



Nonlinear optical properties of some polymer/multi-walled carbon nanotube composites

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Abstract

Several polymer-coated and polymer-grafted multi-walled carbon nanotubes (MWNTs) were synthesized and characterized using TEM and HRTEM. The polymer-coated or polymer-grafted MWNTs formed stable solutions in DMF. Their nonlinear optical properties were investigated using 532 nm nanosecond laser pulses. These polymer–MWNT composites still possess strong nonlinear optical properties. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Carbon nanotubes have attracted considerable attention because of their unique physical properties and many potential applications [1–4]. Our previous investigations [5,6] showed that multi-walled carbon nanotubes (MWNTs) possess optical-limiting properties with a broadband response covering the visible to infrared region. The limiting action was also observed for single-walled carbon nanotubes (SWNTs) [7]. Such nonlinear optical (NLO) effects have potential applications in the protection of optical sensors from high-intensity laser beams. It should be noted that the above observations were made on carbon nanotubes suspended in liquids due to their

poor solubility in most solvents, and such suspensions were unstable at high concentrations. Hence it is highly desirable to obtain stable solutions containing carbon nanotubes.

Polymers are attractive materials since they can be easily processed and fabricated into solid-state forms such as thin films [8] which are often required in most applications. Composites that contain both carbon nanotubes and polymers have been the subject of several studies due to their better solubility in many organic solvents [9–11]. Tang and Xu reported the preparation of carbon-nanotube-containing poly(phenylacetylenes) (PPAs) by in-situ polymerization of phenylacetylene in the presence of carbon nanotubes [11]. Recent studies showed that only special polymers like poly(*p*-phenylenevinylene-*co*-2,5-dioctoxy-*m*-phenylenevinylene) (PmPV) can ‘trap’ the nanotubes from their mixtures with nanoparticles [9,10]. Here we present two methods to obtain stable solutions containing both MWNTs and

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commercially available polymers. The NLO responses of various polymer–MWNT solutions are compared.

2. Experimental

2.1. Materials

Poly(ethylene glycol) (PEG, MW = 1000) was obtained from Merck. Poly(2-vinylpyridine) (P2VP), poly(4-vinylpyridine) (P4VP) and poly(4-vinylphenol) (PVPPh) were obtained from Scientific Polymer Products. These polymers were used without further purification. Poly(ethylene oxide) (PEO, MW = 4600) was obtained from Aldrich Chemical and dried in vacuo at 50°C before use. MWNTs were synthesized using the arc-discharge method. Thionyl chloride (Merck) was used without further purification. Dimethylformamide (DMF) and benzene were refluxed for 2 h over CaH₂ and then distilled under nitrogen. Triethylamine (Fluka) was dried using sodium hydroxide pellets.

2.2. Method 1: synthesis of polymer-coated MWNTs

PEG, P2VP, P4VP and PVPPh were dissolved in DMF separately. The MWNTs were added to the polymer solutions and then sonicated for 1 h. The suspensions were filtered using a Millipore nylon membrane with a pore size of 0.45 μm. The filtrates were deep grayish solutions and remained stable after several months. A drop of each solution was used in HRTEM measurements (Philips CM300). Each solution was evaporated on a hot-plate and the resulting thin film was ground to a powder. The powder was fixed in a poly(methyl methacrylate) matrix which was then cut using an ultrathin tom. The ultrathin films were used for TEM measurements (Philips CM100). The NLO measurements were made directly on polymer solutions.

2.3. Method 2: synthesis of polymer-grafted MWNTs

MWNTs (54 mg), SOCl₂ (15 ml) and benzene (15 ml) were mixed together and refluxed for 5 days under nitrogen. After the reaction, the solvent was distilled out and the resulting MWNT–COCl were dried in vacuum for 4 h at 90°C. MWNT–COCl (20

mg), triethylamine (1 ml) and PEO (5 g) were then charged into a flask and stirred at 140°C under nitrogen for 2 days. The mixture was then poured into DMF to wash out free PEO molecules. The remaining MWNTs in DMF were centrifuged. The light-gray solution was used in the NLO experiment.

