CHAPTER 8

OPTICAL LIMITING PROPERTIES OF IC-PVA, PR-PVA AND LG-PVA NANOCOMPOSITE FILMS AND LOW POWER OPTICAL PHASE CONJUGATION IN LG-PVA NANOCOMPOSITE FILMS

The optical limiting properties of the newly fabricated nanocomposite films of IC-PVA, PR-PVA and LG-PVA systems are discussed in this chapter. Optical limiting curves were plotted from the OA Z-scan data of IC-PVA and LG-PVA nanocomposite films, as these films exhibited RSA type of nonlinear absorption under nanosecond Nd:YAG laser light excitation at 532 nm. Since the nanocomposite films exhibited self-defocusing under CW laser light excitation at 632.8 nm and 442 nm, nonlinear refraction based optical limiting of CW laser light was studied using an aperture limited geometry. The low limiting thresholds obtained for the nanocomposite films suggest that these materials can be efficiently used as optical limiters by utilizing their high refractive nonlinearity. Low power optical phase conjugation (OPC) in a saturable absorber organic-polymer nanocomposite system (LG-PVA), studied under CW laser light excitation at 632.8 nm, is also presented in this chapter. The temporal behavior of the PC waves generated from LG-PVA nanocomposite films signify that they are potential candidates for applications like PC interferometries, involving low power optical phase conjugation.
8.1 Introduction

The ability to control the intensity of light in predetermined and predictable manner is one of the most fundamental and important application in the field of optical communication. This has motivated many researchers to search for efficient NLO materials exhibiting optical power limiting (OPL) behaviour. As discussed in chapter 1, a practical optical limiter should have low limiting threshold, high optical damage threshold and stability, fast response time, high linear transmission throughout the sensor band width, low optical scattering, high attenuation, optical clarity and robustness [Senge et al., 2007; Rao et al., 2000].

The laser damage protection of human eyes remains a challenging problem, due to the ever-increasing use of lasers for scientific, industrial and technological purposes on one hand, and the unavailability of practical low threshold optical limiters, on the other hand. The need for passive laser protectors to protect human eyes and all optical sensors from intense laser beams is not limited to the military but is rather a growing societal problem that can only escalate.

Significant progress has been made over recent decades in the development of optical limiters with large NLO responses, particularly in carbon-based materials [Lim et al., 2011]. These include graphitic systems such as carbon black suspensions (CBS), single-walled and multiwalled carbon nanotubes (CNTs) and small π-electron systems such as fullerenes, porphyrins and phthalocyanines [Mansour et al., 1992; Riggs et al., 2000; Tutt and Kost, 1992; Perry et al., 1996; Senge et al., 2007; Lim et al., 2011]. Until recently, C60 and phthalocyanine derivatives were considered as (standard limiters) candidate materials for optical limiting device applications [Sathiyamoorthy et al., 2008]. These small π-electron systems can provide optical-limiting properties by means of excited-state absorption of long-lived triplet states formed in the sub-nanosecond timescale. The mechanism can provide highly effective optical limiting in liquid cells and solid films, but only over narrow wavelength bands because of the strong wavelength dependence of the ratio of excited-state to
ground-state absorption cross-sections. Various nonlinear optical mechanisms, including self-focusing, self-defocusing, photo-induced scattering, photorefraction, excited state absorption, two-photon absorption, photorefractive and free-carrier absorption, occurring in nonlinear optical materials can contribute to optical limiting (Chapter 1, section 1.5.4). For over a decade now, the optical-limiting benchmark for broadband (wide spectrum) limiting has been held by CBS and CNT suspensions. These materials limit the transmission of optical energy by nonlinear scattering mechanisms. Although CNTs have unique properties such as stiffness, strength and tenacity compared to other materials, they possess several disadvantages like high production cost and lack of technology for mass production. Poor dispersion, lack of alignment of CNTs and agglomeration in the matrix materials are the major challenges to the improved performance of nanocomposites (Gradi, 2011).

