

# Optical Limiting Characteristics for Thin Film of Orcein Dye Doped with PVA Polymer and Nanoparticles

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**Abstract.** It has studied involves the investigation of the spectrum, linear, and nonlinear optical characteristics of (Orcein) organic laser dye at condensations ( $10^{-5}M$ ), doped with polymer and nanomaterials, to apply it in the field of nonlinear optical properties. It is possible to improve and enhance many of the characteristics of organic dyes by performing them with polymer and nanoparticle substances, that is advantageous for practical applications. The spectral optical properties for all prepared samples have been studied using a spectrophotometer for all prepared samples. The measured nonlinear is involved utilizing (Z - Scan) method in two cases (Open aperture) and (Close aperture) to get nonlinear refractive index ( $n_2$ ) and nonlinear absorption factor ( $\beta$ ). A (457nm) wavelength solid-state laser was used to conduct the experiments. The findings revealed that increasing the nonlinear refractive index caused the nonlinear absorption coefficient to decrease, but that raising the nonlinear refractive index caused the nonlinear absorption coefficient to increase for all of the produced samples. The nonlinear characteristics of the doped samples with the polymer were found to be improved, and the nonlinear refractive index of all samples increased as the power of the laser was increased. The nonlinear absorption coefficient of all samples, on the other hand, falls as the power of the sample increases.

**Key words:** Linear Optical Coefficients, Z-Scan Method, Non-linear optical characteristics, Nonlinear Refractive Index.

## 1. Introduction

A simple method called Z- Scan can be used to explore nonlinear optical features. For identifying nonlinear optical characteristics, it is a sensitive and widely used experimental approach. It can be used to calculate nonlinear absorption (NLA) and nonlinear refraction (NLR) in solids and liquids, as well as to investigate materials' optical limiting behavior [1].

By employing the Z-Scan approach, it is possible to study the optical nonlinearity of a variety of organic materials. The Z-Scan approach is a straightforward and sensitive method for measuring the nonlinear refractive index of optical materials that was first introduced in 1990. When a sample is moved in the direction of the strongest form created lengthways on the z-axis, a detector positioned behind a tiny aperture detects changes in the refractive index owing to optical nonlinearities in the model. Low-power continuous wave (CW) lasers were used in combination with the Z-Scan technology to detect small linear absorption. Optical limiters, which are organic materials or devices whose transmission diminishes with increasing light intensity, are used in the protection of the eyes and sensors to limit the transmission of light. When exposed to low incoming light, an optical limiter should have linear transmittance; nevertheless, when exposed to strong incident light, the limiter should become opaque [2].

Hydrocarbons and their derivatives are considered organic substances. Saturated and unsaturated chemicals can be separated from them [3]. High molecular weight organic laser dyes have extended conjugated double bond systems which make them luminous. They're dispersed in an organic solvent using a dye laser, which uses an organic solvent. It is common for them to have a large absorption band [4]. Laser dyes are chemical compounds with a variety of ring configurations that result in a wide range of absorption and emanation spectra. It can be divided into several groups based on structural chemistry similarities. Three simple examples are coumarin, xanthene, and pyrromethene. The structure and arrangement of the molecules have a significant impact on spectrum emission [5].

A (CW) diode solid state laser operating at ( $\lambda=457$  nm) wavelength and (56,70,84,102 mW) power was used in this work to explore the nonlinear optical characteristics of an organic laser dye at condensations ( $10^{-5}$ M) to determine whether it may be utilized as an effective limiter device for various applications.

## 2. Theory

### 2.1 Z-Scan Technique and Nonlinear Optical Properties Measurements

The Z-Scan method is a simple and straightforward approach for detecting nonlinear refraction and nonlinear absorption. A single beam is used in this procedure. Inserting a sample into a concentrated Gaussian beam and translating it along the beam axis through a focal area is known as vocalization. Wavefront distortion generated by self-focusing or self-defocusing causes Kerr nonlinearity. At far-field, the beam power propagating through a narrow aperture varies with sample position. Nonlinearity can be determined using the output power versus position sample approach. Closed-aperture and open-aperture systems are the two forms of Z-Scans [6].

#### 2.1.1 Closed-aperture Z-Scan

The shift in a beam density focused by lens L as the sample passes through the focal plane is investigated using a Z-Scan with a closed aperture. The far-field photodetector PD collects light passing via an axially centered aperture A." As you can see in "In a nonlinear sample, sample S self-focusing or self-defocusing induces a change in the index of refraction, resulting in the creation of a lens [7].

