Appl. Phys. B (2014) 115:401–406
DOI 10.1007/s00340-013-5615-y

Applied Physics B
Lasers and Optics

Optical limiting of high-repetition-rate laser pulses by carbon nanofibers suspended in polydimethylsiloxane

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Received: 2 May 2013 / Accepted: 10 August 2013 / Published online: 22 August 2013

Abstract The optical limiting (OL) behavior of carbon nanofibers (CNFs) in polydimethylsiloxane (PDMS) was studied and compared with that of CNFs in water, and polyhedral multi-shell fullerene-like nanostructures (PMFNs) also in water. It was shown that when switching from single-shot to pulse-periodic regime of laser pulses (10 Hz), the CNF in PDMS suspension retains its OL characteristics, while in the aqueous suspensions, considerable degradation of OL characteristics is observed. It was also observed that a powerful laser pulse causes the CNF in PDMS suspension to become opaque for at least three seconds, while such a pulse brings out a bleaching effect in aqueous PMFN and CNF suspensions. The processes of OL degradation in aqueous suspensions, bleaching and darkening of the studied materials are discussed herein.

1 Introduction

The construction of practical optical limiters is still a challenging problem, which has been engaging researchers in this field for many years. The start of these studies takes us back to the 1980s when the first works were published [1–3]. The qualities required of optical limiters turned out to be extremely demanding, namely the low energy level of the nonlinearity threshold, the high figure of merit and dynamic range, the wide spectral range of performance, colorlessness, high initial transmittance and last but not least, the ability not to downgrade the parameters listed above under pulse-periodic laser irradiation. Diverse classes of materials were tried in order to complete the task, viz solutions of fullerenes [4] and their derivatives, organic chromophores [5, 6], metal-based materials and composites [7], carbon nanoparticles [8, 9] suspended in various liquids [10, 11] and others. Among the mentioned, suspensions of carbon nanoparticles, carbon black particles [12], both single-walled and multi-walled carbon nanotubes [13–16], onion-like carbon (OLC) particles [9], polyhedral multi-shell fullerene-like nanostructures (PMFNs) [17] and others are of particular interest owing to their colorlessness, high photopic transmittance and the ability of broadband [12, 18, 19] optical limiting (OL) in visible and near IR regions. The main and broadly accepted mechanism of optical nonlinearity in such materials is intense light scattering [12, 16, 19, 20] from light-induced micro-plasma and micro-bubbles filled with carbon and host matrix material vapor. The formation rate of these nonhomogeneities is what determines the time delay when the transmittance of the material becomes nonlinear. The authors of [21] showed that the limiting mechanism in carbon black suspension (CBS) can be initiated in a time shorter than 0.2 ns; however, an efficient OL can be realized within pulse lengths of a few nanoseconds. The performance of the optical limiter can be characterized by such parameters as "limiting threshold energy" (E_{th}) and "figure of merit" (FOM). The E_{th} is an incident energy at which the transmittance drops by 50 % of its initial linear value T_L. The FOM is defined [22] as the ratio of linear transmittance to minimum transmittance at high energy T_L/T_{min}; the input energy at which the limiting device suffers damage is what determines T_{min}. As a matter of fact, the nonlinearity in carbon liquid suspensions is fluence dependent [12]; that is

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why to lower E_{th}, the limiters are usually placed in intermediate focal plane of the Kepler telescope. The E_{th} thus usually lies within the range from 10^{-5} to 10^{-6} J. FOM usually has value of about 10^3. These values of E_{th} and FOM are typical for the single-shot mode of the laser irradiation. However, real applications may require optical limiters to supply protection against pulse-periodic laser irradiation. This requirement turned out to be a serious obstacle in the use of the carbon-based liquids. The problem is that under repetitive irradiation, their OL performance degrades significantly. This repetition rate dependence was evidenced in aqueous CBS [12, 21, 23–25], in PMFN aqueous suspension [17], in OLC suspension in *N*,*N*-dimethylformamide [26] and in graphene suspension in water and polyvinyl alcohol [27].