OPL based on nonlinear absorption mechanisms like reverse saturable absorption (RSA), multiphoton absorption (MPA) etc. have been a subject of extensive investigations for the last few decades. This is because nonlinear absorption (NLA) renders the possibility to make devices that are transparent under non-harmful conditions, but become opaque as the intensity exceeds some threshold [Westlund et al., 2008]. Wide range of materials exhibiting reverse saturable absorption has been investigated for optical limiting applications. Harilal et al. [1999] reported optical limiting in toluene solution of C60 under excitation with 532 nm laser pulses of duration 8 ns. They concluded that RSA is the major mechanism for optical limiting in these molecules. Optical limiting in Indium tetra (tert-butyl) phthalocyanine [Perry et al., 1996] has been investigated under optical excitation with nanosecond (8 ns) laser pulses at 532 nm. The observed optical limiting is explained in terms of an excited state absorption mechanism. Optical limiting in toluene solution of C60, investigated under excitation with 10 ns laser light pulses in the wavelength region 710-740 nm has been reported by Mishra et al. [1997]. The observed optical limiting is explained on the basis of RSA, involving triplet states. He et al. [1998] have reported optical limiting and stabilization based on nonlinear absorption (TPA) mechanism occurring in a novel polymer compound (EHO-OPPE) under nanosecond (7 ns) laser pulses from a Q-switched Nd:YAG laser operating at 810 nm. Optical limiting in C60 and higher fullerenes has been reported by
Koudoumas et al. [2005]. Riggs et al. [2004] have reported the concentration and medium dependence on the optical limiting properties of a series of organic dyes under nanosecond pulsed laser excitation at 532 nm. Newly synthesized copolymers containing alternating substituted thiophene & 1,3,4-oxadiazole units have been investigated by J.Kiran et al. [2006]. They have observed optical limiting based on RSA occurring in these compounds. Optical limiting based on RSA in a bischalcone derivative doped PMMA films have been reported by the same group [J.Kiran et al., 2008]. Venkatram et al. [2008] reported optical limiting behavior based on nonlinear absorption (ESA) mechanism of alkoxy phthalocyanines in solution at 532 nm Nd:YAG laser light excitation (6 ns). Axially substituted Indium phthalocyanines have been synthesized and their optical limiting behavior has been investigated under nanosecond laser excitation at 532 nm by Dini et al. [2008]. Westlund et al. [2008] reported optical limiting in Platinum(II) acetylides incorporated into poly(methyl methacrylate) (PMMA) glasses. Optical limiting response of copper phthalocyanine embedded into a polymer host (PMMA) has been reported by Kürüm et al. [2009]. Strong optical limiting property of a ball-type supramolecular zinc-phthalocyanine in polymer-phthalocyanine composite film has been reported recently by Özdağ et al. [2010]. The observed optical limiting has been explained on the basis of a nonlinear absorption mechanism arising from excited state absorption. From our research group, George et al. [2008] have reported optical limiting in an organic dye, Neutral Red, in solution and solid film form under excitation with 20 ns Nd:YAG laser pulses at 532 nm. The observed optical limiting is ascribed to nonlinear absorption (TPA) process. Geetha et al. [2002] has reported optical limiting behaviour of Congo-red and Crystal violet dye films under pulsed laser excitation at 532 nm. Optical limiting behaviour of newly synthesized chromophore 4(2-hydroxy naphthyl azo) antipyrine has also been reported [2004].

Optical limiting based on refractive nonlinearities has also been of significant research interest. Defocusing optical limiters based on nonlinear refractive effects make use of the ensuing distortion of the incident beam, termed thermal lensing, which causes a reduction in the fluence on the detector to be protected [Valsalamilka et al., 2005]. At low intensity levels, this change can be neglected and all laser beam can be detected through a properly placed aperture, whereas, at high intensity levels, this change becomes more prominent and only
a small portion of beam energy can pass through the aperture and finally be detected. The devices based on these mechanisms are called energy spreading type of optical limiter. The physical origin of nonlinear refraction can be electronic, molecular, electrostrictive or thermal. Under continuous wave (CW) laser irradiation, thermal effects play a major role. A laser beam, while passing through an absorbing media, induces temperature gradient that changes the refractive index profile. This intensity-induced localized change in the refractive index results in a lensing effect on the optical beam above certain power threshold values and can be used to clamp an outgoing optical beam at a constant fluence when the input beam is above a certain threshold. Such thermal effects can be exploited for the design of optical limiters in the CW regime. Optical limiters for low power CW lasers are also very important as they could be used for protection of human eyes from intense laser effect, as the maximum permissible exposure for human eyes even with a laser pointer is ~ 2.5 mW/cm² in the visible spectral region [Mathews et al., 2007b]. Information about the damage level of a sensor is necessary to determine the required limiting level of the device.

