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Nonlinear optical studies of inorganic nanoparticles–polymer nanocomposite coatings fabricated by electron beam curing

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ABSTRACT

The optical nonlinearity of metal nanoparticles in dielectrics is of special interest because of their high polarizability and ultrafast response that can be utilized in potential device applications. In this study nanocomposite thin films containing in situ generated Ag nanoparticles dispersed in an aliphatic urethane acrylate (AUA) matrix were synthesized using electron beam curing technique, in presence of an optimized concentration of diluent Trimethylolpropanetriacrylate (TMPTA). The metal nanocomposite films were characterized using UV–visible spectrophotometry, transmission electron microscope (TEM) and field emission scanning electron microscope (FE-SEM) techniques. Ag nanoparticle impregnated films demonstrated an absorption peak at ~420 nm whose intensity increased with increase in the Ag concentration. The optical limiting property of the coatings was tested using a nanosecond Nd-YAG laser operated at third harmonic wavelength of 355 nm. For a 25 ns pulse and 10 Hz cycle, Ag-polymer coatings showed good optical limiting property and the threshold fluence for optical limiting was found to be ~3.8×10^{-2} J/cm^2 while the transmission decreased to 82%. The nonlinear optical coefficients were also determined using the standard Z-scan technique with picosecond (~2 ps, 1 kHz) and femtosecond (~150 fs, 100 MHz) pulses. Open aperture Z-scan data clearly suggested two-photon absorption as the dominant nonlinear absorption mechanism. Our detailed studies suggest these composites are potential candidates for optical limiting applications.

1. Introduction

The use of high power lasers operating over a wide range of wavelengths and pulse durations has become widespread in recent years. This increase in the applications of lasers has led to a simultaneous growth in the need for optical limiters, which are indispensable in the context of protection of optical components and the human eye from laser-induced damages. An ideal optical limiter is defined as a device which exhibits appreciable linear transmission below a threshold input fluence and a constant transmission above it [1]. Therefore, over the years numerous materials have been discovered and developed for use as optical limiters. These include materials such as phthalocyanines, porphyrins, fullerenes, carbon nanotubes, organic dyes, metal nanoclusters, etc. [2–7]. Metal nanoparticles and nanocomposites have, in recent years, received significant attention owing to their unique nonlinear optical (NLO) properties, such as two-photon absorption (TPA), saturable absorption (SA), reverse saturable absorption (RSA), and self-focusing/defocusing arising from nonlinear refraction [8–14]. These NLO properties find application in the design and development of many photonics based devices for optical switching and optical signal processing of information at an enhanced speed compared to electronic counterparts. Materials with ultrafast time response (ideally in the sub-picosecond regime), strong nonlinearity (high value of nonlinear refractive index for optical switching applications and high value of nonlinear absorption for optical limiting and Q-switching kind of applications) combined with high resistance to bulk and surface laser damage are the key requirements for implementation of such high end applications. Therefore, detailed studies of novel materials are essential wherein the effects of pulse duration, wavelength, etc. should be thoroughly investigated. In this regard metal nanoparticles dispersed in polymer matrices have resulted in the development of a new class of materials viz. polymer–metal

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nanocomposites which combine the properties of both the inorganic and polymer components thereby yielding enhanced or completely new properties [15]. The polymer matrix provides the platform for maintaining the size, shape and dispersion of the metal nanoparticles – parameters which play a vital role in deciding the properties exhibited by the particles. The NLO properties of nanocomposites containing metal nanoparticle fillers arise from the dependence of their refractive index and nonlinear absorption on incident light intensity. Significant enhancement of the NLO response in such nanocomposite materials is often associated with the optical excitation of surface plasmon resonances (SPR) which are collective electromagnetic modes and strongly dependent on the overall morphology of the system [16]. Therefore, such nanoparticles embedded polymer nanocomposites can be effectively applied in novel integrated optoelectronic devices.