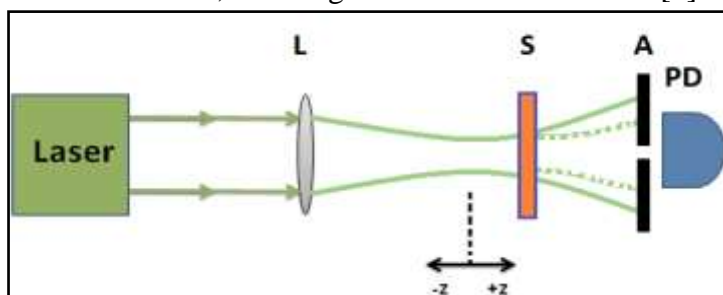
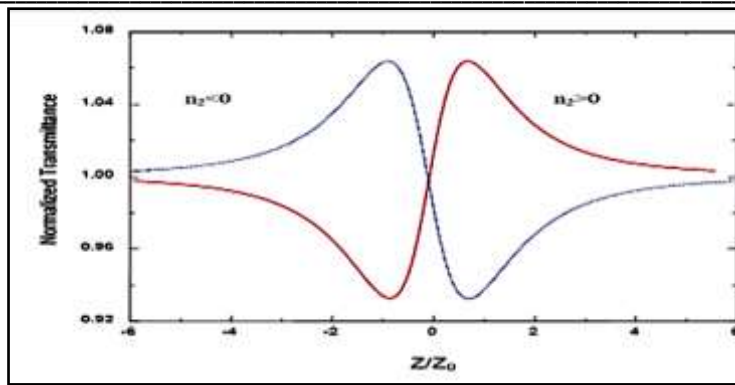


Figure 1. Closed aperture Z-Scan [ 7]

If a material with a negative nonlinear refractive index and a density less than the focused beam's deflection length is used, the Z-Scan transference as a function of Z is linked to the sample's nonlinear refraction. This is an example of a lens with a narrow focal length that can be changed. In addition to the effort, the beam brightness and nonlinear refraction are both low ( $Z_0$ ). "The calculated transference is constant in this situation" (i.e., Z-independent)." Like the sample tactics the beam, the irradiance rises, generating self-lensing in the sample. In the far-field, a negative self-lens in front of the focal plane attempts to collimate the beam on the aperture, boosting iris position transmission. The same self-defocusing that follows the focal plane enhances beam variety, causing the beam to spread at the aperture and decreasing calculated transference. Far from the focus, nonlinear refraction is negligible ( $Z > 0$ ), resulting in Z-independent transmission. A Z-Scan feature of a negative nonlinearity is a transference "maximum (peak)" followed by a transference "minimum (valley)." The inverse Z-Scan curve of a positive nonlinearity (i.e., a peak follows a valley). These two scenarios are depicted in "Figure 2" [ 8].



**Figure 2. Measured Z-Scan transference curves for a cubic nonlinearity [8].**

The following formula is used to compute the nonlinear refractive coefficient from the standardized transmittance peak to valley difference [9].

$$n_2 = \frac{\Delta\Phi_o}{I_o L_{eff} k} \quad (1)$$

Where,  $k = 2\pi/\lambda$ ,  $k$  represents wave number,  $I_o$  refers to the density at the focal spot and  $\Delta\Phi_o$  is the nonlinear phase shift:

$$\Delta T_{p-v} = 0.406 |\Delta\Phi_o| \quad (2)$$

$\Delta T_{p-v}$  the distinction between the standardized peak and valley transferences,  $L_{eff}$  is the effective length of the sample, determined from [10].

$$L_{eff} = \frac{(1 - \exp^{-\alpha_o L})}{\alpha_o} \quad (3)$$

Where  $L$  points out to the length of the sample and  $\alpha_o$  represents linear absorption coefficient which is given as [11].

$$\alpha_o = \frac{\ln\left(\frac{1}{T}\right)}{t} \quad (4)$$

Where  $T$  is the transmittance. The linear refractive index ( $n_o$ ) gotten from equation [10].

$$n_o = \frac{1}{T} + \left[ \left( \frac{1}{T^2} - 1 \right) \right]^{1/2} \quad (5)$$

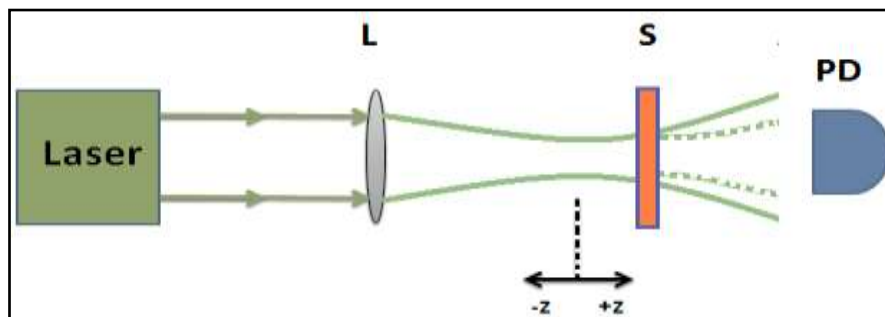
The density at the focal spot is provided by [12].

$$I_o = \frac{2P_{peak}}{\pi\omega_o^2} \quad (6)$$

Where  $\omega_o$  refers to the beam radius at the focal point, the concentrated sample is defined as the peak density.

