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Synthesis of nanocomposites based on carbon nanotube/smart copolymer with nonlinear optical properties

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ABSTRACT

In this study new nanocompoites based on polyglycidylmethacrylate grafted 4-[(4-methoxyphenyl) diazenyl] phenol (Azo-PGMA) and Carboxylicacid functionalized multi-walled carbon nanotubes (MWCNT-COOH) were prepared. The nanocomposites structure was characterized by FT-IR, TGA and SEM. The Z-scan technique was applied for measuring the nonlinear parameters of nanocomposites. The samples after solving in AWM solution (equal ratio of acetone, deionized water and methanol) were investigated by using closed aperture Z-scan technique and a diode-pumped laser at the line 532 nm. All the nonlinear refractive index of the samples at three concentrations of carbon nanotubes in three different intensities of the laser beam were investigated and the nonlinear optical response of them are compared under the same condition. Because of high order of nonlinear refractive coefficient and good nonlinearity, these compounds are suitable candidate for optical switching, optical limiting and electro-optical devices.

1. Introduction

For decades a great attention has been paid to the organization of material properties using external stimuli such as pH, electricity, light and temperature [1,2]. Significantly, photosensitive polymers can exhibit significant changes in their optical properties when exposed to laser irradiation [3,4]. Typical photosensitive moieties are spiropyran, azobenzene, triphenyl methane derivatives, and cinnamoyl groups. Push–pull azobenzene based chromophore is a photo-addressable moiety capable of being incorporated into polymer matrices. It is well established that light irradiation can transform azobenzene and its derivatives from trans to cis isomer, and less stable cis isomer spontaneously relaxes back to the trans isomer in dark [5–7]. The ratio of cis and trans isomers depends on the light intensity, the reaction rates of different isomerization reactions, the quantum yields of photochemical cis–trans and trans–cis isomerizations and also on the extinction coefficients of the respective isomers at the irradiation wavelength [8,9].

Recently, nanoscale bolstering fillers for creating polymeric nanocomposite materials, due to their controllable chemical, physical and electronic properties are favorite issue for scientists [10–12]. In polymer nanocomposites (PNCs), polymers both stabilize the nano fillers and modify nano filler surfaces by passivating the dangling bonds and defect states. Also, polymer chains serve as linkers and help obtain the extended framework of nano fillers in the polymer matrix [13,14]. Various methods have been reported for producing nano particle/polymer composites. Two major synthesis methods are as (1) in-situ technique: the NPs are fabricated in the presence of polymer and (2) ex-situ technique: dispersion of separately fabricated NPs are into the polymer matrix. Ex-situ technique is preferred over in-situ technique since it provides the possibility of controlling the amount of nanoparticle loading in the polymer matrix [15]. Carbon nanotubes (CNTs) possess unique mechanical, electrical, and optical properties, therefore they have been considered as the nanofiller of choice in numerous composites. The CNT nanocomposites have extraordinary properties compared to their neat matrix materials and are applicable in one-dimensional quantum wires, nano transistors, optical switchers, and other electronic components [16,17]. Multi-walled carbon nanotubes (MWNTs) are used due to their lower price compared to single walled carbon nanotubes.

Investigating nano fillers such as carbon nanotubes, nanoparticles, quantum dots, etc. embedded into the polymer matrices

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have attracted significant attention because of their nonlinear optical susceptibilities [18]. There are many materials with nonlinear optical properties, including inorganic and organic materials [19,20], conjugated polymers [21] and composite thin films [22] that are studied by continous wave [22,23] or pulsed lasers [24,25]. The azobanzene containing polymers have many applications such as optical data storage, holographic memories, waveguide switches, photonics, electroptics and optical limiters because of their special properties at processability and low dielectric constants. Among the organic NLO molecules, polymer -MWCNTs are more important due to existing delocalization of the π-electronic clouds [22]. Furthermore reversible photoisomerization of azobanzene allows to change reversibly molecular properties such as absorbance, dipole moment, polarity, geometric shape, and finally to control their macroscopic properties. These compounds have significant optical and nonlinear optical (NLO) properties in resonant and non resonant interaction of laser light including nonlinear refractive index, anisotropic response by absorbing laser light, second harmonic generation, and electro optics in transparent region of the spectrum. They have been most frequently either grafted into the polymeric matrix or incorporated as a guest in the polymeric matrix. However, because of thermal motion of the polymer chains, the ordered state of NLO active molecules induced by the electric field poling process would normally decay to an equilibrium isotropic state [26,27]. Different approaches such as an interpenetration polymer network method, the incorporation of the chromophore into the polymer backbone (a main-chain or embedded side-chain system), and a cross-linking method have been used to suppress the relaxation of NLO chromophores resulting from the motion of polymer chains. Because the latter methods have relatively lower glass transition temperature, the use of embedded side-chain polymers has been chosen as the best NLO matrix method for stabilizing poled chromophores and retaining thermal stability of the polyimide backbone [27,28].