A number of studies have been reported on optical limiting in the CW regime. Sendhil et al. [2005] have investigated the low-threshold optical power limiting based on nonlinear refraction in Zinc tetraphenyl porphyrins incorporated in Nafion polymer and in toluene solution under CW laser light excitation at 632.8 nm. The origin of nonlinearity is explained on the basis of thermal nonlinear refraction. Also, it was shown that the effective optical limiting at desired threshold values can be achieved by the optimal choice of aperture size and experimental geometry. Ghaleh et al. [2007] have analyzed the nonlinear responses and optical limiting behaviour of the dye Fast green FCF dye under CW laser irradiation at 632 nm. A stable low power optical limiter in the CW regime (632 nm) has been designed by Sathiyamoorthy et al. [2007]. Optical limiting based on nonlinear refractive properties of symmetrical and unsymmetrical phthalocyanines in the CW regime have been demonstrated by Mathews et al. [2007b]. The same group [Mathews et al., 2007] has reported optical limiting based on nonlinear refraction in tetra tert-butyl phthalocyanine and zinc tert-butyl phthalocyanine in solution and thin film form under the same experimental conditions. Optical limiting based on thermal nonlinear refraction
displayed by Chloro Aluminium phthalocyanine as studied under optical excitation at 632.8 nm CW laser light has been reported by Sathiyamoorthy et al. [2008b]. Rashidian et al. [2009] have studied the nonlinear response and optical limiting behaviour in Basic Violet 16 dye. Optical limiting behavior of Acid Blue 29 in ethanol solution under low power CW He-Ne laser excitation at 632.8 nm has been reported by Zidan et al. [2009]. Girisuń et al. [2010] have reported optical limiting of 532 nm CW laser light, arising from refractive nonlinearities of thermal origin occurring in diglycinyl thiourea under.

Organic dyes embedded in rigid environment find applications in low power optical phase conjugation (OPC). Saturable absorption as well as photorefractive effect which enhances the effective third-order nonlinear susceptibility make it possible to realize phase conjugation even with low power lasers [Sreedhar et al., 1993]. Organic dye doped polymer films exhibiting saturable absorption with relatively low intensity laser beams are of intense interest in this respect. They have been demonstrated as materials available for phase conjugation by degenerate four-wave mixing (DFWM), for two-wave coupling by nearly degenerate two-wave mixing and for possible applications in the field of real-time optical information processing [Sharma et al., 1994; Nitani et al., 1998]. Low power phase conjugation has been demonstrated by degenerate four-wave mixing (DFWM) in numerous organic materials. Fujiwara et al. [1985] observed two contributions to the OPC signal in fluorescein-doped gelatin. Kramer et al. [1986] have demonstrated OPC in fluorescein-doped boric acid glass. Miyanaga et al. [1988] observed OPC in erythrosine B doped in a planar wave guide of PVA. OPC in Rhodamine 6G doped boric acid has been observed by Kumar et al. [1989]. Moosad et al. [1990] studied low power optical phase conjugation in xanthene dyes doped in polymer matrices. Generation of PC wave in Eosin yellow-doped polymer films have been reported by Nakatsuka et al. [Nakatsuka et al., 1991]. Low power phase conjugation in phenosafranin dye-doped gelatin and PVA films has been demonstrated by Sreedhar et al. [1993]. Phase conjugation in colour additive doped PVA films has been demonstrated by Keinonen et al. [1997]. The simultaneous generation of PC signals by DFWM and holographic process using nanosecond and CW lasers in PVA films doped with saturable absorber dyes has been reported by Tanaka et al. [2002].
Geethakrishnan et al. [2005] have reported the generation of phase conjugated wave in acid blue 5 dye-doped gelatin films.

The optical limiting properties of the new organic-polymer nanocomposite films (IC-PVA, PR-PVA and LG-PVA) were investigated using both nanosecond laser pulses and CW laser light. Phase conjugation studies were also carried out on a saturable absorber nanocomposite system (LG-PVA) with a CW He-Ne laser source at 632.8 nm.

8.2 Optical limiting behaviour of IC-PVA and LG-PVA nanocomposite films for 532 nm nanosecond laser light pulses

OA Z-scan profiles of IC-PVA and LG-PVA nanocomposite films revealed reverse saturable absorption behavior under pulsed laser light excitation at 532 nm (see Chapter 4 and 6). Materials exhibiting RSA find applications in optical limiting. In this context, the optical limiting behavior of IC-PVA and LG-PVA nanocomposite films was further investigated using OA Z-scan data, as has been done by many researchers [Kurum et al., 2009; Özdağ et al., 2010; Sandeep et al., 2010].

