Low-threshold Optical limiting and Nonlinear refraction in Nanocomposite films of Light Green dye-polymer system

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Abstract. Poly(vinyl alcohol) (PVA) /Light Green (LG) dye nanocomposites were fabricated and their structure, microstructure, linear and nonlinear optical properties were investigated. The samples were characterized as nanocomposites with dye molecules encapsulated between the larger molecules (molecular chains) of the polymer host PVA. The nonlinear refraction behaviour was investigated employing the Z-scan technique, using a continuous wave (cw) He-Ne laser operating at 632.8 nm, as the excitation source. The samples displayed negative nonlinear refraction (self-defocusing) under the experimental conditions. Low-threshold optical limiting behaviour exhibited by the PVA based nanocomposites was demonstrated using an aperture limited geometry. The low limiting thresholds (~4 mW and ~2.4 mW) observed for the samples indicate that these low cost and durable nanocomposite films are potential media for optical limiting application under cw laser light excitation.

1. Introduction
The growth of photonic technology during the past decade has intensified research activities for developing new materials that display unusual and interesting NLO properties. This has lead to the design and synthesis of new molecular architectures and hybrid materials with nanoscale dimensions, including nanocomposites with various structures and multiple functions. Polymer matrix nanocomposites (PMNC) have opened up enormous scope for utilizing NLO active materials in various diverse applications ranging from optical limiters and optical wave guides to polymer based nanodevices and OLEDs and, also in many recent significant applications in medical and biological sciences, without causing much health and environmental hazards. Polymer matrices reinforced with micro and nanoparticles have been proven to possess properties superior to those of the starting materials and exhibit good thermal stability, high optical damage threshold, micro-hardness, etc. Organic dye polymer nanocomposites have been generating significant research interest by way of their high degree of compatibility, easy mode of preparation, flexibility in molecular design strategy, versatility and diverse functionality. The vinyl hydroxy polymer PVA has been proven to be a high performance matrix for polymer composites and it is largely in use in medical, biomedical and industrial fields because of its many interesting physical properties such as high transparency, good gas-barrier property against ambient gases, high dielectric strength, bio-degradability, biocompatibility etc. In the present work, we report the results of the structure, morphology, linear and nonlinear optical properties of a PVA based nanocomposite system comprising an organic dye Light Green (LG).
2. Experimental
The PVA based nanocomposite films for the present work were prepared by the solution-cast method, incorporating very small wt% of the organic dye Light Green (LG) (Loba Chemie, Mumbai) in the host polymer PVA (molecular weight = 125,000 g/mol s.d. Fine chemicals, Mumbai, India), as has been adopted by many researchers [1]. However, the method was improved to allow film formation in a dark, dust free environment, for NLO study. Good quality transparent films with uniform surface finish and, thickness in the range 30-35 μm were obtained within about five to six days.

The structure and crystallinity of the composite films were examined by X-ray diffraction (XRD) technique. A Bruker AXIS-D8 Advance diffractometer with Ni-filtered CuKα radiation of wavelength 1.54 Å was used to record the X-ray diffractograms of the samples. The composite films were characterized for details of their microstructure and surface homogeneity employing atomic force microscopy (AFM) (Digital Instruments Nanoscope E, with Si3N4 100 μm cantilever, 0.58 N/m force constant in the contact mode). The linear absorption spectra of the nanocomposite films were recorded using a UV-visible spectrophotometer (SHIMADZU UV-2450). The Z-scan technique [2] was employed to investigate the nonlinear refraction behaviour exhibited by LG-PVA composite films. For this, a continuous wave (cw), He-Ne laser operating at 632.8 nm was used as the excitation source. Optical limiting based on nonlinear refraction is demonstrated with an aperture limited geometry [3].

3. Results and Discussion
The XRD patterns of the LG-PVA nanocomposite films along with that of an unfilled PVA film and LG dye molecules in the powder form (inset) are shown in figure 1. The observed XRD pattern of the PVA film characterizes a semicrystalline polymer possessing a clear crystalline peak at 2θ=19.6°, corresponding to 101 spacing. This semicrystalline nature is due to the inter-molecular hydrogen bonding between the PVA chains [4]. The crystalline phase of this polymer may be treated as an imperfect crystalline lattice, in which free volumes/interstitials are filled with amorphous phase [4]. Even though the dye LG is crystalline in nature, it loses its crystallinity when incorporated into the polymer PVA. The dye molecules when incorporated into this matrix may occupy the interstitial space between the polymer chains and lose the crystallinity of their powder form. For the PVA based nanocomposites, the intensity of the peak at 2θ=19.6°, characteristic of the host matrix PVA increases, suggesting an enhancement in the degree of crystallinity of PVA. The increase in crystallinity of the composite films with respect to that of clean (unfilled) PVA may be due to the interactions of LG dye molecules probably with the hydroxyl groups of PVA.

![Figure 1](image1.png)
**Figure 1.** XRD pattern of (a)LG dye in powder form (b) PVA film (c & d) LG-PVA nanocomposite films.

