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Nonlinear optical characteristics of Nile blue films doped with the polymers PMMA, PVC and their blend by using z-scan technique

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Abstract

The nonlinear optical characteristics of the laser dye Nile blue doped with Polyvinyl chloride (Nb /PVC), poly methylmethacrylate Nb/ (PMMA) and their blend N /(blend of PMMA 50 %+PVC 50%) was studded. Free-casting technique method was used for deposited the films. The nonlinear properties of the films studded by using Z- scan technique .Z-scan experiment was performed using continuous wave (CW) diode laser at 650 nm in two parts with power of 50 mw . The first part was done using a closed-aperture placed in front of the detector to measure the nonlinear refractive index ,with the second part; the aperture in front the detector was removed (open aperture) to measure the nonlinear absorption coefficient. The open-aperture curve exhibits a normalized transmittance (valley), indicating the presence of induced absorption. The observed nonlinearity is found to be of the third order, as it fits to two photon absorption process (TPA). The closed-aperture curve exhibits a peak to valley shape, indicating a negative value of the nonlinear refractive index n_2. The effective values of the nonlinear refractive index n_2, the nonlinear absorption coefficient β_2, real and imaginary parts of the third-order optical nonlinearity, $\chi(3)$ for Nb/PMMA+PVC films comparatively with that of Nb/PMMA and Nb/PVC has much lower optical transmittance value obtained shows that these films can be used as efficient optical limiters.

Keywords: Nonlinearity, doped dye polymer films, z-scan.

الصفات البصرية اللاخطية لاغشية صبغة النيل المطعمة مع البوليمرات كلوريد متعدد الفاينيل والبوليمربولي ميثيل ميثاكريليت ومزيجهما باستخدام تقنية المسح على البعد الثالث

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الخلاصة

الصفات البصرية اللاخطية للاغشية الرقيقة للصبغة الليزرية صبغة النيل المطعمة مع البوليمر كلوريد متعدد الفاينيل (Nb /PVC) والبوليمربولي ميثيل ميثاكريليت (Nb/PMMA) ومزيجهما (Nb/(PMMA 50 +PVC 50%)تم دراستها .استخدمت تقنية الطرح الحرلترسيب الاغشية .الصفات اللاخطية لها درست باستخدام تقنية المسح على المحور الثالث '(z–scan). اجريت تقنية المسح على المحور الثالث باستخدام ليزر الموجات المستمرة وبطول موجي 650 نانومتر بطريقتين:. في الطريقة الأولى تم وضع فتحة أمام الكاشف لغرض د ا رسة معامل الانكسار اللاخطي (n2).في الجزء الثاني أزيلت الفتحة من أمام الكاشف لغرض حساب معامل الامتصاص اللاخطي (β2).اظهرت الرسوم البيانية لا ا زلة الفتحة نفاذية تطبيع (قعر)

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دالة على وجود امتصاص محتث .وجد أن اللاخطية الملاحظة هي من المرتبة الثالثة،لانها تتطابق مع عملية إمتصاص فوتونين .أظهرت منحنيات الفتحة المغلقة شكل قمة الى قعر دالة الى وجود معامل انكسار لاخطي ذو قيمة سالبة. القيم الفعالة لمعامل الانكسار اللاخطي، ومعامل الامتصاص اللاخطي والاجزاء الحقيقية والخيالية للصفات اللاخطية من المرتبة الثالثة $\chi(3)$ لاغشية, NB/PMMA+ PVC مقارنة مع اغشية Nb/PMMA واغشية Nb/PVC مع القيمة الواطئة جداً للنفاذية التي تم الحصول عليها اوضحت بإمكانية استخدم هذه الاغشية كمحددات بصرية فعالة.

1. Introduction

With the large advancement in the technological field of photincs and bio-photincs, the need for organic materials with large nonlinear optical properties and having applications in low power nonlinear optical devices is being very important as a source of practical challenges [1]. Organic dyes are the most attractive optical materials for studying nonlinear optical properties for the point of view understanding their photo-physics and impending applications [2]. Polymer blends have been considered the most important in the recent past due to the lower cost of the product than those of a new polymer [3]. Many organic dyes have shown considerable third order nonlinearity for intense laser light and new primary nonlinear properties have been demonstrated when doped with polymer or a combination of polymers like Mercurochrome dye is studied for potential application in optical limiting by Krishnamurthy et. al. (2010 [4]). Oxazine Dye Doped Films in PMMA,Amal jaffar(2015 [5]) .Disperse Yellow Dye-doped PMMA-MA Polymer Shubrajyotsna et al (2016[6]). Orange G Dye in Solution and Polymer Film,Furat A. Al-Saymari et al (2016 [7])

A great advantage and improvement can be getting from the polymeric material by selection of suitable ingredients and their ratios. Blending of two polymers having different characteristic is usually produced a new polymeric material. These new polymeric material may possess the properties of both the polymers. The properties of polymer blends such as toughness, strength, etc have close relationships with their internal microphase morphology [2, 3, and 8].