In an open aperture Z-scan scheme using a Gaussian beam, at each position $z$, the sample faces a different value of laser fluence, which will be maximum at the focal point. The laser fluence at each $z$ positions could be calculated from the value of the fluence at the focus using the standard equations for Gaussian beam waist [Irirman et al., 2008]. So to further investigate the optical limiting, the normalized transmittance is plotted against the incident laser pulse energy density ($J/m^2$). Such plots are generated from Z-scan traces and represent a better comparison of the nonlinear absorption or transmission in these samples. Figures 8.1 and 8.2 depict the optical limiting curves of the IC-PVA composite films (linear transmission ~70% - 80%) and LG-PVA composite films (linear transmission ~50% - 68%) respectively, deduced from the Z-scan data. From the figures, it is clear that for high input irradiances, there is marked deviation from linearity. For an input fluence greater than 1.4 $J/cm^2$ (Fig. 8.1), the output intensity drops steadily for IC-PVA composite films with higher dye concentration, whereas, for LG-PVA composite films (figure 8.2), the output drops steadily at 1.8 $J/cm^2$. This clearly indicates optical limiting.
Figure 8.1: Optical limiting behavior of IC-PVA nanocomposite films for Dye concentrations (a) 6.1x10⁻⁴ M (b) 8.3x10⁻⁴ M (c) 2.0x10⁻³ M and (d) Different concentrations of dye content) for 532 nm nanosecond laser light. Solid lines are the theoretical fits to the experimental data.

In general, optical limiting behavior of a medium can have contributions from various nonlinear optical effects such as ESA (including excited singlet or triplet absorption, free-carrier absorption etc.), multi-photon absorption (2PA, 3PA), self-focusing/defocusing, thermal blooming, nonlinear scattering etc. The predominant mechanism for the observed optical limiting behaviour of IC-PVA and LG-PVA nanocomposite films is attributed to excited state absorption, as discussed earlier in the case of nonlinear absorption (RSA) behaviour of the nanocomposite films.
Figure 8.2: Optical limiting behavior of LG-PVA nanocomposite films. (Concentrations (a) $3.1 \times 10^{-4}$M (b) $5.1 \times 10^{-4}$M (c) $7 \times 10^{-4}$M and (d) Different concentrations of the dye content) for 532 nm nanosecond laser light. Solid lines are the theoretical fits to the experimental data.

Table 8.1: The NLA parameters and optical limiting thresholds of the nanocomposite films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration(M)</th>
<th>Linear Transmission</th>
<th>Incident intensity, $I_0$</th>
<th>$\beta$ (cm/GW)</th>
<th>Optical limiting Threshold</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC-PVA</td>
<td>$6.1 \times 10^{-4}$</td>
<td>80 %</td>
<td>$4.4 \times 10^9$</td>
<td>17</td>
<td>3.6 J/cm$^2$</td>
</tr>
<tr>
<td>IC-PVA</td>
<td>$8.3 \times 10^{-4}$</td>
<td>77 %</td>
<td>$4.4 \times 10^9$</td>
<td>105</td>
<td>2.45 J/cm$^2$</td>
</tr>
<tr>
<td>IC-PVA</td>
<td>$2.0 \times 10^{-3}$</td>
<td>70 %</td>
<td>$4.4 \times 10^9$</td>
<td>130</td>
<td>1.4 J/cm$^2$</td>
</tr>
<tr>
<td>LG-PVA</td>
<td>$3.1 \times 10^{-3}$</td>
<td>68 %</td>
<td>$4.4 \times 10^9$</td>
<td>30</td>
<td>2.5 J/cm$^2$</td>
</tr>
<tr>
<td>LG-PVA</td>
<td>$5.1 \times 10^{-3}$</td>
<td>62 %</td>
<td>$4.4 \times 10^9$</td>
<td>73</td>
<td>2.3 J/cm$^2$</td>
</tr>
<tr>
<td>LG-PVA</td>
<td>$7.0 \times 10^{-3}$</td>
<td>50 %</td>
<td>$4.4 \times 10^9$</td>
<td>145</td>
<td>1.8 J/cm$^2$</td>
</tr>
</tbody>
</table>

observed under the experimental conditions (section 4.3.1 and section 6.3.1). The normalized transmittance for the standard open aperture Z-scan is expressed by the relation [Sheik-Bahae et al., 1990].