### 2.1.2 Open-aperture Z-Scan

An example might be "The open-aperture Z-Scan examines the density shift of a far-field beam at photodetector PD, which holds the entire beam as concentrated a lens (L) in "Figure 3".



**Figure 3. Z-Scan that is Open-aperture [13]**

There is a great deal of interest in discovering materials that exhibit rapid nonlinearities.

### 3. Employed Materials

#### A. Orcein Dye

The structural formula ( $C_{28}H_{24}N_2O_7$ ), its molecular weight is (500.51g/Mol), dissolves in water to give an acid aqueous solution, but it is rarely soluble in ethyl alcohol. "Figure 4". shows the chemical structure of the Orcein dye.

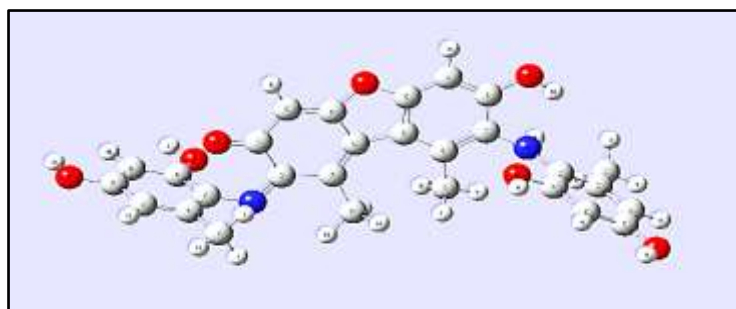


Figure 4. molecular composition of Orcein organic dye

#### B- Ethanol Solvent

Ethanol, commonly known as (ethyl alcohol), is a colorless liquid that is composed entirely of pure alcohol. When Ethanol is ingested, it has the potential to induce alcohol intoxication. It has a blue flame that burns. The presence of the hydroxyl group in ethanol, as well as the length of its carbon chain, are responsible for the majority of its physical characteristics. A volatile colorless liquid having a density of (0.789) grams per cubic centimeter and a molecular weight of (46.07) (gm / Mol).

#### C- Polyvinyl alcohol (PVA)

Previously, polyvinyl alcohol (PVA) was utilized; the parameters of this polymer are provided in "Table 1". Since the early 1930s, polyvinyl alcohols (PVA) have been used in an extensive variety of manufacturing, commercial, medical, and food applications, including resins, lacquers, medical threads, and food interaction requests. It can dissolve in water, is resistant to solvents and oils, and has an exceptional ability to adhere cellulosic materials, so it has a wide range of applications in the paper and textile industries, as well as in industry resistance to oxygen membranes in photographic film coating, and in high-voltage applications to have high tensile strength and storage capacity. "Figure 5" depicts the structure of polyvinyl alcohol.

Figure 5. The construction of polyvinyl alcohol (PVA)

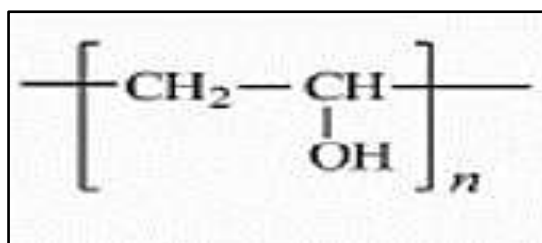


Table 1. The principal qualities of polymer

Formula for a molecule	Avantor (Netherlands)
Solubility	Water soluble
Physical Appearance	White, odorless

#### D- Silver nanoparticles (Ag NPs)

Laboratory Reagent LTD supplied the silver nanoparticles, which have the following major characteristics are shown in "Table 2". Silver nanoparticles are silver nanoparticles with a size of (1 to 100) nm. While many are referred to as "silver," some include a high percentage of silver oxide due to their high surface-to-bulk silver atom ratio. Nanoparticles can be made in a variety of shapes, depending on the study's applicability.

**Table 2. The main characteristics of Ag NPs nanoparticles.**

<b>Nanoparticles of silver</b>	<i>Description</i>
<b>Productive company</b>	<i>SIGMA-ALDRICH, Germany</i>
<b>Molecular formula</b>	<i>Ag NPs</i>
<b>form</b>	<i>Nano powder</i>
<b>the area of the surface</b>	<i>&gt; 40 m<sup>2</sup>/g</i>
<b>Size of the particles</b>	<i>(1-100) nm</i>

#### 4. The Preparation of Samples

Dissolve (0.05005gm) of the dye powder in a volume of Ethanol solvent (10 cm<sup>3</sup>) using solutions with a concentration of (10<sup>-5</sup>) M of Orcein. To determine the concentration of the dye powder, a four-digit sensitivity electronic balance (BL 210 S) from Germany was used according to the equation.

$$W = \frac{M_W \times V \times C}{1000} \quad (7)$$

There are four factors to consider: weight (g), molecular weight (g/mol) of the substance, volume (mL) of the solvent, and concentration (M).