Z-scan is simple, sensitive well-elaborated theory technique depend on the spatial distortion of a laser beam passed through a NLO material. This technique it is helped for obtaining several measurements of nonlinear parameters for different materials, in one set of experiments. It help to measure the sign and magnitude of the nonlinear refractive index and the kind of the nonlinear absorption if it is saturation absorption or reverse saturation absorption (two photon absorption)[9 and 10].

This work is an attempt to investigate in detail the nonlinear optical properties of the free casting Nb/PMMA+PVC films and see how the kind of the polymer and their blend is influencing the linear and nonlinear optical properties. The results obtained are compared with those of the Nb/PVC and Nb /PMMA doped films.

2. The practical part

Nonlinear optical properties of dye doped film were studded by using z- scan technique. Closed aperture z-scan is used to determine nonlinear refractive index $n_{2.}$. Figure-1 Show the setup of the experiment, Figure-2 show the photographic picture for the experiment setup:

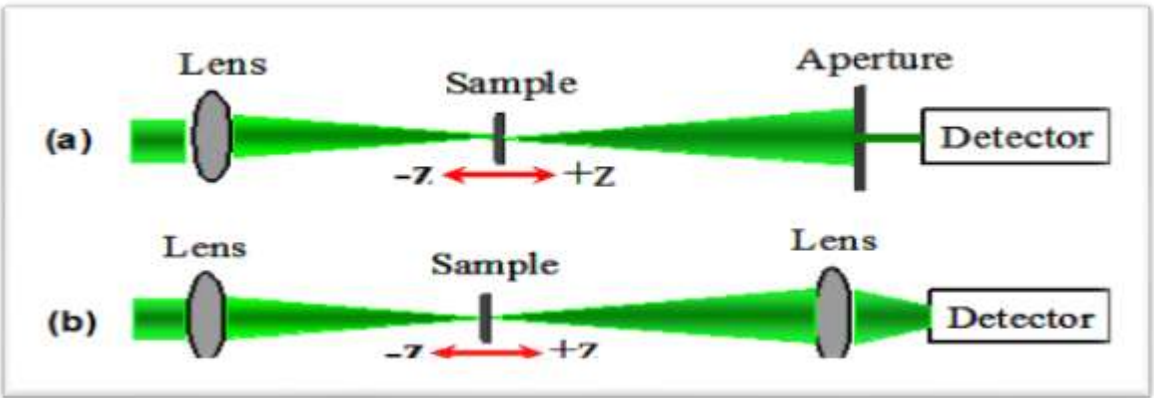

Figure 1- the setup of closed aperture Z-scan,(a)closed aperture z-scan and (b) open aperture z-scan.[11].