![Figure 2](image2.png)
**Figure 2.** AFM images of 1x1μm² regions of LG-PVA nanocomposite film (dye concentration: 5.1x10⁻⁴ M)

The results of AFM analysis are also in agreement with the above observations. Figure 2 shows the 2D and 3D AFM images of LG-PVA composite films with dye concentration 2.02x10⁻⁴ M. The
average roughness of the surface was measured to be ~1.3 nm for the LG-PVA composite film. The surface roughness was found to be much less than those reported for many nanostructured materials and nanocomposite films. This suggests that by dispersing the dye molecules/particles in the PVA matrix, the dye molecules get inside the voids/free volume present in the polymer PVA, as a result of which the free volume of the matrix decreases. Encapsulation of dye molecules in these microscopic/nanoscopic free volumes/interstitials of molecular dimension available between the polymer chains reduces the porosity, and hence the surface roughness also decreases.

![Figure 3](image3.png)

**Figure 3.** Linear absorption spectra of (a-c) LG-PVA composite films for different concentrations and (d) aqueous solution of LG dye

Figure 4. CA Z-scan profiles for different dye concentrations of LG-PVA nanocomposite films (a) 1.0×10⁻³M (b) 3×10⁻³M (c) 5×10⁻³M

The linear absorption spectra of LG-PVA nanocomposite films for different concentrations of the dye content are illustrated in figure 3. The spectra indicate well structured and wide absorption band centered at 649 nm, red shifted by ~11 nm compared to that of aqueous solution of LG dye, as has been observed for other solvatochromic dyes.

Closed aperture (CA) Z-scan experiments were performed to study the nonlinear refraction behaviour of the PVA based nanocomposite films. The normalized closed aperture Z-scans (Fig. 4) exhibit a pre-focal peak followed by a post-focal valley, indicating self-defocusing effect (negative nonlinear refraction). Nonlinear refraction in a medium can be due to different physical mechanisms (Kerr effect, thermal self-focusing, defocusing, photo refraction, molecular reorientation etc). The peak-valley separation of the CA Z-scan curves for the composite films is found to be ~2.3 – 2.4 z₀ in contrast to 1.7 z₀ that is observed for Kerr nonlinearity. According to the literature on nonlinear refraction, the positive deviation of the peak-valley separation from the Kerr value of 1.7 z₀ indicates the presence of thermal contributions [5]. Localized absorption of tightly focused laser beam propagating through an absorbing dye medium produces spatial distribution of temperature and consequently a spatial variation of refractive index, that act as a thermal lens resulting in the phase distortion of the propagating beam. This is a predominant mechanism of nonlinearity for excitation under cw laser light where the experimental data were analysed using Thermal lens model [5], good fitting was obtained for the theoretically obtained curves (shown as solid lines of fig. 4) with experimental ones. The on-axis phase shift θ can be obtained from the best theoretical fit. Assuming θ<<1, the on-axis normalized transmittance can be expressed as:

\[
T_{NL}^{TLM} (z) = \frac{1}{1 + \theta \frac{2}{1 + \frac{x}{z_0}}} \tag{1}
\]

where, \( x = z/z_0 \), and \( \theta \), the nonlinear phase shift. From the value of \( \theta \), the nonlinear refractive index of the sample can be calculated using the expressions,
0 = k n^2 L_{eff} I_0 

(2)

where, \( L_{eff} = \frac{1 - \exp(-\alpha L)}{\alpha} \), \( I_0 \) is the on-axis irradiance at the focus, \( k \), the wave vector (\( k=2\pi/\lambda \)), \( L \), the sample thickness and \( \alpha \), the linear absorption coefficient at the wavelength used for excitation. The estimated values of \( n^2 \) for LG-PVA composite films are found to be 0.5 - 1.36 x10^{-6} cm^2/W.

The defocusing effect under cw laser irradiation, associated with nonlinearity of thermo-optic origin, can be used for the design of an optical limiting device [3]. Optical limiting based on nonlinear refraction is studied keeping an aperture (2 mm) in front of the detector, which is placed at a distance of 60 cm from the lens of focal length 5 cm. Figure 5 shows the optical limiting performance of LG-PVA samples for two different dye concentrations. The samples were placed at the valley position of the Z-scan trace and the output power from the sample was monitored varying the input power in steps. At low input powers, the output varies linearly with input power, obeying Beers law. With further increase in the input power, the transmitted power get saturated and the limiting thresholds were found to be ~4 mW and ~2.4 mW for LG-PVA composite films (Dye concentrations: 1.1×10^{-3}M and 3.1×10^{-3}M) under cw laser excitation at 632.8 nm. This indicates that the nanocomposite film samples are good candidates for optical limiting of 632.8 nm cw laser light.

### 4. Conclusion

Good quality nanocomposite films comprising Light Green dye and PVA were prepared by a simple processing technique and their structure, morphology, linear and nonlinear optical properties were investigated. Employing the techniques of XRD and AFM, the samples were characterized as nanocomposites with dye molecules encapsulated between the larger molecules (molecular chains) of the polymer host PVA. The low-threshold nonlinear refraction behaviour exhibited by the PVA based nanocomposites on excitation with 632.8 nm, cw He-Ne laser light were investigated employing the Z-scan technique. Since the nanocomposite films exhibited self-defocusing under cw laser light excitation at 632.8 nm, nonlinear refraction based optical limiting of cw laser light was demonstrated with an aperture limited geometry. The low threshold optical nonlinearities exhibited by these LG-PVA composite films signify the scope for utilizing these nanocomposites as a potential material for photonic device applications.

### References

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