There are many practical methods for measuring the nonlinear parameters of nanocomposites based on photosensitive polymers and the MWCNT such as degenerate four-wave mixing [29], ellipse rotation [30], beam-distortion [31], Z-scan technique and etc. Except of Z-scan technique that present by Sheik-Bahae and et al. for the first time in 1989 [32], other techniques require complex experimental setups and low sensitivity. High accuracy and simplicity and ability in determining the sign of optical nonlinearity from a single experiment are the advantages of this technique and the nonlinear refraction (NLR) of PNC/MWCNT compounds can be analyzed perfectly.

In this paper firstly the PGMA and Azo-PGMA were synthesized according to our previous work [33]. After that nanocompoites based on Azo-PGMA and MWCNT-COOH were prepared. The Z-scan technique was applied for measuring the nonlinear parameters of nanocomposites. Also the nonlinear refractive index of the samples at three concentrations of carbon nanotubes in three different intensities of the laser beam were investigated and the nonlinear optical response of them are compared under the same condition.

2. Experimental

2.1. Material

4-Methoxybenzeneamine was purchased from Sigma-aldrich and used without further purification. Glycidylmethacrylate (GMA) (Sigma-Aldrich) was distilled before use. Benzoyl peroxide (BPO) (Fluka) was purified by recrystalization from methanol. Tetrahydrofuran (THF) was purchased from Merck and dried before use. 4-Hydroxy-4'-methoxy-azobenzene, Polyglycidylmethacrylate and polyglycidylmethacrylate grafted 4-[(4-methoxyphenyl) diazenyl] phenol (Azo-PGMA) were prepared according to our previous work [26]. Carboxylicacid functionalized multi-walled carbon nanotubes (MWCNT COOH) were used as received from Sigma-Aldrich. Other reagents such as phenol, NaOH, sodium nitrite, acetone, N, N-dimethylformamide (DMF) and methanol were purchased from Merck and were used without further purification.

2.2. Instruments and measurements

IR spectra were measured with a Fourier transform infrared spectrophotometer (Nexus-670, Thermo Nicolet, USA). ^{1}HNMR spectra were recorded on a BRUKER 300 MHz spectrometer at room temperature with DMSO-d_6 as solvent and TMS as internal standard. UV–vis spectra were recorded with a UV–vis spectrophotometer (PGI-T60, UK). Dilute solution of Azo- PGMA in a mixture of three solvents, acetone, deionized water and methanol, with equal ratio (AWM solution) was prepared for measuringits photosensitivity under the irradiation of a UV lamp (8 W, $\lambda = 365$ nm). A sonicator (CPX 600, 20 kHz, 600 W, Cole-parmer instrument, USA) was used for in the preparation of the nanocomposite. A differential scanning calorimeter (DCS, Mettler 822) was used to determine phase transition temperatures at the heating and cooling rates of 10 °C/min. Temperature and heat flow were calibrated using benzoic acid and indium. Thermogravimetric analysis (TGA) was performed on a TGA-SDVA 851 instrument at a heating rate of 10 °C/min under air atmosphere. The morphology of the as-prepared nanocomposites was analyzed with a Scanning Electron Microscopy (SEM-3200). The normalized transmittance as a function of sample's place was recorded on a continuous wave Nd: YAG laser at 532 nm.

2.3. Preparation of nanocomposites

The Azo-PGMA (0.01 g) was dissolved in the AWM solution (15 ml, same ratio of Acetone, deionized water and methanol). Then the MWCNTs COOH (0.0001 g. 1% w/wAzo-PGMA) was added to above solution with constant stirring. Then the mixture was ultrasonicated (600 w probe sonicator) for 4 h along with magnetic stirring at room temperature. Finally the solution was evaporated to achieve powder form of nanocomposite. The same procedure was repeated for preparation of 2% and 5% w/w MWCNTs COOH to Azo-PGMA nanocomposites.

3. Results and discussion

3.1. Synthesis and characterization of Azo-PGMA/MWCNT COOH nanocomposites

For preparation of nanocomposites, the Azo-PGMA was dissolved in the AWM solution. Then 1%, 2% and 5% w/w MWCNTs COOH was added to the Azo-PGMA solution respectively with constant stirring. The mixture was ultrasonicated with a 600w probe sonicator for 4 h along with constant magnetic stirring at room temperature. To achieve nanocomposites in powder form the suspensions were heated to evaporate the solvent completely.

The FT-IR spectrum of functionalized carbon nanotubes (MWCNT-COOH), the Azo-PGMA and prepared nanocomposites are depicted in Fig. 1.

In Fig. 1a the broad and sharp peak at 3434 cm^{-1} is related to the stretching vibrations of the –OH groups in the carboxylic acid moieties of carbon nanotubes. The sharp peaks at 2924 and 2854 cm^{-1} are associated with symmetric and asymmetric vibrations of the aliphatic –CH groups on the repeated carbon nanotube walls. The band at 1739 cm^{-1} is associated with carbonyl of carboxylic acid groups by resonance between conjugated C=C in