$$T(z, s = 1) = \sum_{m=0}^{\infty} \left[ -q_0(z) \right]^m \left[ m + 1 \right]^{3/2}, \quad \text{for } |q_0(0)| < 1 \quad (8.1)$$
where, 

\[
q_0(z) = \frac{\beta_{\text{eff}} l_0 L_{\text{eff}}}{1 + z^2 / z_0^2}
\]  

(8.2)

L_{\text{eff}} is the effective length of the sample given by, \( L_{\text{eff}} = (1 - \exp(-\alpha L))/\alpha \), with \( L \), the sample length and \( \alpha \), the linear absorption coefficient; \( l_0 \) is the on axis intensity at the focus and \( z_0 \), the diffraction length of the beam. Solid lines are the theoretical fits generated using equation (8.1) [Venkatram et al., 2008; Unnikrishnan et al., 2002; Henari et al., 2008b]. The values of \( \beta_{\text{eff}} \) extracted from the best fits to the experimental data, together with the respective threshold values of input intensity for the onset of optical limiting (optical limiting threshold) are given in table 8.1. The obtained values are comparable to or greater than those reported for many materials in the nanosecond excitation regime [J.Kiran et al., 2008; Santhi et al., 2006; Unnikrishnan et al., 2001; Auger et al., 2003; Unnikrishnan et al., 2003].

8.3 Optical limiting behaviour of organic dye-PVA nanocomposite films for CW laser light excitation

Optical limiters based on refractive nonlinearities operate by refracting light away from the sensor or the object to be protected; in contrast to the absorption based limiter where, the incident radiation is simply absorbed. This results in a large dynamic range before the limiter itself gets damaged. As nonlinear refraction and thermal lensing properties play dominant roles in the overall nonlinearities of the material in the case of continuous wave (CW) pumping [Mathews et al., 2007b], optical limiting studies based on nonlinear refraction are carried out for the organic-polymer nanocomposite films under CW laser light irradiation at 442 nm and 632.8 nm.

8.3.1 Experimental Details

The nonlinear refraction based optical limiting of CW laser light is studied using an aperture limited geometry [Sathiyamoorthy et al., 2008; Dhanuskodi et al., 2011]. The setup is essentially the same as that for closed aperture (CA) Z-scan; the only difference is that, in optical limiting experiments, the input intensity is varied using a combination of neutral density filters. The samples are kept at the Z position where the valley falls in the closed aperture Z-scan (just after the focus), because it is at this position the beam is maximum defocused by the sample [Mathews et al., 2007].
Figure 8.3: Experimental arrangement for nonlinear transmission studies under CW laser light excitation

The aperture kept in front of the detector reduces the cross-section of the beam entering the detector. The input power of the laser beam was varied systematically and the corresponding output power through the aperture was detected using power meter and, the characteristic curve with output power as a function of input power is obtained. The aperture-detector distance from the sample and, the aperture size were optimized for better limiting performance. This allows the control of overall output transmittance to a great extend, which is difficult with limiters based on absorptive nonlinearities. The laser sources used for excitation are:

- A low power CW He-Ne laser operating at 632 nm (Maximum power output: 22 mW).
- A CW He-Cd laser operating at 442 nm wavelength with a maximum output power of 135 mW

8.3.2 Results and Discussion

For Z-positions very close to the focus, the gradual formation of concentric ring patterns attributed to induced self-phase modulation was observed (See Chapter 7). With CW laser illumination, such effects indicate the domination of thermal effects in the medium [Mathews et al., 2007b]. Therefore, to keep away from the irregularities, the samples were placed away from the focus, but still in the nonlinear regime, to ensure the absence of ring pattern formation.