Our MWNT samples contain hydroxyl and carboxyl groups on their surface because of the use of a mixed acid (H₂SO₄ + HNO₃) during the purification process [12]. The carboxyl groups can be transformed to acid chloride groups by thionyl chloride [13]. PEO can then be grafted to the MWNT samples by reacting the terminal hydroxyl groups of PEO and the acid chloride groups.

2.4. Nonlinear optical (NLO) measurements

The polymer/MWNT solutions in DMF were contained in 1 cm thick quartz cells. For comparison, the suspension of MWNTs in DMF was also measured under the same condition. The concentrations of all the samples were adjusted so that their linear transmittances are ~ 50%. Their NLO responses were measured with linearly polarized 7 ns optical pulses from a Q-switched frequency-doubled Nd:YAG laser. The spatial distribution of the pulses was nearly Gaussian after passing through a spatial filter. The laser was operated at single shots so that the response of the sample to each pulse was monitored. The pulse was divided by a beam splitter into two parts. The reflected part was taken as the reference representing the incident light energy and the transmitted beam was focused through the sample. Both the incident and transmitted pulse energies were measured simultaneously by two energy detectors (Laser Precision RjP-735). The sample was mounted on a translation stage, which was controlled by a computer to adjust the sample's position along the Z-axis with respect to the focal point. By keeping the incident laser energy constant, the light transmission through the sample was measured with respect to the sample Z-position, with (and without) an aperture (transmittance, $S = 0.5$) placed in front of the transmission detector. The minimum beam waist of the focused laser beam was (30 ± 5) μm, measured by the standard Z-scan method [14]. The optical limiting measurements were conducted with the sample fixed at the focus.

3. Results and discussion

The ultrathin films of the PVPh–MWNT composites made by the first method were examined by TEM. The MWNTs still retain their straight tubular morphology in the composites. However, the MWNTs in these samples are shorter than the ordinary tubes. The average diameters (D), lengths (L) and the L/D ratios of the PVPh–MWNT composites in the TEM images are listed in Table 1.

The L/D ratios of these PVPh-coated MWNTs are around 20–40, which are significantly smaller than the typical carbon nanotubes' aspect ratio of around 100–1000. This result is in agreement with an earlier study by Liu et al. [15], who showed that strong sonication could chop a SWNT thread into shorter pipes and these pipes could be soluble in some organic solvents. Therefore, shorter carbon nanotubes are more readily soluble in solvents or form polymer composites.

The same PVPh–MWNT sample was characterized by HRTEM. The HRTEM image in Fig. 1 shows a typical tube coated by PVPh. The tube was completely covered by PVPh with a thickness of ~ 2 –3 nm. Tang and Xu [11] showed a similar image of PPA-wrapped MWNTs. They considered that these tubes were chemically linked to the polymer. The initiators adsorbed on the surface of carbon nanotubes led to the polymerization of monomer molecules. The polymer chains could then wrap the whole MWNT. In our case, the mechanism of wrapping is different. We believe that sonication is effective in dispersion because the collapses of cavitation of bubbles in ultrasonication produce microscopic domains of high temperature [16]. This effect is very

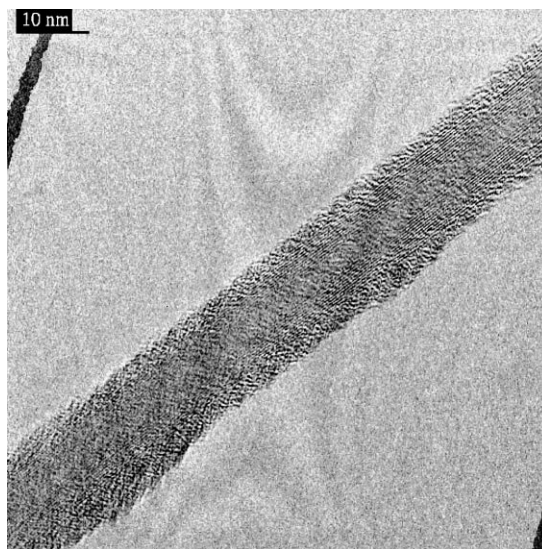


Fig. 1. A HRTEM image of a PVPh-coated multi-walled carbon nanotube.