Seeking for materials maintaining their OL characteristics in pulse-periodic regime of laser irradiation, we found CNF suspension in PDMS. In the present paper, we report our observations of optical limiting performance of CNF in PDMS suspension in single-shot and pulse-periodic regime. We compare its performance with the performance of aqueous CNF suspension and aqueous PMFN suspension. Using a pump-probe technique, we show the long-term bleaching of the aqueous suspensions and long-term darkening of the PDMS suspension under the action of a powerful laser pulse. We discuss possible mechanisms of the observed bleaching and darkening of the studied media.

2 Experimental

Our CNFs were synthesized in D. Mendeleev University of Chemical Technology of Russia by catalytic pyrolysis of methane [28]. CNFs are particles with a high length/diameter ratio, in our case, about 300. The prevalent diameter of our CNFs was from 25 to 35 nm and the length of about 1–10 µm. An aqueous suspension of CNFs was prepared as follows: 10 mg of CNFs was added to 10 ml of 0.5 wt%. water–surfactant solution (sodium oleate) and ultra-sonicated for 60 min by a tip sonicator (80 W) and then centrifuged ($3{,}000\times g$, LMC4200R, Biosan) for 30 min. The supernatant (9 ml) was used for further experiments. To prepare a suspension of CNFs in PDMS, we first made a suspension in toluene in accord with the same procedure as in water and then mixed the prepared suspension with PDMS (Sigma-Aldrich) in a ratio 2:1 (PDMS/toluene suspension).

For preparation of PMFN aqueous suspensions, we used commercially available PMFNs trademarked "astralene" [29]. PMFNs are quasi-spherical particles with an average diameter of about 40 nm. More details about their structure can be found in the paper by Shames et al. [30]. To render the suspension stable, we used sodium dodecylbenzene sulfonate (SDBS) as a dispersant. The solid feed material was placed in a vial (4 ml) with an aqueous solution of SDBS (0.01 g of a surfactant per 1 g of water), the net concentration of the added PMFNs being 1 mg/ml. The system was ultra-sonicated (120 W, UP200H, Hielscher) for 60 min. To segregate individual PFMNs from the impurities, their conglomerates and other carbon nanomaterial remaining after ultra-sonication, we employed 40 min of centrifugation (Optima MaxE, Beckman Coulter) at acceleration equal to 30,000 g. We used 3 ml as a supernatant from the overall volume of 4 ml of the centrifuged solution for experiments. The linear transmittance at 532 nm of all suspensions was adjusted to the value of about 50 %. The prepared suspensions were subjected to further optical measurements on the day of their preparation.

Two experimental techniques, viz recording of nonlinear transmittance and pump-probe, were employed for optical measurements. The experimental setup allowing both techniques to work simultaneously is charted in Fig. 1. The Q-switched, frequency-doubled Nd:YAG laser (532 nm, 7 ns) (1) was used as a pumping source in single-shot and pulse-periodic (10 Hz) modes. Pumping radiation (beam diameter 8 mm) was focused into a sample (10) with the help of a concave lens (8) (focal length 40 mm) and then re-collimated by another lens (9) (focal length 40 mm). The sample was a 10-mm fused silica spectrophotometric cell filled with the studied suspension. The system of lenses (8) and (9) and apertures (2) and (11) (both of 8 mm in diameter) provided $1\times$ magnification of the telescopic system and an aperture ratio 1/5. The incident pulse was split by a beam splitter (3) to measure its energy by a detector (4). The incident energy was controlled by neutral density filters (5). The detection of a signal transmitted through the sample was performed by the detector (22) in a 1.6-mrad viewing field, set by the lens (19) (focal length 620 mm) and the aperture (21) (1 mm in diameter). Neutral density filters (20) were used to protect the detector (22) if needed.

