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Optical limiting properties of magenta doped PMMA under CW laser illumination

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ABSTRACT

The optical limiting properties of the magenta doped PMMA film were measured using cw laser beam at 532 nm wavelength. The optical limiting behavior is investigated via transmission measurement through the sample at different concentrations. The results showed that the sample has obvious optical limiting effect. 0.65 mM concentration has the best limiting effect among the four concentrations chosen. Absence of photochemical or photothermal destruction processes in the studied materials suggests their perspective application as a stable optical limiter in photonic devices.

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Key words: Optical limiting, dye, polymer, limiting threshold

INTRODUCTION

It is well-known that intense laser beam can easily damage delicate optical instruments, especially the human eye, and consequently the field of optical limiting has invested much effort into the research of materials and processes in an attempt to afford some measure of protection from such beams. The need for materials to protect optical sensors from intense laser is not only limited to the military, but also is rather a growing societal problem that can only escalate [1]. Basically "optical limiters" are systems that permit transmission of ambient light levels but which strongly attenuate high intensity, potentially damaging light such as focused laser beams. Previous researches on optical limiting materials were focused on nonlinear, organic [2-11] and semiconductor materials [12]. Since it was found that organic materials have large nonlinearity and ultra-fast response time, the research on optical limiting organic materials is of great importance. Nonlinear absorptive organic dyes are among the most widely studied optical limiting materials. Recently, Palanisamy et al. studied the third-order nonlinear optical response of a triphenylmethane dye (Acid blue 7) using the Z-scan technique with a continuous-wave He–Ne laser radiation at 633nm [13]. The third-order nonlinear optical properties and the optical power limiting behavior of 3-phenyl sydnones doped PMMA were investigated using nanosecond Nd–YAG laser pulses at 532nm wavelength [14]. The nonlinear optical absorption, refraction and optical limiting behavior of an organic dye, neutral red, were investigated under excitation with nanosecond laser pulses at 532 nm [15]. Alaa et al. studied the optical limiting behavior of Phenazinediamine,N8,3-trimethyl-hydrochloride (1:1) dye solution using cw laser light[16].The third-order nonlinear optical properties, $\chi(3)$,of malachite green thin films are evaluated from changes of index of refraction using Millers rule[17].

Magenta being an organic molecule that cannot be used directly in practical photonics device applications because of the possibility of getting degraded or bleached when exposed to intense optical signals. In order to overcome this drawback, they can be doped into a polymer matrix. This enhances the chemical and physical stability of the organic materials, while retaining the nonlinear optical (NLO) properties and linear optical transmittance [18, 19]. The main requirement of polymer matrix when serving as hosts for the organics are, it should possess high laser damage threshold, good optical quality with high transparency, good thermal and photochemical stability. Polymer matrices offer advantages such as ease of processing which allows the fabrication of devices at low cost and have better compatibility with the organic molecules. Poly (methylmethacrylate) (PMMA) is a hard, rigid and transparent polymer with a glass transition temperature of 125°C. PMMA is a polar material and has larger dielectric constant than other thermoplastics [20-21]. We have, therefore, selected PMMA as a solid matrix into which the molecules are incorporated.

This paper presents the results of the investigations on the optical limiting behavior of magenta dye doped PMMA polymer with four different concentrations, using a continuous wave (cw) laser at 532 nm wavelength.

MATERIALS AND METHODS

2-1 Preparation of the films

The chemical structure of magenta is shown in Fig.1. To prepare the solid films, PMMA was selected as the host material. A known quantity of PMMA and magenta were dissolved in chloroform separately, the concentration of the orcein in chloroform is 0.5 mM, later both solutions were mixed and stirred for 2 hr using a magnetic stirrer. The ratio of PMMA solution and dye solution is 1:1. The film was prepared on a clean glass slide by the casting method and dried at 20 °C for 24 hr. The film sample has a good purity and uniform thickness. The other films for magenta doped PMMA with 0.5mM, 0.55 mM; 0.6 mM and 0.65 mM concentrations were also prepared in a similar manner. The thickness of the films were measured using digital micrometer and are found to be 71.3 μ m,73.2,74.9 and 77.1 μm for 0.5 mM, 0.55 mM, 0.6 mM and 0.65 mM concentrations, respectively.