similar to a new purification method, the hydrothermally initiated dynamic extraction (HIDE), reported by Tohji et al. [17]. The water molecules break the network between SWNTs, amorphous carbon and metal particles, contributing to the overall performance of the purification process. In sonication, solvent molecules also attack the surface of the MWNT threads and break the network between MWNTs and other nanoparticles, thus helping PEO or other polymer molecules penetrate into the MWNT threads to form a coating on the surface of the tube. After being wrapped by polymer chains, these MWNTs become a microdomain that could easily be dispersed in the solvent of the polymer.

To assess the potential application of these polymer/MWNT composites, NLO measurements were made. Fig. 2 displays the Z-scan results of a MWNT–DMF suspension at peak irradiances of 50, 165, and 840 MW cm⁻². The filled circles are the Z-scan data measured without the aperture, and the open circles are the results obtained from dividing the Z-scan measured with the aperture by the Z-scan measured without the aperture. The data in Fig. 2a and b are vertically shifted for presentation. All the DMF solutions of the polymer/MWNT composites still possess similar NLO effects in the Z-scan measurements. The Z-scan data of PEO/MWNT (pre-

Table 1

The average diameters (D), lengths (L) and the L/D ratios of the PVPh-coated MWNTs

D (nm)	L (nm)	L/D
24	340	14.2
23	652	28.3
7	240	34.3
17	470	27.6
15	413	27.5
10	380	38.0

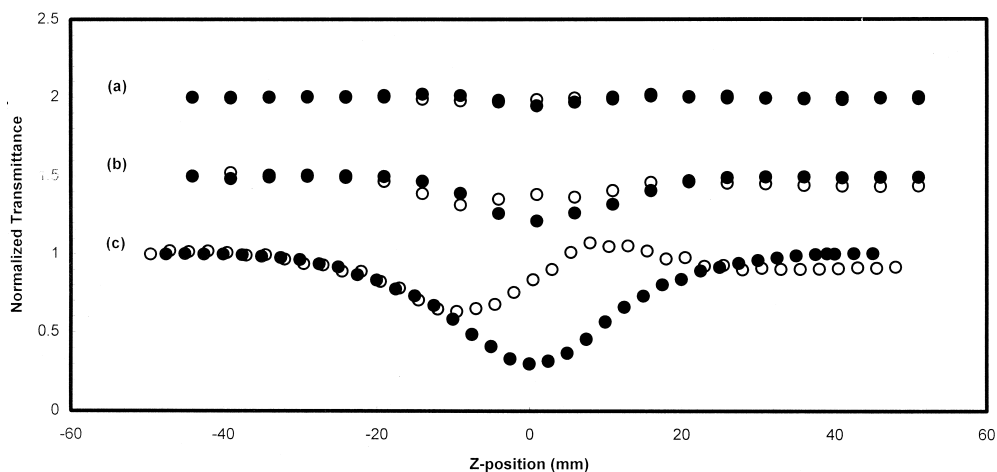


Fig. 2. Z-scan measurements on the MWNT–DMF suspension at peak irradiances of: (a) 50 MW cm^{-2} ; (b) 165 MW cm^{-2} ; and (c) 840 MW cm^{-2} , by using the 7 ns, 532 nm laser pulses. The filled circles are measured without the aperture. The open circles are those obtained from dividing the data measured with the aperture by the data measured without the aperture. The data in (a) and (b) are vertically shifted for presentation.