The process of preparing a less intense focus (10<sup>-5</sup>M) The dilution relationship, which is derived from the concentration, is utilized [2].

$$C_1 V_1 = C_2 V_2 \quad (8)$$

Where (C<sub>1</sub>) denotes the primary concentration and (C<sub>2</sub>) denotes the new concentration. (V<sub>1</sub>) refers to the volume before dilution, whereas (V<sub>2</sub>) refers to the volume after dilution.

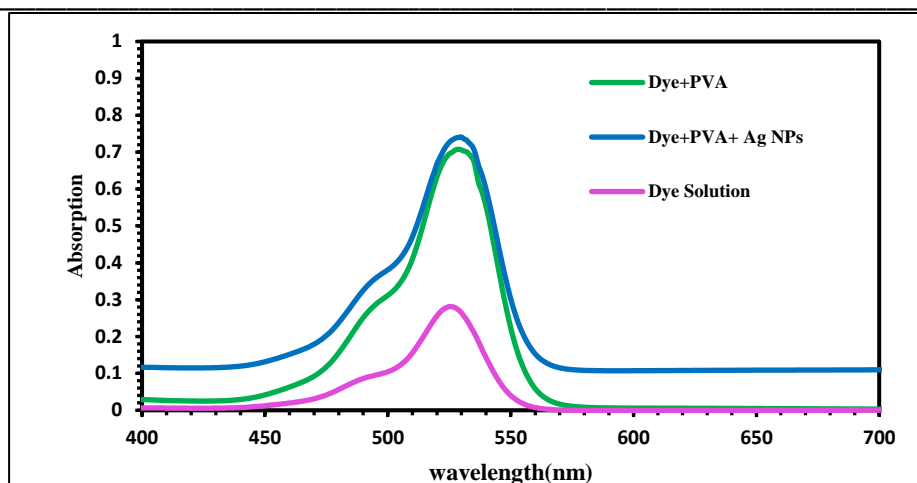
Using the drop casting method, on a clean glass slide, thin films of Orcein were produced, with a solution at a concentration of (10<sup>-3</sup>) M for each of them, and then allowed to dry at room temperature for three days. There is a wide variety of thicknesses for these thin films between (150-250) nm. A dye doped thin film was measured using a Michelson's interferometer. A paralleled beam of light is separated into two pieces via partial reflection in Michelson's interferometer. Drop casting was used to create the dye doped polymer films, which were at a concentration of (10<sup>-3</sup>) M. It is necessary to dissolve the needed amount of polymer in order to produce the solution of the polymer ( 2 mg in 50 mL of Ethanol solvent ). To determine the thickness of a dye doped thin film, the method was utilized [14].

#### 4. Conclusion and Discussion

##### A. Linear Optical Coefficients

Measurements of optical properties such as absorbance (A) made using a spectrophotometer (Shimadzu UV-VIS) over a wavelength range of (190-1100) nm are known as orcein measurements. A computer programmer conducts a scan of all wavelengths, and the wavelength at which the greatest amount of absorption happens and the least amount of transmission occurs is identified.

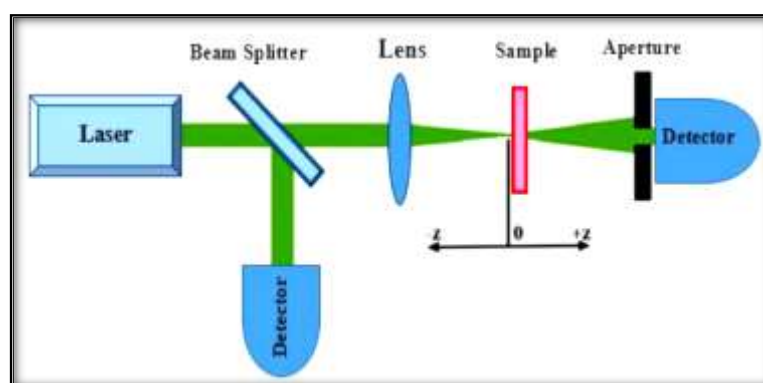
At room temperature, the drop casting procedure was employed to make thin films with a thickness of (10<sup>-3</sup>) M. "Figure 6" shows the linear absorption ranges of thin films of (Orcein) at a concentration of (10<sup>-3</sup>) M. The absorption maxima for (PVA and Nano) "at (10<sup>-3</sup>) M in Ethanol solvent were pushed toward longer wavelengths after the addition of" (PVA) polymer and nanoparticles to pure dye, as shown in this work.



**Figure 6.** The absorption spectra for (solution dye, dye +PVA, Dye +PVA+ Nano) of Orcein.

### B. Z-Scan Technique

The nonlinear refractive index ( $n_2$ ) and coefficient of nonlinear absorption for all samples under a particular set of conditions are computed using Z-scan analysis. The light source was an unremitting wave diode pump solid-state laser operating at (457 nm) and the closed aperture Z-scan method was used. In continuous-wave mode, vertical polarization and high laser output power (56,70,84,102) mW. The laser ray was fixated on the model using a convex lens by a central distance of (15) cm. You must move your sample along the Z-axis around the laser's minimal ray middle to determine how much transmittance you have in respect to your sample position [15]. In “Figure 7”, you can see the design of the arrangement for the Z-scan experiment.