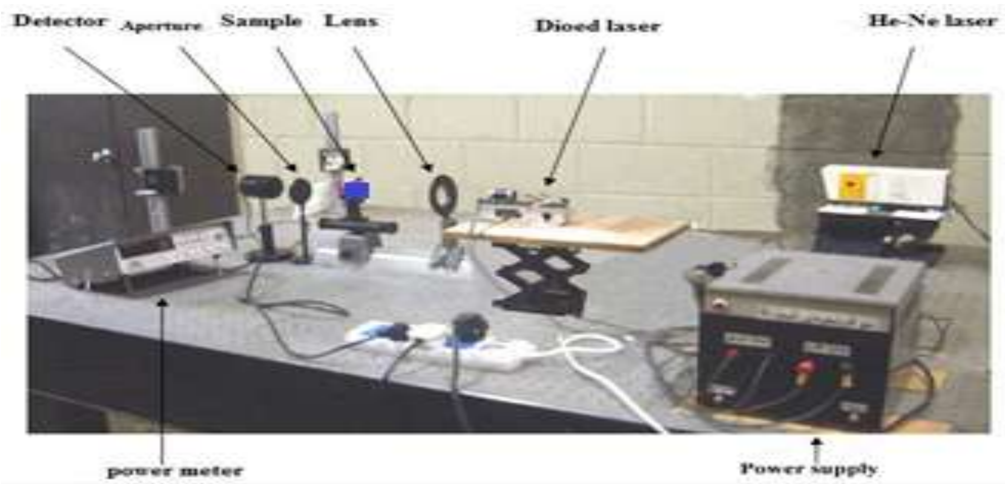

Figure 2- Photographic picture for the experiment setup

"There are two parts of Z-scan experiment: closed and open aperture z - scan. Closed aperture z-scan started by scanning the sample from a distance far away from the focus point (-Z), Figure- (1a) where the beam irradiance is low and negligible and this lead to linear transmittance. Moving the sample near and before the focus point will produce self-defocusing (or negative self-lensing), the irradiance will increased the beam to collimate at the aperture and the transmittance is increasing. As the scan continues and the sample crosses to (+Z) to the right of the focal plane, the same negative self-lensing effect will tend to increase diffraction and reduce the aperture transmittance. A peak (pre-focal transmittance maximum) and valley (post- focal transmittance minimum) will be the signature of negative nonlinearity Z-scan. A vally (pre-focal transmittance minimum) and peak (post- focal transmittance maximum) will be the signature of positive nonlinearity Z-scan (positive self -lensing)". [12, 13].

The change in transmittance between the peak and valley in the Z-scan can be defined as:

$\Delta T_{pv} = T_p - T_V$ .... (1)

Where T_p and T_v are the normalized peak and valley transmittances.

"The relation between the induced on axis phase shift, $\Delta\Phi_0$, and ΔT_{pv} for a third-order nonlinear refractive process in the absence of nonlinear absorption (NLA) is",

□T_{PV} □□0.406□□□$_o$ □.. (2) [14]

The nonlinear refractive index of the used substance (n_2) can be calculated from equation (3):

$n_2 = \Delta\Phi^o / k \ I_o \ L_{eff}$ ……………………………………………………………………………..…(3)

where: $k = 2\pi / \lambda$ ..……………………………………………………………………….………(4)

k: is the wave number, λ: is the wavelength of the beam.

I_0: the intensity of the incident beam at focus,

L_{eff} the effective length of the material can be determined from EQ (5):

$L_{eff} = (1 - e^{-\alpha_o L}) / \alpha o$……………………………………………………………………..…..(5)[15]

$\alpha_\circ = \frac{1}{L \ln(\frac{1}{T})}$………………………………………………………………………………… (6)

Where T: linear transmittance

$I_o = 2P_{peak} / \pi \omega_0$ ………………………………………………………………………………..(7)

Where ω_0: the beam radius of the focal point.

By removing the aperture in front the detector (open-aperture *Z*-Scan) the z-scan transmittance is insensitive to nonlinear refraction so the nonlinear absorption coefficient can be determined.[16] Figure- (1b) .By measuring the change in intensity of the beam which focused by the lens in the far field by a detector PD, which captures the entire beam, and gives the estimate of the absorptive nonlinearity of a sample [17]. The change in intensity is caused by multi-photon absorption in the sample as it travels through the focal plane (beam waist) where the intensity is the greatest; which caused largest nonlinear absorption. In the far field where $|Z| >> Z_o$, the beam intensity is too weak to extract nonlinearity. The measurement the higher order of multi-photon absorption depends on the wavelength of light and the energy levels of the sample [5, 18]. It is found that the absorptive

nonlinearity cans either (saturable absorption SA): the absorption coefficient decreases and the transmittance increase with increase in the input laser intensity, and (reverse saturable absorption RSA): the absorption coefficient increases and the transmittance decrease [19]. The normalized change in transmitted intensity can be calculated by the equations
(6-8), [15, 19, and 20]:

$\beta_1 = 2.83\ T_{min} / I_{\circ}\ L_{eff}$ ……………………………………………………………………….(6)

$\beta_2 = (5.2\ T_{min} / (I_{\circ}\ L_{eff})^2)^{1/2}$ …………………………………………………………………..(7)

$\beta = \beta_1 + \beta_2$……. (8)

3. Materials and methods:

"Nile blue (Nb) obtained from Lambdacxhrome was used in this study directly without any further purification. Nile blue has a positively charged, oxidized, phenoxazine system [21], the high fluorescence and intensity of Nile blue are good indicators of the polarity of the dye's circumference. Nile blue exhibted progressively high absorption and emission as the solvent polarity is increased. The spectroscopic characteristics of Nile blue are pH dependent".