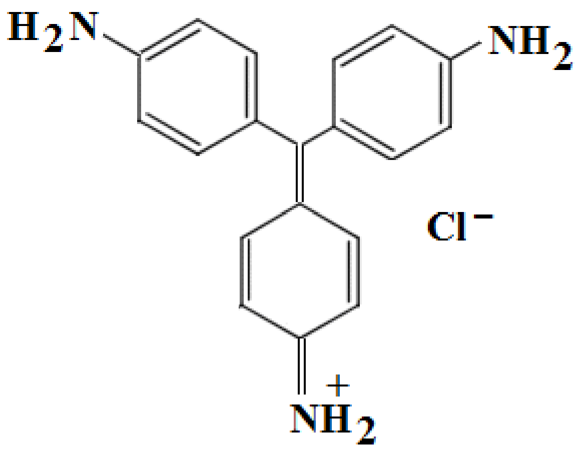

Fig. 1. Chemical structure of magenta dye.

2-2 UV-Visible spectroscopic studies.

A UV–visible spectroscopy has been used to characterize the magenta doped PMMA films in the spectral range (350–900nm).The transmittance (T) and the absorbance (A) of the sample measured using Cecil Reflected-Scan CE 3055 reflectance spectrometer. These measured were performed at room temperature. Fig. 2 and 3 shows the spectral distribution of absorbance and transmittance of samples with different concentrations .The optical absorption for the magenta doped PMMA film with different concentrations shows an absorption peak at 558 nm, as can seen in Fig.2. Also we can see from the Fig. 2 that the absorbance of the sample increases with increasing the concentration this due to increase number of molecular per unit volume, so the absorbance will be increased.

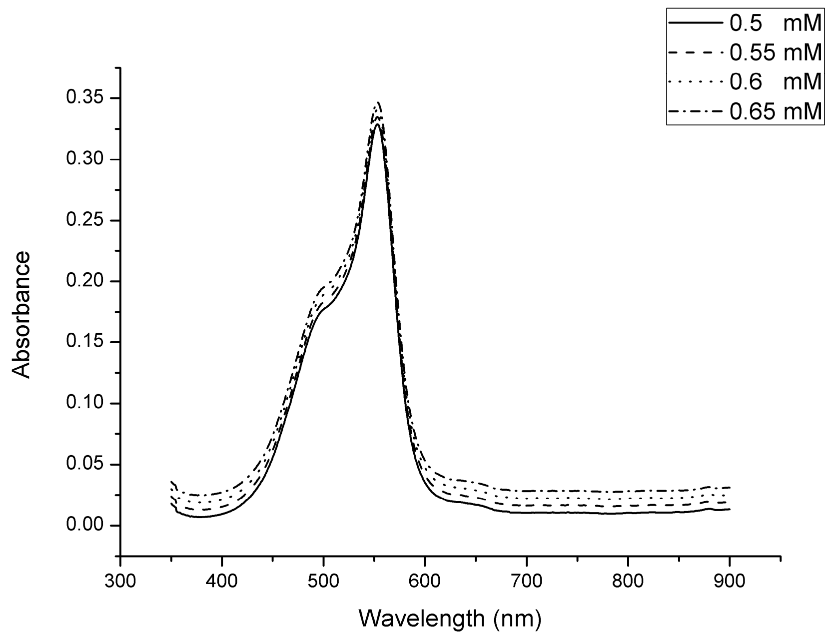

Fig. 2. Optical absorption spectra of magenta doped PMMA films with different concentrations.

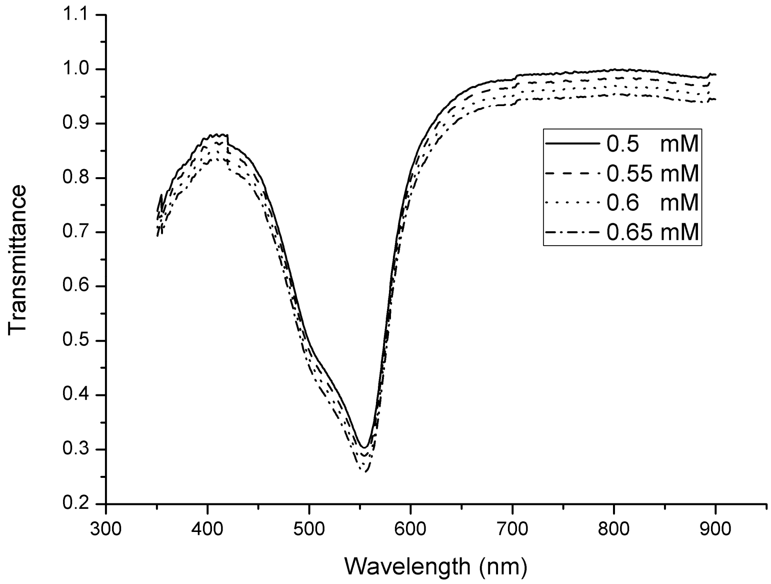

Fig. 3. Optical transmittance spectra of magenta doped PMMA films with different concentrations.