**Figure 7.** Schematic diagram of the experimental setup for closed aperture z-scan technique

### C. The Optical Characteristics of Nonlinear

The open-aperture Z-Scan method was employed to evaluate the nonlinear absorption coefficient of (Orcein) for various powers (56,70,84,102) mW in Ethanol solvent. The transmission around the lens's focus increases when the open aperture Z-Scan is conducted. “Figures 8” show open-aperture Z-scans of samples in (Ethanol) solvent at (457) nm. The phenomena of two photon absorption have been seen. When the sample position is changed, transmission begins to act linearly at varying distances from the far-field of the model point (-Z). The transmittance curve continues to decline in the near field and eventually achieves its minimum value ( $T_{min}$ ) at the focal point, where ( $Z=0$  mm). While in the distant field (+Z), transmittance begins to grow in a linear fashion and then continues to do so. There are two photon absorptions that occur when the model passes through the beam waist in this specific case, which results in a change in the intensity level. You may generate variable transmittance values using a Z-Scan with an open aperture and then use them to determine the absorption coefficient. The maximum nonlinear absorption is found at the focal plane, which is also where the intensity is the highest.

According to “Figure 9” and “Figure 10”, saturable absorption was found for thin films of compounds under investigation using an open-aperture Z-Scan with an open-aperture Z-Scan. Depending on the distance

from the far field of the model site, transmittance curves begin to behave linearly ( $-Z$ ). The transmittance curve begins to grow in the near field and continues to climb until it achieves its maximum value ( $T_{max}$ ) at the focal point, where  $Z=0$  mm. Following that, the transmittance begins to decline in a linear fashion toward the far-field of the sample point ( $+Z$ ) and eventually to zero. The transmittance is proportional to the power input and is subject to nonlinear absorption. Saturation absorption in the sample occurs when the sample goes through the beam waist, causing the shift in intensity to occur. The maximum nonlinear absorption is found at the focal plane, which is also where the intensity is the highest. Because of the absence of intensity in the far-field of a Gaussian beam, nonlinear effects can only be observed. The negative nonlinear absorption coefficient is augmented by asymmetric peak value due to the sample's bleaching-like behavior (saturation of absorption).