Figure-3 Shows its molecular structure. It's chemical formula is ($C_{20}H_{20}N_3O_5Cl$)with molecular Mw=: 417.85 gm/mol [22].

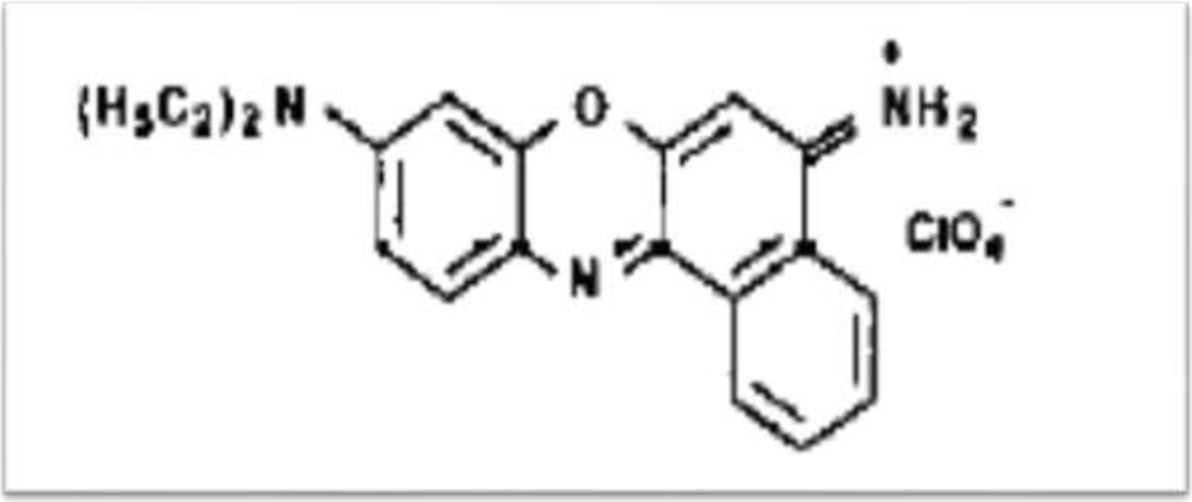

Figure 3- The molecular structure of Nile blue, [22].

"The polymers which were chosen as a host material for the laser dye are PMMA and PVC (Vinyl chloride) due to their high optical properties. PVC polymer has molecular weight of 93.93 g / mole (obtained from Sigma, Aldrich Germany) was chosen owing to its many important properties like high laser damage threshold, good process ability, low flammability, and low cost [23]. PMMA (poly methyl methacrylate) of molecular weight 45, 000 gm/ mole is a member in the family of poly (acrylic esters), from ICI Company, has poor heat resistance, it has been widely used in many fields, because of its transparent optical property, chemical stability, and high biocompatibility. When the dyes were doped with PMMA one can get thin films more colorful and functional. Incorporating dyes into polymer supported matrices, and could keep them far away from the disturbance of external environments". [15, 23 and 24].

The spectroscopic grade solvent Chloroform is from Lab-Scan LTd. Analytical Science HPLC Ireland-Dublin. Films thicknesses were measured with an electrical device (Mini-test 3000 microprocessor coating thickness) from electro, phyisk, Germany (ERICHSEN). The films had thickness of (1.151-1.733) µm. The *Z*-scan experiments were performed using (650) nm CW diode laser: "(max.power is (50) mW, Ac: (220-240) volt, Frequency: (50-60) Hz (250) mA, beam diameter: (1.5) mm, beam divergent (1.5) mrad, focused by (10) cm focal length lens". The laser beam waist ω_o at the focus is measured to be (0.015) mm and the Rayleigh length $Z_0$to be (0.915) cm.
Casting method is used to prepare dye doped polymer films was performed according to the method mentioned in ref. [5 and 8].