2-3 Optical limiting technique

The limiting effect of the magenta dye doped PMMA was studied using a continuous wave (cw) from solid state laser (SDL) at 532 nm wavelength. The experimental set-up for the demonstration of optical limiting effect is shown in Fig. 4.The laser beam was focus by a lens with focal length +5 cm. The sample is kept at the position away from focus. A variable beam splitter (VBS) was used to vary the input power. The input laser intensity is varied systematically and the corresponding output intensity values are measured by the photo detector connected to power meter (Field Max II-To+OP-2 Vis Senser). At very high peak intensities (closer to the focus) we could observe diffraction type pattern of concentric ring structures probably due to self-phase modulation. However, in limiting experiments we have ensured that there is no ring pattern formed by placing the sample away from focus.

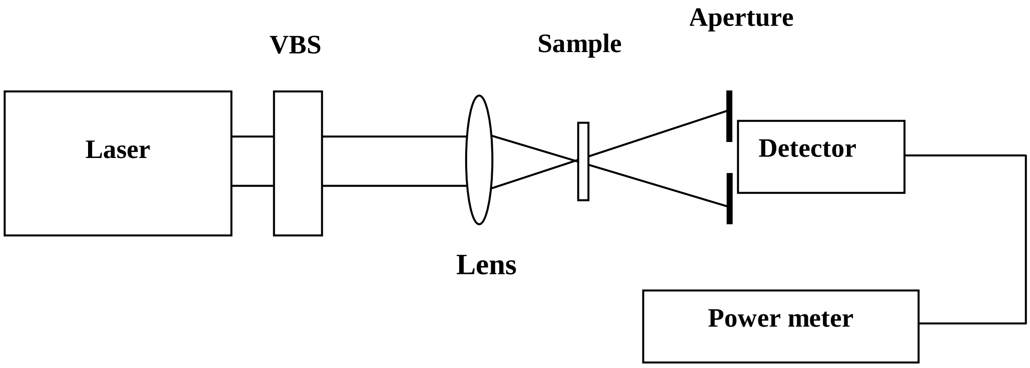

Fig. 4. Experimental set-up for optical limiting effect.

RESULTS AND DISCUSSION

3-1 The absorption coefficient (α)

The spectrum of the optical absorption was computed from the absorbance data. The absorption coefficient (α) has been obtained directly from the absorbance against wavelength curves using the relation [22,23,24,25]

$$\alpha = 2.303A/d \qquad (1)$$

Where d is the sample thickness and A is the absorbance.

The values of absorption coefficient (α) at wavelength 532 nm for magenta doped PMMA film with different concentrations have been calculated using Eq. 1 and they are given in Table 1.

3-2 Optical density

UV-vis absorption spectra values (optical density values) were taken to study the linearity of the sample with different concentrations[. Since complete absorption occurs around 558 nm for magenta doped PMMA film, the absorption values were taken at λ = 450 nm. As expected, the optical density increases with the increase in concentration as shown in Fig. 5.

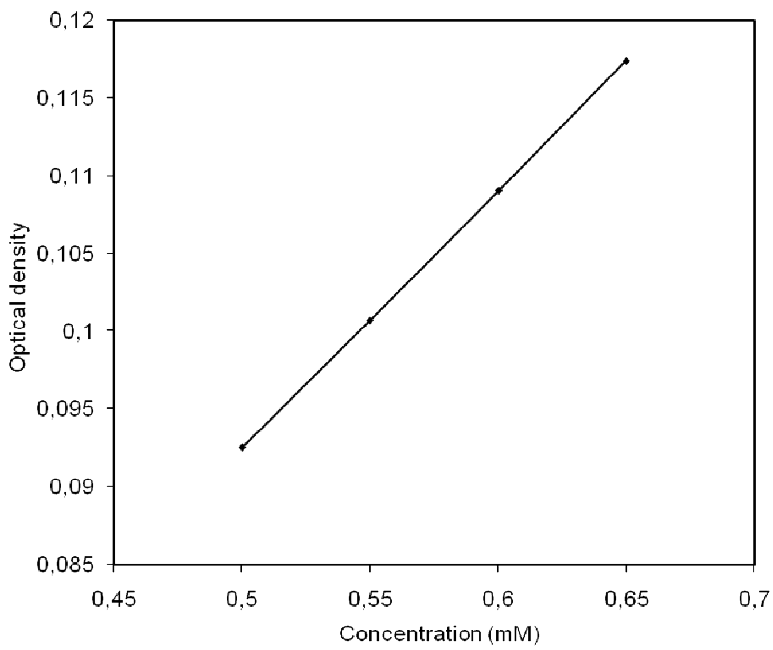

Fig. 5. Variation of optical density with concentration for magenta doped PMMA film.