Figure 8.4 shows the optical limiting behaviour of IC-PVA nanocomposite films for CW laser light excitation at 632.8 nm and 442 nm. The straight lines indicate the linear transmission of the samples at the respective wavelengths of excitation. At very low incident power, the output power varies linearly according to Beer’s law. As the incident power is increased above a particular value (threshold value), the beam starts diverging. The transmitted intensity through
the aperture decreases and a marked deviation from linearity is observed. For IC-PVA nanocomposite films, the threshold values are found to be \( \sim 2.5 \) mW (for the composite film with linear transmission 77\%, for CW laser light excitation at 632.8 nm) and \( \sim 13 \) mW and 10 mW for the composite films having linear transmission 90\% and 84\% respectively, for CW laser light excitation at 442 nm. This suggests that the nanocomposite films can be used as optical limiting media in the CW regime for the protection of optical sensors like night vision devices [Girisun et al., 2010]. It may be noted that low limiting threshold (\( \sim 2.5 \) mW) was obtained for IC-PVA nanocomposite film (Concentration of dye content: \( 6.1 \times 10^{-4} \) M), for 632.8 nm CW laser light. For IC-PVA nanocomposite films, the saturation of output intensity occurs at an incident intensity of \( \sim 10 \) mW for 632.8 nm (He-Ne) laser light and, \( \sim 40 \) mW for 442 nm (He-Cd) laser light.

![Figure 8.4: Optical limiting behaviour of IC-PVA nanocomposite films for CW laser Light excitation at (a) 632.8 nm and (b) 442 nm](image)

![Figure 8.5: Optical limiting behaviour of (a)PR-PVA nanocomposite films for CW laser light excitation at 442 nm(b)LG-PVA nanocomposite films for CW laser light at 632.8 nm.](image)
The optical limiting materials rely on one or more of the nonlinear optical mechanisms like two-photon absorption (TPA), excited state absorption (ESA), free carrier absorption (FCA), thermal defocusing and self diffraction, photorefraction, nonlinear refraction, nonlinear scattering etc. [Tutt and Boggess, 1993]. The OA Z-scan profiles of IC-PVA nanocomposite films (Chapter 4, section 4.3.2) exhibited reverse saturable absorption process occurring under excitation with CW laser light at 632.8 nm. However, it may be noted that the real part of the third-order nonlinear susceptibility ($\chi^{(3)}$) is much greater than that of the imaginary part for 632.8 nm CW laser light excitation (See table 7.4, Chapter 7). i.e., the absolute values of $\chi^{(3)}$ has major contribution from its real part. Nonlinear refraction mechanisms are, therefore, assumed to give greater contribution to the third-order nonlinearity, compared to that of the absorptive nonlinearity. Under CW laser irradiation, the major contribution to the observed nonlinear refraction is expected to be of thermo-optic origin [Grisun et al., 2010; Sathiyamoorthy et al., 2008; Mathews et al., 2007]. The energy from the focused laser beam is transferred to the sample through linear absorption and is manifested in terms of heating of the medium resulting in a temperature gradient, thereby changing the refractive index across the sample and the sample then acts as a lens [Mathews et al., 2007], as explained in Chapter 7. The phase of the propagating beam will be distorted due to this thermal lens formation. The occurrence of thermal effects in all the nanocomposite films has been confirmed in CA Z-scan analysis and was discussed in detail in Chapter 7. However, according to literature, the presence of more than one mechanism can enhance optical limiting performance. The intense optical limiting performance of IC-PVA nanocomposite films (at 632.8 nm) may arise from a combination of refractive nonlinearities as well as reverse saturable absorption (though occurring at two different temporal scales), the predominant mechanism being thermal induced change in refractive index. Optical limiting in the case of thermal nonlinearities arise from defocusing of the beam, when the incident intensity exceeds a critical threshold value which results in a greater part of the beam cross-section being cut off by the aperture [Sendhil et al., 2005].

The optical limiting behaviour of PR-PVA and LG-PVA nanocomposite films for CW laser light at 442 nm and 632.8 nm, respectively is presented in figure 8.5. Since the samples exhibited saturable absorption type of behaviour
(sections 6.3.1 and 6.3.2), which could not yield optical limiting, the observed optical limiting effect can be attributed to thermally induced nonlinear refraction. The limiting thresholds of the PR-PVA nanocomposite films (Dye concentrations: $3.4 \times 10^{-3} \text{M}$ and $5 \times 10^{-3} \text{M}$) were found to be $\sim 15$ mW for 442 nm He-Cd laser light. Low limiting thresholds of $\sim 4$ mW and $\sim 2.4$ mW were observed for LG-PVA nanocomposite films (Dye concentrations: $1.1 \times 10^{-3} \text{M}$ and $3.1 \times 10^{-3} \text{M}$) for 632.8 nm CW laser light at. It is worth noticing that, for LG-PVA nanocomposite films, when incident laser power exceeds 10 mW, the saturation of output intensity occurs at $\sim 3.5$ mW and $\sim 1.5$ mW for dye concentrations $1.1 \times 10^{-3} \text{M}$ and $3.1 \times 10^{-3} \text{M}$ respectively. The limiting threshold values obtained for the organic dye-PVA nanocomposite films, for 632.8 nm CW laser light excitation at 632.8 nm is comparable to or even better than those reported for phthalocyanine solutions, and an organic crystal (2APS) under similar experimental conditions [Mathews et al., 2007; Sathiyamoorthy et al., 2008; Ramamurthy et al., 2011]. The optical limiting action of the nanocomposite films is similar to that observed for C$\text{C}_6$, the standard optical limiter, in toluene solution [Mishra et al., 1997]. These observations indicate that LG-PVA nanocomposite films can be an efficient optical limiter at this wavelength.