"Nb solution of concentrations (10^{-5}) M in chloroform was prepared by weighting the dye by using a matter balance having a sensitivity of (10^{-4}) gm. For the preparation of polymer blend : 1gm of

PMMA, 1 gm of PVC was dissolved in 10ml of Chloroform separately to obtain a 10% w/v solution at room temperature and for 24 hour with stirring. Nb was added to the two homopolymers separately and also to their blend (PVC/PMMA 50%/50%). The solutions were cast on pettry dish which kept open at room temperature to evaporate the solution to get thin films".

4. Results and Discussion

UV-Visible absorption spectra of the laser dye Nile blue and its doped polymer films were carried out by using (UV/Vis SP – 3000, plus, 2003) Spectrophotometer Optima/Japan, which operates in wavelength range of (190- 1100) nm [25].

Figure-4 shows the absorption spectrum at room temperature for Nb solution 10^{-5} M in Chloroform where λ_{max}.was 633 nm, and that because When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength.

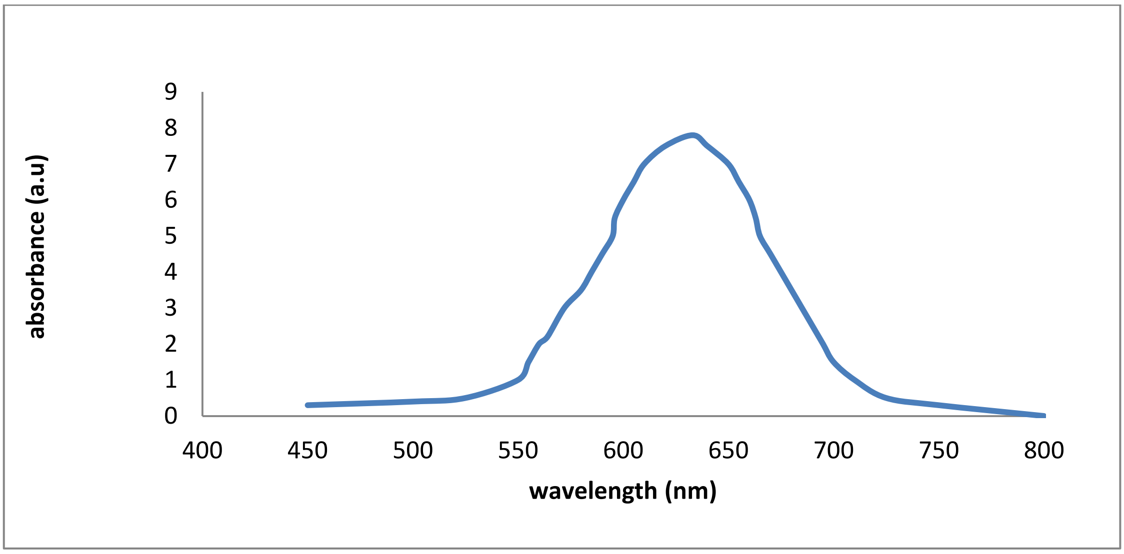

Figure 4-The opical absorption spectrum of Nile blue solution.