3-3 Optical limiting

The optical limiting curve for the magenta doped PMMA film with different concentration is shown in Fig.6. The output power rises initially with an increase in input power for all samples, but after a certain threshold value the samples start defocusing the beam, resulting in a greater part of the beam cross-section being cut off by the aperture. Thus the transmittance recorded by the photo-detector remained reasonably constant showing a plateau region and is saturated at a point defined as the limiting amplitude. i.e., the maximum output intensity, showing obvious limiting property. The saturated output value at which limiting occurs for the magenta doped PMMA film is shown in Fig.7 for different concentrations. We can see from Fig. 7 that the saturated output value decreases with increasing concentration.

Fig. 8 shows the normalized transmission curves as a function of incident input power for 0. 5, 0.55, 0.6 and 0.65 mM concentrations of magenta doped PMMA. The optical limiting abilities are quantitatively different. The optical limiting thresholds (defined as the incident input power where the transmission reduces by 50%) are measured and they are given in Table 1.

It is well known that concentration plays very important role in the optical limiting action. The optical limiting effect is enhanced and the transmittance decreases with increasing concentration. This is because a sample with high concentration has more molecules per unit volume participating in the interaction during the nonlinear absorption processes. So the optical limiting responses of the low concentration sample are generally much weaker than those of high concentrated samples, while high concentrated samples exhibits strong optical limiting with the range of this study. However, the concentration of the sample should be chosen carefully in order to reach the concentration threshold, which is an important factor in the investigation of optical limiting.

The limiting behavior observed in all samples is attributed mainly to nonlinear refraction. Since the samples were pumped with cw laser beam the arising nonlinearities are predominantly thermal in nature. Due to change in refractive index of the material self-focusing and self-defocusing can be observed in the material, leading to reduction of transmittance at far field (due to distortion of spatial profile of Gaussian beam). Reduced transmittance in the far field gives better optical limiting performance.

The UV-visible absorption spectrum of the samples before and after the laser irradiation shows that the pattern and intensity of the spectrum does not show any change, indicating that the samples possesses good photo-stability.

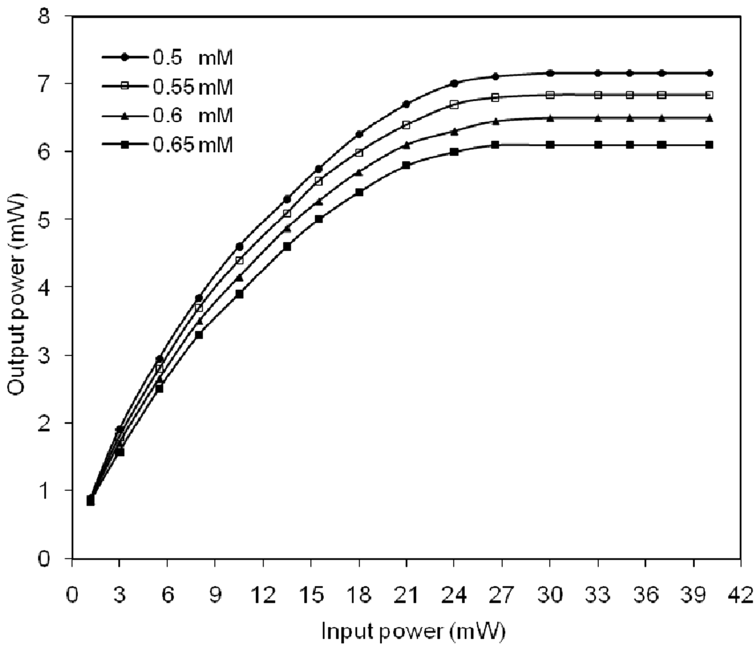

Fig. 6. Optical limiting curves for magenta doped PMMA film for different concentrations.

