiency with increasing concentration.

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