pared by method 1) in DMF, measured at a peak irradiance of 840 MW cm^{-2} , are shown in Fig. 3 as an example. The effective nonlinear refractive index and nonlinear absorption coefficient are $\sim 1.2 \times 10^{-17} \text{ m}^2 \text{ W}^{-1}$ and $\sim 2.1 \times 10^{-10} \text{ mW}^{-1}$, respectively. This indicates that the coating of polymer does not alter the NLO properties of the MWNTs. The effective refractive nonlinearity in all the samples has a positive sign, which can result in self-

focusing and hence can be exploited to enhance the limiting effectiveness.

The measurements of optical limiting effects in the DMF solutions of various polymer/MWNT composites are depicted in Fig. 4. It is obvious that the PEO/MWNT composites prepared by the two methods both behave similarly and their behavior is also similar to that of the MWNT–DMF suspension as shown in Fig. 4a. The limiting threshold is de-

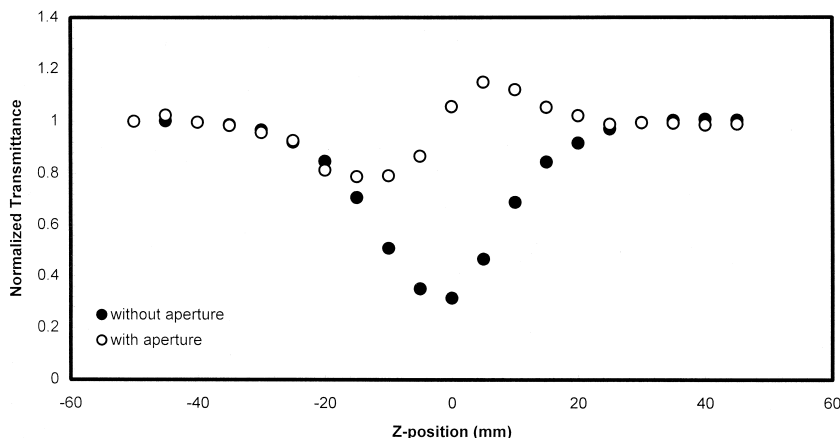


Fig. 3. Z scans conducted on PEO/MWNT composite (prepared by method 1) dissolved in DMF solution at a peak irradiance of 840 MW cm^{-2} . The filled circles are the data measured without the aperture. The open circles are those obtained from dividing the data measured with the aperture by the data measured without the aperture.