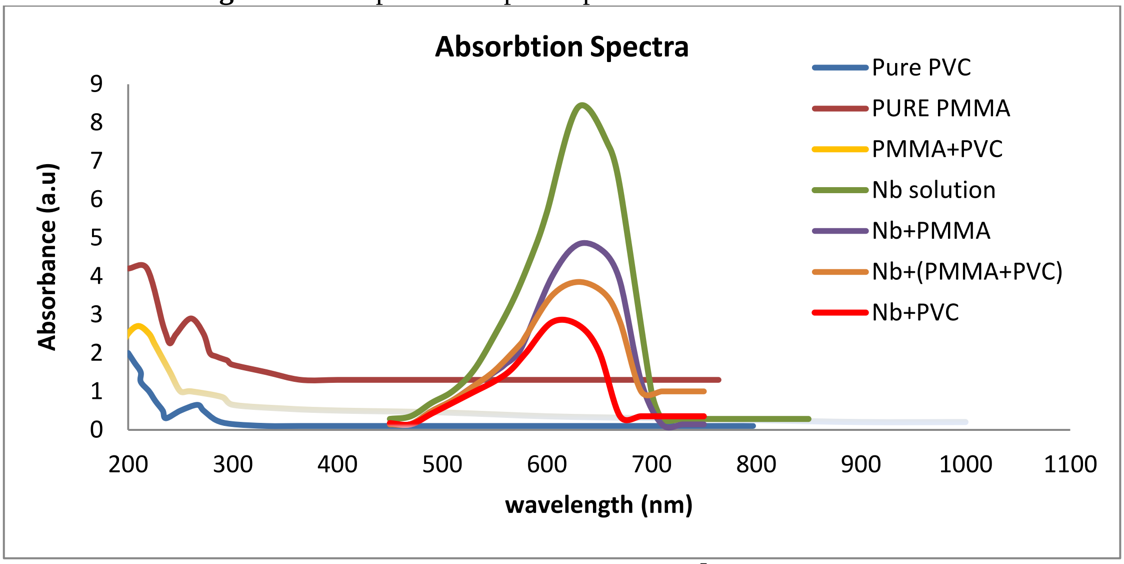

Figure 5- UV/Vis. spectra of Nb solution of concentration10^{-5} M ,pure PVC , pure PMMA ,Blend of PMMA and PVC,Nb films doped with PMMA ,PVC, and their blends (50/50)%.,

Figure- 5: Shows the UV/Vis. spectra of of Nb solution of concentration10^{-5} M, pure PVC, pure PMMA, Blend of PMMA and PVC (50/50) %, Nb films doped with PMMA , PVC, and their blends. It has been shown that the Nb doped polymer films have less absorption than the Nb solution, (The presence of Nb thus, enhances the UV absorption of the doped films and modifies the overall optical behavior of polymer blend films [26]. Also it has been shown that for Nb solutions and the doped films with the two polymers there is a wide absorption bands between 480- 700 nm and there is the same behavior of absorption peaks at 633 nm. “For the polymer and their blend there is red shifting of peak absorption after doping (bathochromic) where the molecular aggregates have different spectroscopic characteristics than individual molecules” . The presence of Nb, enhances the UV absorption of the doping films and modifies the overall optical behaviour of polymer blend films [27]. “Each additional double bond in the conjugated π-electron system shifts the absorption maximum $\lambda_{max.}$ about 30 nm in the same direction and, the molar absorptivity (ε) roughly doubles with each new conjugated double bond”[27]. It can be seen also that the absorption peak value for Nb / PMMA was greater than that in Nb/PMMA-PVC 50/50), which were also greater than that in Nb/PVC, for the same concentrations of the doped dye.

Nonlinear optical properties(the third-order nonlinear refractive index n_2 the nonlinear absorption coefficient β), used for finding the real and imaginary parts of the third-order nonlinear optical susceptibility (χ^{3}): [5,7 , and 8]

$$\text{Re}\,\chi^3\ (\text{esu}) = 10^{-4}\ \varepsilon_0 c^2 n_0^{\ 2}\ n^2/\pi\ (\text{cm}^2/\text{W}) \quad \ldots\ldots (10)$$

$$\text{Im}\chi^{3}\ (\text{esu}) = 10^{-2}\ \varepsilon_0 c^2 n_0^{\ 2}\lambda\beta\ /4\pi^2\ (\text{cm/W}) \quad \ldots\ldots (11)$$

Nile blue doped films with PMMA, PVC and their blend were investigated by Z-scan technique using CW diode laser of 650 nm where the pumping wavelength 650 nm chosen to adjusted the excitation of the dye for optimal usage of the dye. Incident intensity I_0= 510W/cm2.

Figure-6 Shows the closed aperture Z-scan profiles of the films indicating the negative refractive index” is referred to a thermal nonlinearity formed by the absorption of radiation from the source of excitation diode laser of wavelength 650 nm”.

“As the intensity depended on the refractive index this make the beam radius of the transmitted beam changed while maintaing the Gaussian profile. In the beginning of the scan far away from the focus (-ve z), the beam irradiance is low and there was no nonlinear refraction occurs and that lead to linear transmittance.