8.4 Low power optical phase conjugation in LG-PVA nanocomposite films

Optical phase conjugation (OPC) plays a significant role in technological applications such as real-time image processing, phase-conjugate interferometries, adaptive optics and spectral filtering [Nakatsuka et al., 1991; Tanaka et al., 2002; Sreedhar and Sirohi, 1993]. Degenerate four-wave mixing (DFWM), a third-order NLO process, is a simple and elegant method for generating a phase conjugate wave. Organic dyes exhibiting large third-order nonlinearities were investigated in this respect [Sillberg and Bar Joseph, 1981; Tanaka et al., 2002; Sreedhar and Sirohi, 1993; Nakatsuka et al., 1991; Nitanai and Miyanaga, 1998; Geethakrishnan et al., 2005; Cerdan et al., 2012; Thakur et al., 2012; Zou et al., 2012]. The phase conjugate of a given input wave is a wave whose spatial part is the complex conjugate of the spatial part of the input wave (section 1.5.5).
Optical phase conjugation (OPC) in organic dyes embedded in solid matrices has been described by a few authors [Moosad et al., 1990]. Compared with other nonlinear materials such as oxide crystals, semiconductors, liquid crystals, etc., the dye-doped films have the advantage of easy fabrication of large size elements and provide a wide variety of dye/polymer combinations which enable the development of functional phase conjugators suitable for many practical applications [Tanaka et al., 2002]. Most of these experiments utilized high peak power pulsed lasers. The photorefractive effect and the saturable absorption which enhance the effective third-order optical susceptibility make it possible to realize phase conjugation with low power lasers [Sreedhar and Sirohi, 1993]. Low power phase conjugation has been demonstrated in a number of organic and inorganic materials. Organic dyes have emerged as materials with good potential for OPC because of their large third-order optical nonlinearity.

8.4.1 Experimental Details

The phase conjugate wave generated by DFWM involves the interaction of three coherent input waves of same frequency in a nonlinear medium to create a fourth output wave that is phase conjugate to one of the input waves [Sharma et al., 1994]. Detailed experimental setup is given in Chapter-2.

In the present case, the standard degenerate four-wave-mixing (DFWM) configuration was used for the generation of phase conjugate signal. A CW He-Ne laser operating at 632.8 nm was used as the excitation source. The entire experimental setup was arranged on a vibration-free optical table. The output beam (figure 2.5) from the laser was first split by a beam-splitter BS1 (~5: 90). The beam reflected off from BS1 was used as the probe beam $E_3$ after reflected by the beam-splitter BS3. The transmitted beam from BS1 was further divided by another beam-splitter BS2 (50 : 50) to provide the counter-propagating pump beams, called forward-pump wave $E_1$ and backward-pump wave $E_2$ respectively. Beam-splitter BS3 was used to direct the probe beam to the organic dye nanocomposite sample and to transmit the PC signal, which was opposite to the direction of the probe beam. The constant intensity ratio of the probe beam ($E_3$), forward-pump beam ($E_1$), and backward-pump beam ($E_2$) used in this study was ~1: 10: 10. The incident angle ($\theta$) between the probe beam and forward-pump beam is fixed at ~10°. The optical path lengths of all the three beams were made equal.
that they were coherent at the sample. The intensity of PC wave was measured by a photo-detector fed to the digital power meter.

8.4.2 Results and Discussion

Figure 8.6: Temporal behavior of PC signals generated from LG-PVA composite films (i) for a concentration of $3.1 \times 10^{-3}$ M and (ii) showing the effect of dye concentration on PC signal generation using CW laser at 632.8 nm.