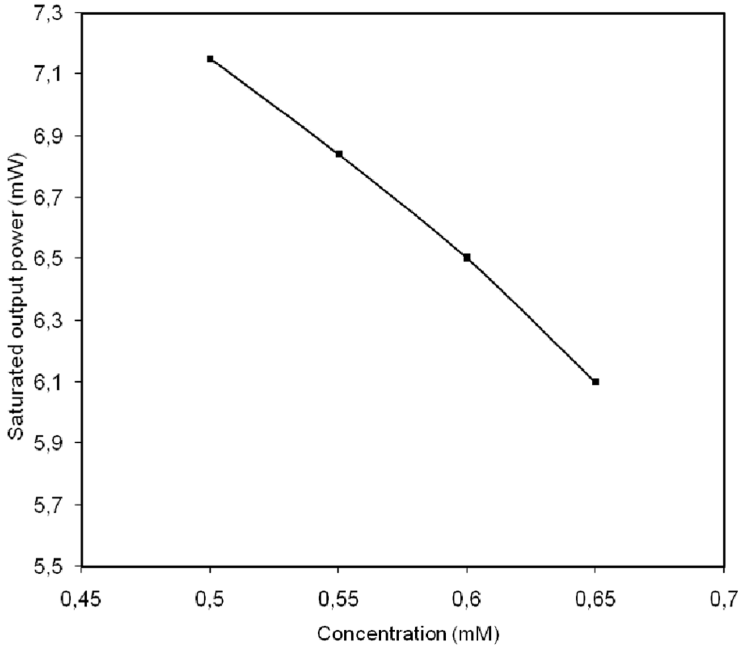

Fig.7.Concentration dependence of saturated output value of magenta doped PMMA film.

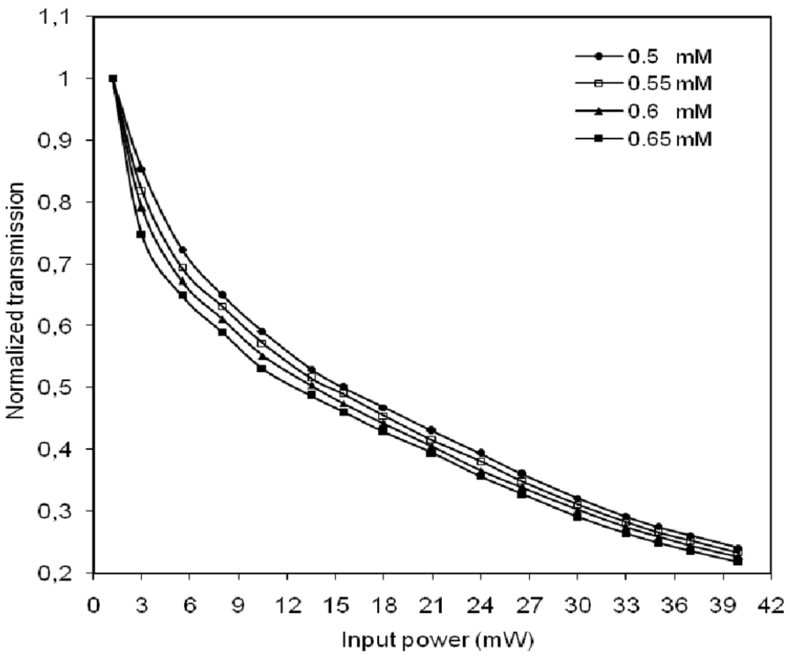

Fig.8. Normalized transmission curves of optical limiting for magenta doped PMMA film for different concentrations.

Table 1: Optical parameters and limiting thresholds of magenta doped PMMA film at λ=532 nm.

concentration (mM)	Absorbance (A)	absorption coefficient (α) (cm^{-1})	limiting threshold (mW)
0.5	0.3629	117.21	16.6
0.55	0.3779	118.89	16
0.6	0.3929	120.80	14.7
0.65	0.4079	121.84	13.7

CONCLUSION

The optical limiting performances of magenta doped PMMA film have been investigated at 0.5, 0.55, 0.6 and 0.65 mM concentrations, using cw laser beam at 532 nm wavelength. The results show that the optical limiting efficiency is concentration dependent. Excellent optical limiting performances with relatively good stability for magenta doped PMMA film have been observed until the incident input power approaches 40 mW without sample damaging. The experimental results show that the optical limiting threshold and saturated values of magenta doped PMMA film with 0.65 mM concentration are much lower than those of other films with 0.5, 0.55, and 0.6 mM concentrations. These materials can find potential applications in various optical limiting devices.

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