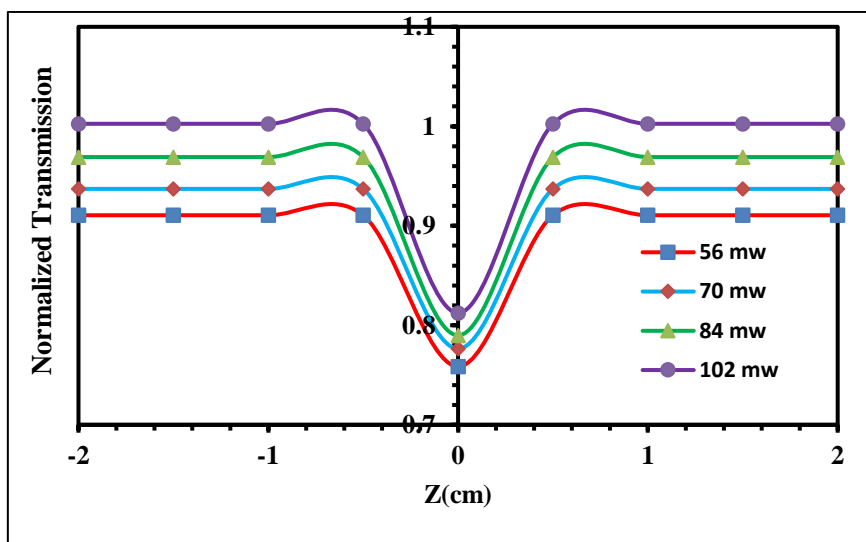


Figure 8. Open-aperture Z-Scan data of Orcein as solution

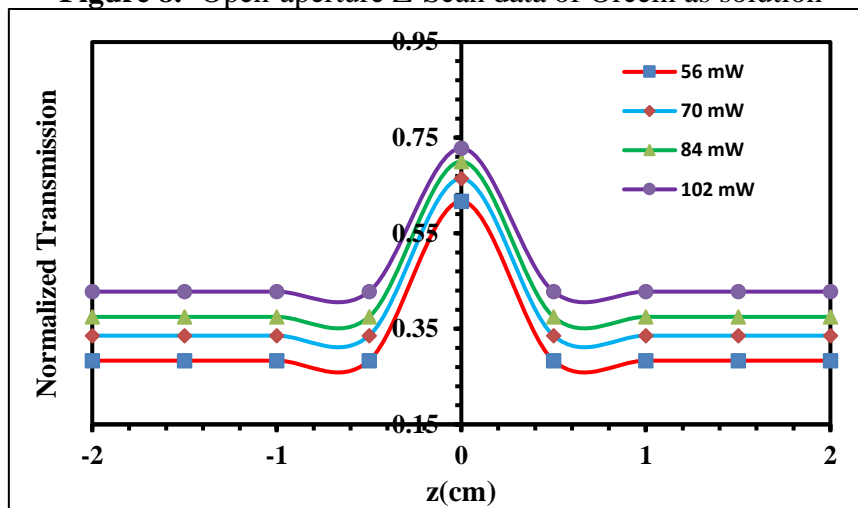
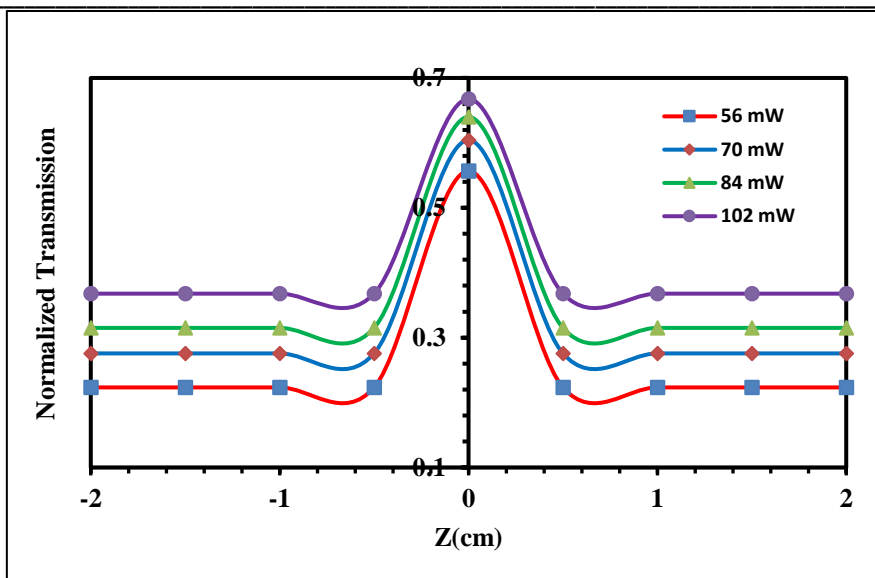


Figure 9. Data from an open-aperture Z-scan for a thin layer of Orcein + PVA with varying laser powers



**Figure 10.** Open-aperture Z-Scan data for thin film of (Orcein +PVA+ Nano) with various laser power

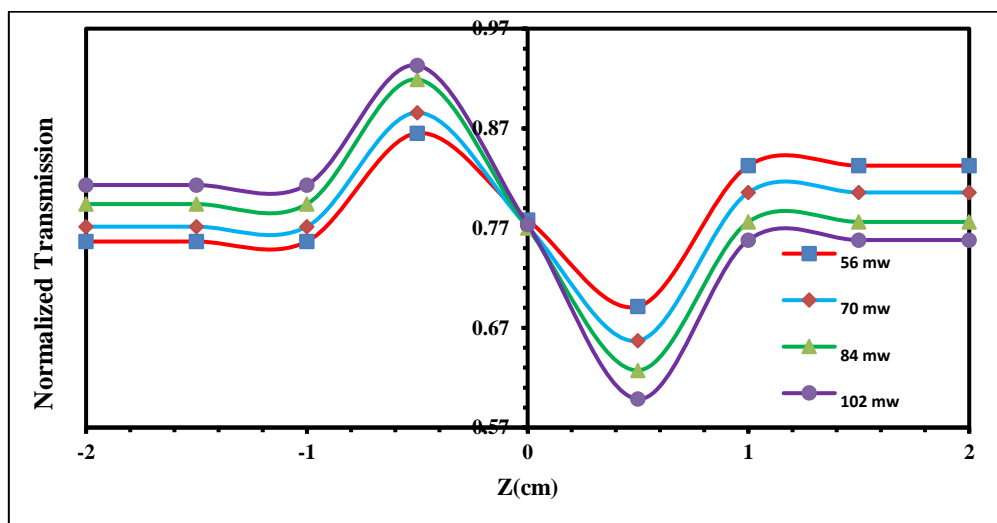
#### D. Nonlinear Refractive Index

The dye's nonlinear refractive index was determined by the Z-Scan closed-aperture way at a concentration of ( $10^{-5}$ ) M in Ethanol solvent. Z-Scan normalized transmissions on the right. “Figure 11” shows observations for (Orcein) dye at the concentration ( $10^{-5}$  M) as a function of distance. The nonlinear impact zone has been expanded from (-2) cm to (2) cm in this Figure.

“Figure 12” and “Figure 13” show the stabilized transmissions of Z-Scan measurements as a function of distance for thin films of (Orcein)dye at different concentrations ( $10^{-3}$ M) doped with polymer (PVA) and for thin films of (Orcein)dye at different concentrations ( $10^{-3}$ M) doped with polymer (PVA) (Ag NPs).