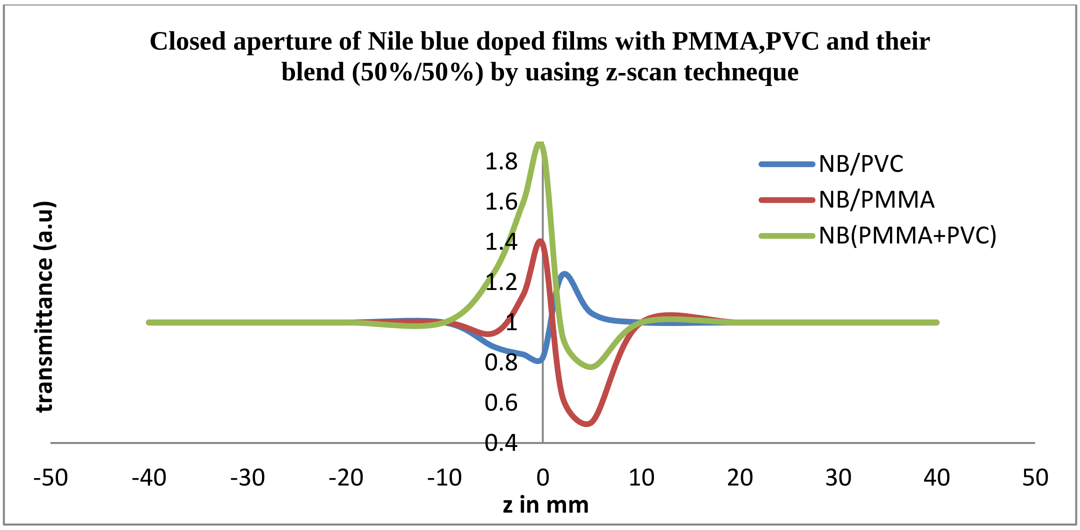

Figure 6- “Closed aperture Z-scan profile of Nile blue doped films indicates to negative nonlinear refractive index”.

When the sample is brought near the focus, the beam irradiance increases causing self-lensing in the sample. This self-lensing (self-defocusing) before the focus works to combine the beam and reduce the diffraction make a smaller beam at the aperture and an increased transmittance. When the sample crosses the focal plane to the right (+ ve z), the same self-defocusing effect will tend to increased diffraction and decreased the aperture transmittance. transmittance maximum (peak) befor the focal and minimum transmittance (valley) a post the focal will be, the z-scan signature of a negative nonlinearity, while a positive one, following the same analogy, will give rise to an opposite valley-peak configuration. [10].”

The third order nonlinear properties and third order susceptibility values of Nb/PS-PMMA doped film are given in Table-1. Higher susceptibility value of Nb/ PMMA+ PVC films measured by the Z-scan technique, compared to both Nb/PVC and Nb/PMMA films, highlight that the Nb/ PMMA+PVC doped films have the best nonlinear optical properties and can be chosen for many applications in nonlinear optics .
Values of T_{p-v}, n_0, n_2, $\Delta\phi_o$ and $R\chi^3$ are listed in Table-1.

Table 1- shows that Nb./PMMA+PVC film has the highest nonlinear parameter

Nb	T_{p-v}	Δφo	n_2	n_o	RX^3(esu)	ImX3	X3
pmma	0.883	2.175	6.32E-06	2.738	7.598E-05	1.60E+00	1.6
pVC	0.412	1.0148	2.584E-06	1.656	4.648E-06	2.04E+00	2.039
pVC+pmma	1.09	2.685	9.740E-06	3.448	2.86E-04	2.22E+00	2.22

Figure-7 Shows Z-scan open aperture films profiles, where there is no aperture in front of the detector in the far field. The experiment begins when the sample moves far away from the focus where the intensity is low and linear so it is normalized to unity. "Near the focal plane (-z, 0, and + z, Figure- 1, the transmission is reduced and be symmetric about the focus Z=0. This is an intensity dependent enhanced absorption termed "reverse saturable absorption (RSA) "or "positive nonlinear absorption" displayed by the nonlinear material"[28].

