ABSTRACT

The ability to control molecular structure on atomic and macroscopic dimensions is a key parameter in designing materials with preprogrammed activity, as demanded by the latest technology. A significant advance that took place in the synthesis of such novel materials with new, improved properties and performance is in the case of nanocomposites, where the structural order within the material can be controlled on nanometer/submicron scales. By the combination of functionalized fillers with a polymeric support, composite materials with outstanding properties and applications can be prepared. Polymer matrix nanocomposites (PMNCs) can offer improved mechanical, electrical, optical, thermal, and catalytic properties than those of its each individual components, due to the nano-size effect of the fillers. Organic chromophores with delocalized π-electrons can act as a functional molecule and its incorporation in a solid-state matrix endows the solid material with the chromophore properties if proper control of the microstructure at a nanometric level is achieved. Organic dye-doped polymer nanocomposites have emerged as prospective materials for applications such as optical limiters, organic light emitting diodes (OLEDs), electroluminescent devices, photovoltaic solar cells, polymer based nanodevices etc. and, in recording and storage of information. However, compared to inorganic-polymeric nanocomposites, organic-polymeric nanocomposites have not yet received much attention. Poly(vinyl alcohol) (PVA) is a water soluble, biodegradable, non-toxic and biocompatible polymer, with large scale use in the medical, biomedical and industrial fields and, regarded as a high performance matrix for polymer composites because of its high transparency, good gas barrier property against ambient gases, excellent chemical resistance, and above all, excellent film forming and adhesive properties.

The work presented in the thesis entitled ‘Organic Dye-PVA Nanocomposites for Photonic Applications: Structure, Morphology, Linear and Nonlinear Optical Properties’ focuses on the fabrication and investigation of the structure, morphology, linear as well as nonlinear optical properties of three
novel, PVA based organic dye nanocomposites incorporated into solid films. The nanocomposite films were fabricated by a simple processing technique based on the solution-cast method, with PVA functioning as a template for the nanostructured growth of the dye molecules. The nonlinear optical properties were evaluated at three wavelengths using the Z-scan technique, under excitation with 532 nm Nd:YAG laser pulses and, also with continuous wave (CW) laser light at 442 nm and 632.8 nm to assess the low threshold response. The optical limiting properties and generation of a phase conjugated (PC) wave in the samples were also studied.

This thesis is constituted of nine chapters. Chapter 1 begins with a brief account of polymer matrix nanocomposites (PMNC) and organic-polymeric systems for nonlinear optics (NLO). A review of nonlinear optical materials, important nonlinear optical processes as well as an account of the materials chosen for the present work are also furnished in this chapter. It concludes with a discussion of the motivation for carrying out such a work, the objectives of the study and, a highlight of the present contribution.

The fabrication method of the nanocomposite films and a brief discussion on the characterization tools and techniques employed for the structural, surface morphological and linear optical characterization of the composite films are included in the second chapter. This chapter concludes with a concise discussion of the Z-scan technique and its theory and, other techniques employed for the study.

The results of the investigation of the structure, morphology as well as linear optical properties of the three newly fabricated PVA based organic dye nanocomposites, carried out employing the techniques of X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), optical microscopy, UV-Vis and photoluminescence emission spectroscopy are presented in chapter 3. The samples were characterized as nanocomposites with dye molecules encapsulated between the larger molecules/molecular chains of the polymer host PVA. Structural analysis revealed the occurrence of weak interactions between the dye molecules and PVA chains. These interactions account for the different filler-
induced property enhancements (crystallinity, conductivity, morphological properties, and optical, thermal and chemical stability etc.) exhibited by the nanocomposites.

In chapter 4 the results and discussion of the reverse saturable absorption (RSA) behavior observed in a novel nanocomposite system comprising Indigo Carmine dye and PVA for excitations with nanosecond laser pulses (532 nm) and continuous wave laser light (632.8 nm) are presented. The nonlinear absorption coefficients were evaluated and the effect of varying dye concentrations on the nonlinear absorption behavior has been discussed.

Chapter 5 furnishes an account of the nonlinear absorption behaviour displayed by another new nanocomposite system consisting of Phenol Red dye and PVA under excitation with 532 nm Nd:YAG laser light pulses, and low intensity CW laser light at 442 nm. Z-scan analysis revealed that these composite films can be potential candidates as saturable absorbers for applications in the low threshold (CW) as well as in the nanosecond regime.

In chapter 6, the results of the investigation of the nonlinear absorption exhibited by yet another new organic-polymer nanocomposite system (Light Green dye·PVA) under excitation with nanosecond laser pulses at 532 nm and CW laser light at 632.8 nm are presented. The results imply that with proper choice of filler concentration and excitation wavelengths the NLO properties of the composite films can be fine-tuned for a specific purpose.

The nonlinear refraction studies performed with the three new PVA nanocomposites, under CW laser illumination at 442 nm and 632.8 nm, employing the closed aperture (CA) Z-scan technique are furnished in chapter 7. The negative refractive nonlinearities (defocusing) displayed by the samples were analyzed and evaluated on the basis of thermal nonlinearity.

The optical limiting properties of the novel PVA based nanocomposite films (IC·PVA, PR·PVA and LG·PVA), and their possible applications are discussed in Chapter 8. The generation of a phase conjugated (PC) wave in Light Green·PVA nanocomposite films which exhibited saturable absorption behaviour is also discussed in this chapter.
Chapter 9 summarizes the conclusions and inference drawn from the studies. Perspectives for the future work is also presented at the end of the chapter.

The study presented here, which features the first ever report of the fabrication and determination of NLO parameters of the three new, cost-effective, organic-polymeric nanocomposites, certainly establishes the role of these low-cost organic-polymeric nanocomposites as a promising NLO medium for both low power as well as high power applications. It reveals the tremendous scope for utilizing these novel nanocomposites, all of which exhibited nonlinear absorption and nonlinear refraction behaviour, for applications in optical limiting, pulse shaping, optical data storage, optical switching etc. This study also places emphasis on understanding structure-property relationships in order to design and develop further better materials. These organic-polymeric multifunctional nanocomposites, containing very small wt % of the organic dyes in PVA, satisfy most of the technical requirements such as excellent surface homogeneity, high laser damage threshold, environmental stability, good photostability etc., for industrially applicable NLO materials, and can definitely be of significant use for applications in various photonic devices as well as in biological and medical fields, as already pointed out.