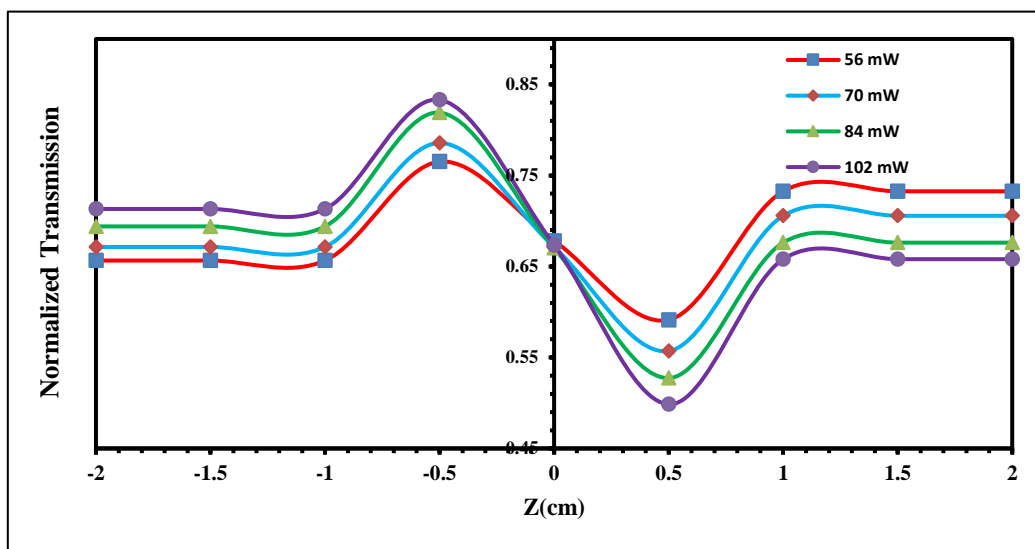
There is a peak and a valley in the transmission curve obtained from Z-Scan data for closed apertures, suggesting that nonlinearity is negative ( $n_2 < 0$ ), which results in self-defocusing lensing for these samples.

A greater amount of nonlinearity exists in doped dye compared to that of solution dye. The non-linear parameters are computed as shown in “Table 3” and are listed in this section. “Table 3” displays that the values of the nonlinear parameter for ( $n_2$ ) raise as the power increase and ( $\beta$ ) is reduced. It is possible to generate variable transmittance values employing the closed-aperture Z-scan, which may then be used for estimating the nonlinear phase shift  $\Delta\Phi_0$ .