Although metal nanoparticle–polymer composites have been conventionally fabricated by mixing preformed nanoparticles with the polymer in solution and casting the composite films (ex-situ), this method puts severe limitations on the homogeneous dispersion of the metal nanoparticles. Therefore, in recent years focus has been shifted to the in situ generation of metal nanoparticles in the polymer matrices [17,18]. One of the methods which has ascended to the fore front in the process is the radiation induced synthesis of polymer nanocomposites. Compared to conventional techniques, the major advantages of using high energy electron beam or gamma irradiation for simultaneous reduction and polymer curing are that they offer a pollution-free work environment, high efficiency and throughput, long service life, uniform cross-linking degree, and excellent heat-resistance and cold-resistance properties. The variation of parameters such as radiation dose, dose rate and metal/polymer ratio facilitates control over the size and dispersion of the metal nanoparticles as well as the overall properties of the nanocomposite material. In this work, we report the fabrication of flexible silver nanoparticles–polyurethane acrylate based polymer nanocomposite films (PNCs) via electron beam irradiation route in an attempt to introduce optical limiting properties in the radiation cured polymer coating films. Aliphatic urethane acrylate was used as the matrix owing to its unique properties, including excellent abrasion resistance, flexibility, hardness, chemical resistance, solvent resistance, and light stability [19]. The PNC samples were tested for their optical limiting properties using an Nd-YAG laser operating at third harmonic wavelength of 355 nm with 25 ns pulse duration and 10 Hz repetition rate. Furthermore, the NLO coefficients of these films were extracted from the standard Z-scan experiments achieved with both picosecond (~2 ps, 1 kHz, 800 nm) and femtosecond (~150 fs, 100 MHz, 800 nm) pulses [20]. Both open aperture and closed aperture data were recorded for retrieving the real and imaginary parts of the third order NLO susceptibility, $\chi^{(3)}$. We have attempted to correlate the obtained NLO results and coefficients in terms of the Ag doping concentration. In both the cases, we observed strong NLO coefficients from the Z-scan data indicating the potential of such nanocomposite system in photonic applications.

2. Experimental

2.1. Materials

Silver nitrate (> 99% purity), Thiophene and Trimethylolpropanetriacrylate (TMPTA) were procured from Sigma Aldrich. Aliphatic urethane acrylate (AUA, Cognis) and Montmorillonite Clay (Cloisite 30B, Southern Clay) were used as received.

2.2. Sample preparation

Different concentrations (w/v) of the precursor ion (Ag^+) solution were added to an optimized mixture of AUA and TMPTA. To achieve uniform dispersion of the filler in the oligomer matrix, each of the samples was subjected to probe ultrasonication (400 W) for 1 h. The formulations obtained were coated onto glass substrates and subjected to electron beam (EB) irradiation technique at ILU6, Vashi, BARC, operated at 2 MeV with power output of 20 kW for a total absorbed dose of 200 kGy to obtain non-tacky, homogeneous thin films. The thickness of the EB cured coatings was found to be ~100 μm as estimated by a thickness gauge 'coat measure M12' (Yuyutsu, Japan).

2.3. UV–visible spectroscopy

The UV–visible absorption spectra were recorded on a UV–visible spectrophotometer (Evolution 300, Thermoelectron, UK) in the wavelength region of 250–800 nm with resolution of 1 nm. The samples were cut into small rectangular sheets, fixed vertically into the sample holder and analyzed in the absorbance mode with a control polymer film of identical dimension as the sample.

2.4. Transmission electron microscopy (TEM)

Transmission Electron Microscopy (TEM) studies were performed on an energy filtering transmission electron microscope (EF-TEM, LIBRA 120, Carl Zeiss) with an accelerating voltage of 120 kV in order to determine the shape and size of the nanofillers. Prior to analysis, the samples were cut into thin sections using an ultramichrotome and placed on the Cu TEM grids.

2.5. Scanning electron microscopy (SEM)

The bulk morphologies of the EB radiation cured polymer coatings were investigated by SEM analysis using field emission scanning electron microscope (JEOL JSM7600) at acceleration voltages of 0.6 kV using a secondary electron detector. The sample cross-sections were pasted onto a conducing surface using silver paste and coated with gold in ion sputter coater, before recording the SEM image.

2.6. NLO Studies

The optical limiting studies were carried out using an Nd-YAG laser operated at third harmonic wavelength of 355 nm (25 ns, 10 Hz) as the excitation source. Samples were mounted on a metal frame and the laser beam focused at the center of the sample for pre-determined time intervals at different incident laser powers till complete burn out of the samples was observed.

The complete experimental details of ps Z-scan were reported elsewhere [21–30]. Briefly, ~2 ps pulses were generated from a regenerative amplifier (Coherent, Legend) seeded by an oscillator (Coherent, Micra). The amplifier was operated at 1 kHz repetition rate and 800 nm and the peak intensities used typically were 16–32 GW/cm^2. The lower peak intensities of the samples were taken into account for the analysis of closed aperture data. A beam diameter of ~3 mm was focused using 20 cm focal length plano-convex lens into the sample. The estimated Rayleigh range calculated was $\sim 3.4 \pm 0.4$ mm. In the fs Z-scan [23,25] ~150 fs pulses with 80 MHz repetition rate were delivered from a tunable oscillator (Chameleon, Coherent), operated at central wavelength 800 nm. An input beam diameter of ~3 mm and plano convex lens (focal length 10 cm) were used to focus on to the sample. The coresponding Rayleigh range was calculated to be 1.4 ± 0.2 mm. A set of neutral density filters were used to attenuate the input