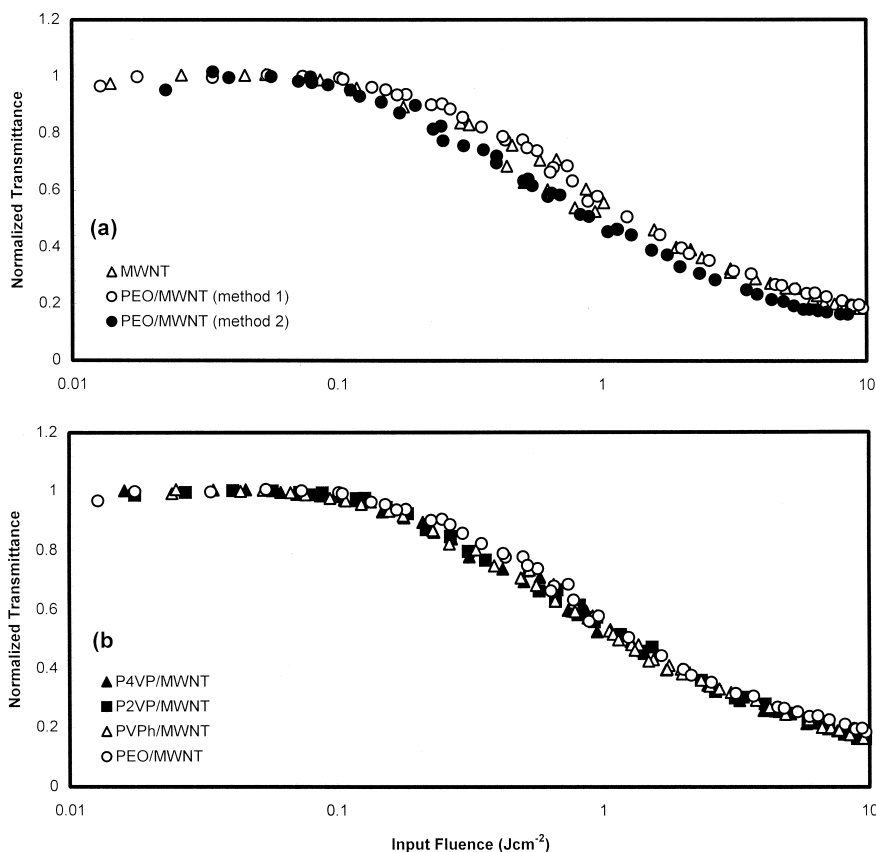


Fig. 4. Optical limiting responses of: (a) MWNT–DMF suspension (open triangles) and DMF solutions of PEO/MWNT composites (method 1, open circles; method 2, filled circles); and (b) P4VP/MWNT, P2VP/MWNT, PVPh/MWNT, PEO/MWNT (method 1) composites, measured with 7 ns, 532 nm laser pulses.

defined as the input fluence at which the transmittance falls to 50% of the linear transmittance. The limiting thresholds of the samples are all $\sim 1 \text{ J cm}^{-2}$. Since there is no optical limiting effect in the polymer–DMF solutions, the optical limiting effects are induced by the components of carbon nanotubes in the composites, showing again that the polymer does not change the NLO properties of MWNTs.

The NLO properties of the PEO–MWNT composites prepared by the two methods are nearly identical. It should be noted that the first method is simpler than the second grafting method or the other reported methods [9–11]. In addition, it is applicable to a variety of commercially available polymers. For demonstration, optical limiting measurements were also made on the other four different polymer/

MWNT composite solutions prepared by the first method, and the results are displayed in Fig. 4b.

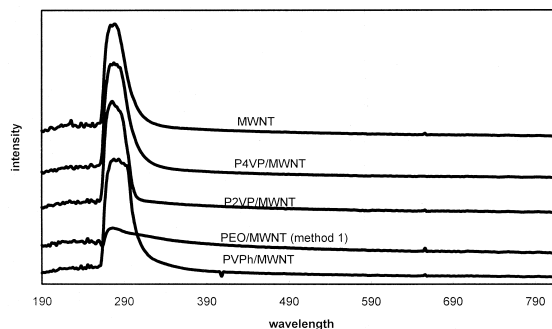


Fig. 5. UV–visible spectra of MWNT suspended in DMF and polymer/MWNT composites dissolved in DMF. The spectra are shifted vertically for clear presentation.

Within experimental errors, there are no significant differences among these measurements. The limiting thresholds of all the composites are also $\sim 1 \text{ J cm}^{-2}$. The results show that a large variety of polymers could be used as the matrix of carbon nanotubes for the limiting application. Fig. 5 shows the UV–visible spectra of the samples. The spectra show a very broad decaying tail covering the entire visible and near-IR region. Considering that MWNT and SWNT are both broadband optical limiters [5–7], the results indicate that these polymer/MWNT composites are also broadband limiters. It is worth noting that the polymer/MWNT solutions are very stable towards air and laser radiation. The optical measurements reported here were conducted over a period of one month, and no differences were observed among these measurements.

4. Conclusions

Two methods were used to prepare polymer–MWNT composites. The first method is simple and can be used with many commercially available polymers. The polymer–MWNT composites possess strong NLO properties, similar to those of MWNT suspension.

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