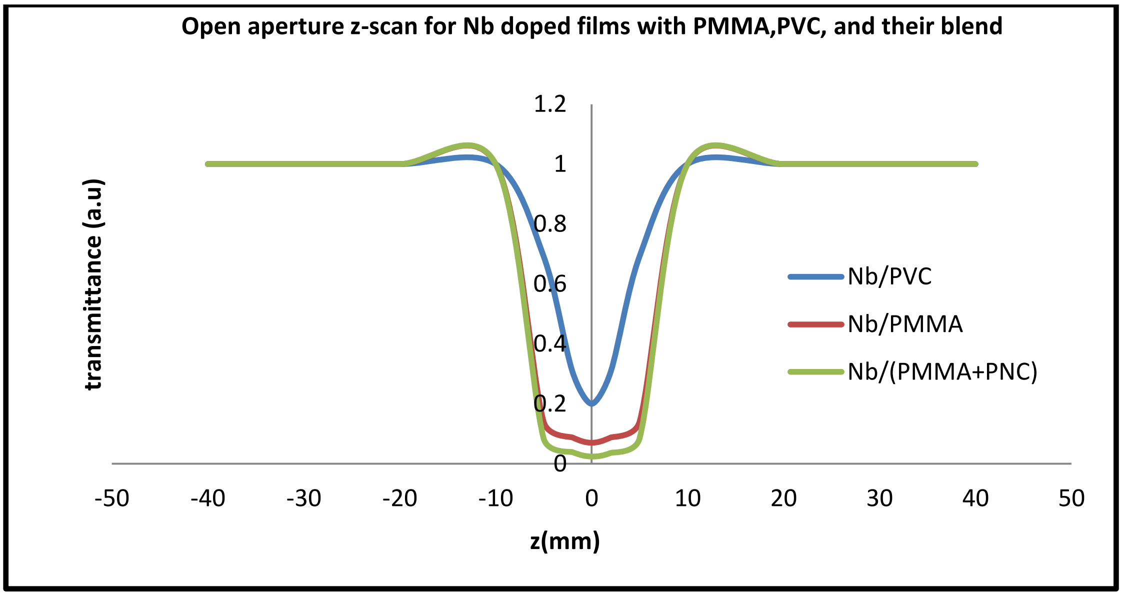

Figure7 -"Open aperture Z-scan profile of Nile blue doped films indicates to two photon absorbtion".

"The observed nonlinearity is found to be of the third order, as it fits to a two photon absorption process (TPA) and the nonlinear absorption coefficient β is positive" [29]. The reverse saturable absorption (RSA) behavior is attributed to absorption of excited states which it is larger than that of the ground states and the molecules of ground and excited states absorb the incident photons of the same wavelength [30, 31]. "Such RSA has been observed to occur in organic materials especially in π-conjugate materials" [32, 33].

From the open aperture Z-scan curve it is found that, the Nb/PVC+PMMA films exhibit large induced absorption behavior (the lowest transmittance). The observed dip in the open aperture curve shows the transmittance limiting efficiency of the films. The three curves of Nb doped films show a better fit to the theoretical equations for TPA, and the'transmittance minimum is about 0.024, which emphasize the better optical limiting efficiency of the Nb/(PMMA+PVC) doped films compared to the two ethers. The calculated nonlinear parameters are given in Table-2, where β_1, β_2, and β calculated from equations (6, 7, and 8).

The much lower transmittance value obtained for Nb/ (PMMA + PVC) doped film Figure-6 compared to the other two films(Nb/PMMA and Nb/ PVC) shows that film Nb/ (PMMA + PVC) can be used as efficient optical limiters and give the importance of the blending between the polymers.

Table-2

Nonlinear parameters of Nb./PMMA, Nb./PVC, Nb./PMMA+ PVC films by using CW diode laser at 650 nm for open aperture z-scan.

Nile blue	Z/Zo	T(z)	Leff(cm)	B_1(cm/w)	B_2(cm/w)	B
pmma	0	0.07	0.0141	0.0258	**0.359**	**0.206**
PVC	0	0.2	0.0161	0.0689	**0.568**	**0.319**
PVC+PMMA	0	0.024	0.01	0.0134	**0.319**	**0.166**

Conclusion

Open aperture Z-scan curves for the three films Nb/PMMA,Nb/PVC and Nb/(PMMA50 % +PVC 50%) showed nonlinearity of third order, as it fits to a two photon absorption process (TPA). Nb /PMMA+PVC films exhibited large induced absorption behavior (little transmittance) which highlights the better optical limiting efficiency compared to Nb/PMMA and Nb/PVC. The improvements in the nonlinear optical properties of Nb/ PMMA+ PVC films compared to NB/PVC and Nb/PMMA films explain the importance of the polymer blend in formation of an interpenetrating network (IPN) of PVC and PMMA in the polymer blend. Closed aperture z-scan showed negative third order refractive index which attributed to a thermal nonlinearity resulting from the absorption of radiation at 650 nm. The observed higher nonlinear susceptibility of Nb/PMMA + PVC films measured by the Z-scan technique, compared to both Nb/PVC and NB/PMMA films, establishes the fact that the Ox/ PMMA+ PVC films have the best nonlinear optical properties and can be chosen as ideal candidates for applications in nonlinear optics".

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