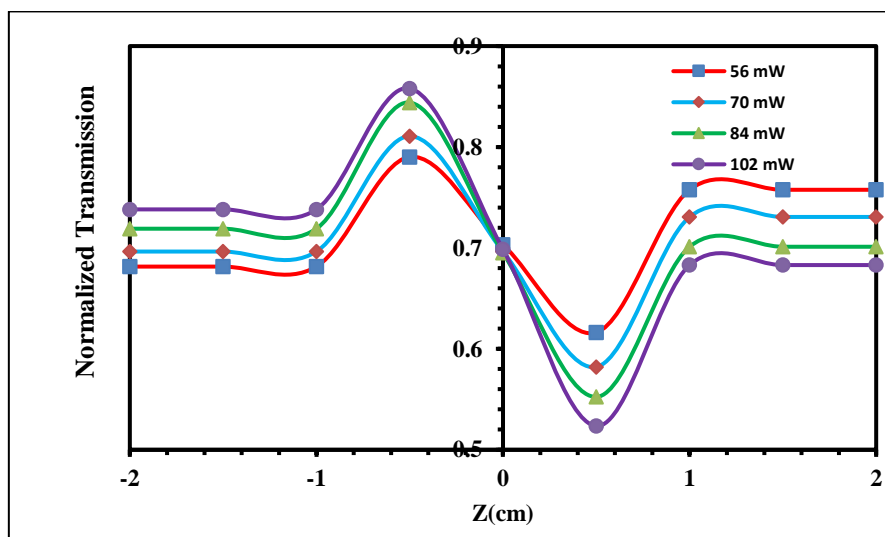


**Figure 11.** Orcein data from a closed-aperture Z-Scan as a solution





**Figure 12.** Data from a closed-aperture Z-Scan for a thin layer of" (Orcein + PVA) with varying laser powers



**Figure 13.** Data from a closed-aperture Z-Scan for a thin layer of" (Orcein + PVA+ Nano) with varying laser powers

**Table 3.** The nonlinear optical characteristics of Orcein at  $\lambda = 457\text{nm}$  with varied laser powers

Material	Power (mW)	$\Delta T_{P-v}$	$\Delta \Phi_0$	$n_2$ ( $\text{cm}^2/\text{mW}$ )	T (z)	$\beta$ ( $\text{cm}/\text{mW}$ )
Orcein	56	0.1739	0.4284	$5.4691 \times 10^{-10}$	0.7585	$0.376 \times 10^{-3}$
	70	0.2285	0.5629	$5.7486 \times 10^{-10}$	0.7765	$0.308 \times 10^{-3}$
	84	0.2916	0.7183	$6.1129 \times 10^{-10}$	0.7898	$0.261 \times 10^{-3}$
	102	0.3345	0.8239	$6.1995 \times 10^{-10}$	0.8123	$0.238 \times 10^{-3}$
Orcein + PVA polymer	56	0.2241	0.5521	$4.9840 \times 10^{-7}$	0.6166	0.2163
	70	0.2785	0.6861	$4.9549 \times 10^{-7}$	0.6642	0.1864
	84	0.3416	0.8415	$5.0643 \times 10^{-7}$	0.7010	0.1639

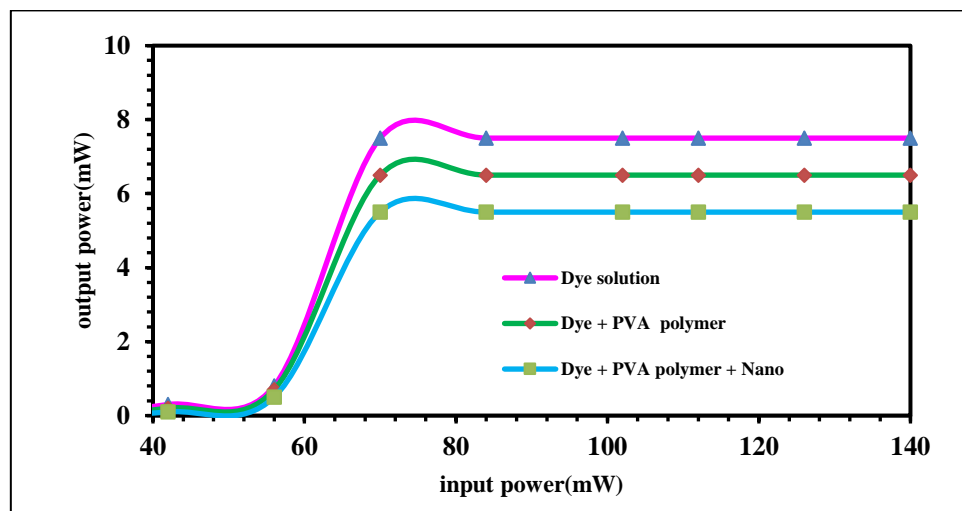
	102	0.3845	0.9471	$5.0397 \times 10^{-7}$	0.7277	0.1505
Orcein	56	0.2439	0.6007	$10.871 \times 10^{-7}$	0.59678	0.4197
+ PVA polymer	70	0.2985	0.7353	$10.645 \times 10^{-7}$	0.64586	0.3633
+ Ag NPs	84	0.3616	0.8908	$10.746 \times 10^{-7}$	0.6812	0.3193
	102	0.4045	0.9963	$10.628 \times 10^{-7}$	0.71786	0.2976

### E. Limiting Optical Behavior

Using a comparable laser closed gap and Z-Scan method, the optical limiting behavior was explored. The optical limiting physical features of the sample are shown in “Figure 14”. The output power increases in proportion to the rise in input power at first, but after a certain threshold is achieved, the samples begin to defocus the beam. Because Orcein thin films have a lower threshold and amplitude than Orcein solutions, this suggests that the optical limiting behavior in thin films, as opposed to liquid specimens, and in the case of polymer and nanoparticle revised dyes in general, has been greatly optimized. When compared to dyes in solution, thin films of Orcein have a lower optical power limiting threshold and limiting amplitude, as shown in “Table 4”.

**Table 4.** The response of the optical limiting of (Orcein) Dye and their thin films doped with PVA polymer and Ag NPs.

Case of organic dye	Limiting threshold	Limiting amplitude
<i>solution</i>	79	7.5
+PVA polymer	78	6.5
PVA polymer+ Ag NPs	76	5.5



**Figure 14.** Optical limiting of Orcein dye (solution, PVA, Nano)

### 6. Conclusions

An organic laser dye solution of (Orcein) organic dye in Ethanol solvent at ( $10^{-5}$  M) condensation was studied using the Z-Scan technique with a (457 nm) continuous-wave laser using the Z-Scan technique. The findings revealed that the material has extremely strong nonlinear optical characteristics. It is possible to

attribute the nonlinear absorption factor to a two-photon absorption mechanism, whereas the nonlinear refraction coefficient may be attributed to self-focusing. Dye films grafted with polymer and nanomaterials exhibit stronger nonlinear characteristics than the other models, as well as superior qualities as an optical limiter when compared to the other models, according to the findings. The behavior of optical limiting has been investigated. All of these investigational results demonstrate that this dye is a potential material for use in nonlinear optical systems and optical power limiting

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