Figure 8.6 depict the temporal behavior of the PC signals generated from LG-PVA nanocomposite films for dye concentrations $3.1 \times 10^{-3}$ M and $5.1 \times 10^{-3}$ M. The PC signal built-up is not instantaneous, but it takes several minutes. The PC signals are found to increase, reach a maximum value and then decrease gradually, as time elapses. For higher concentration of the dye content (figure 8.6 (ii) (b)) in the nanocomposite films, the maximum value of PC signal intensity is found to be high compared to that for the lower dye content, however, the time taken for grating formation is larger than that for the sample with a lower dye content.

In the present case, the LG-PVA nanocomposite films exhibited saturable absorption type of behavior at 632.8 nm, on excitation with CW laser light (Chapter 6) and the estimated values of the saturation intensities were found to be very low ($I_s = 8 \times 10^3$ W/cm$^2$ and $6 \times 10^3$ W/cm$^2$). When an intense light beam impinges continuously on the organic polymer film, the population in the state $S_0$ decreases and the consequent rearrangement of populations (i.e. in $S_0$ and $S_1$ states) may cause a decrease in the absorption coefficient [Keinonen et al., 1997]. As the life time of the triplet state $T_1$ is quite long, the absorption saturates even for low incident intensities, as described in section 6.3.2. PC wave generation can
also have contributions from photoisomerization, holographic components, orientational and thermal effects etc.

According to literature, PC waves generated in organic dye-doped polymer films can have contributions from DFWM and holographic processes under the condition that the polarization states of the probe and two pump beams are mutually parallel [Sreedhar and Sirohi, 1993; Tanaka et al., 2002; Nakagawa et al., 1989]. The PC signals generated by DFWM process (response time ~ms) is a result of the saturable absorption process in the dye molecules, whereas, the PC signals, by holographic process (response time ~s) arises due to irreversible photochemical changes in the absorption and/or refractive index in the medium [Tanaka et al., 2002]. Tanaka et al. [2002] reported that the fading of dye chromophore samples leads to the generation of the holographic component, which governs the temporal behavior of the total PC signals. It has been reported in literature that, the photo-induced bleaching process occurring in organic dye-doped systems may be reversible for lower light intensities, but at higher incident intensities, it may result in complete decomposition of dye molecules [Geethakrishnan et al., 2005]. In the present case, for LG-PVA nanocomposite films, the PC signals decrease gradually after attaining a maximum value (figure 8.6). This reduction in the total PC signal intensity may be attributed to the fading of the organic dye chromophore samples [Tanaka et al., 2002]. The gratings formed may have a semi-permanent holographic component, which may become greater when the recording time is prolonged [Keinonen et al., 1997]. The temporal behaviour of the PC signals generated from LG-PVA nanocomposite films suggests contributions from both DFWM and holographic components. The phase conjugation component decays rapidly after the removal of the irradiation, because it originates from the transient population grating formed in the film [Sreedhar and Sirohi, 1993].

8.5 Conclusion

The optical limiting behaviour of IC-PVA and LG-PVA nanocomposite films was investigated using the Z-scan data. Optical limiting curves were plotted from the OA Z-scan data of IC-PVA and LG-PVA nanocomposite films, as these films exhibited reverse saturable absorption behaviour under nanosecond laser light excitation at 532 nm. The values of intensity at which transmission
begin to drop (optical limiting threshold) decreases with concentration of dye content in the nanocomposite films. Since the nanocomposite films exhibited self-defocusing under CW laser light excitation at 632.8 nm and at 442 nm, nonlinear refraction based optical limiting of CW laser light was studied with an aperture limited geometry. The limiting threshold was found to be 10 mW and 13 mW for IC·PVA nanocomposite films with linear transmission 84% and 90%, respectively, for CW laser light excitation at 442 nm (section 8.3). It should be noted that low limiting threshold (~2.5 mW) was obtained for IC·PVA nanocomposite film with linear transmission 77%, under cw laser light excitation at 632.8 nm. Low limiting thresholds of ~4 mW and ~2.4 mW were also obtained for LG·PVA nanocomposite films with linear transmittance 32% and 22%, respectively.

Generation of PC wave from a saturable absorber organic dye-polymer nanocomposite system (LG·PVA) at 632.8 nm was demonstrated using DFWM geometry. The total PC signals were found to have contributions from both DFWM and the holographic components. Moreover, the nanocomposite films were not permanently bleached. The temporal behavior of the PC waves generated from the films indicated that they could be suitable candidates for applications like PC interferometries, involving low power optical phase conjugation.