The probing beam from the continuous wave He–Ne laser (0.7 W, at 632.8 nm) (7) was deflected and aligned

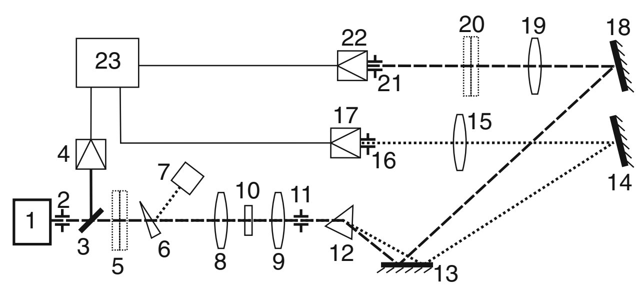

Fig. 1 Experimental setup

co-axially with a pumping beam by the wedge (6). Within the focal point, the diameters of the beams were approximately 30 and 100 µm for the pumping and probing beams, respectively. By means of the prism (12), the pumping and probing beams were separated. Then, the probing beam was detected in the same way as the pumping one, by the detector (17) with a 1.5-mrad viewing field, set by the lens (15) (focal length 250 mm) and the aperture (16) (0.4 mm in diameter). The signals from the detectors were processed in the personal computer (23).

3 Results and discussion

In Fig. 2a, OL behavior in single-shot regime of laser irradiation for three suspensions is presented. The values of E_{th} are 7, 20 and 150 µJ for the aqueous PMFN (line with triangles), the aqueous CNF (line with squares) and the CNF in PDMS (line with circles) suspensions, respectively. FOMs are 1,100, 1,600 and 300 for the aqueous PMFN, the aqueous CNF and the CNF in PDMS suspensions, respectively. The aqueous suspensions of PMFNs and CNFs in the single-shot regime are rather similar in their OL behavior. The suspension of CNFs in PDMS has a weaker OL response, evidently due to the thermodynamic properties of the PDMS. The dependence of OL on the thermodynamic properties of solvents was discussed, among many other articles, in [10]. In pulse-periodic regime, however, the order of things as they occurred in the single-shot regime alters. The results obtained in the pulse-periodic regime at a repetition rate of 10 Hz are shown in Fig. 2b. To obtain the value of transmittance (plotted on the graph) at each energy value, the row of pulses (usually 50–100 pulses) was registered at 10 Hz until the stable value of transmittance was reached. The suspension of the CNF in PDMS (line with circles) retains its single-shot OL parameters (E_{th} and FOM). Meanwhile, E_{th} of aqueous CNF suspension (line with squares) does not change, and its FOM downgrades to the value of 170. The aqueous PMFN suspension (line with triangles) undergoes the most pronounced degradation of OL characteristics, so its E_{th} grows nearly three orders to the value of 3 mJ and its FOM downgrades to the value of 30. The results of OL characteristics obtained in single-shot and pulse-periodic regimes for three suspensions are juxtaposed in Table 1.

The dependence of the nonlinear transmittance of the three studied suspensions on pulse number at a repetition rate of 10 Hz is presented in Fig. 3. The measurements were taken at energy 0.9 mJ at which all three samples behave nonlinearly in single-shot mode.

One can see the growth of nonlinear transmittance from pulse to pulse for the aqueous suspensions of PMFNs and CNFs, which represents the OL degradation. However, it should be noted that the degradation of OL is stronger for the PMFN than for the CNF aqueous suspension. It is also clear that there is no such growth of nonlinear transmittance for the CNF suspension in PDMS. These facts will be discussed further.

The degradation of OL in carbon-based materials is usually attributed to depletion of the suspensions with carbon particles. As proposed and evidenced in the scientific literature, under the action of a powerful laser pulse, the suspended particles in the focal volume heat up to the temperature of about 4,000° K [31]. This temperature increase leads to the vaporization of carbon. As a result, particles diminish in size significantly or atomize [12, 24,

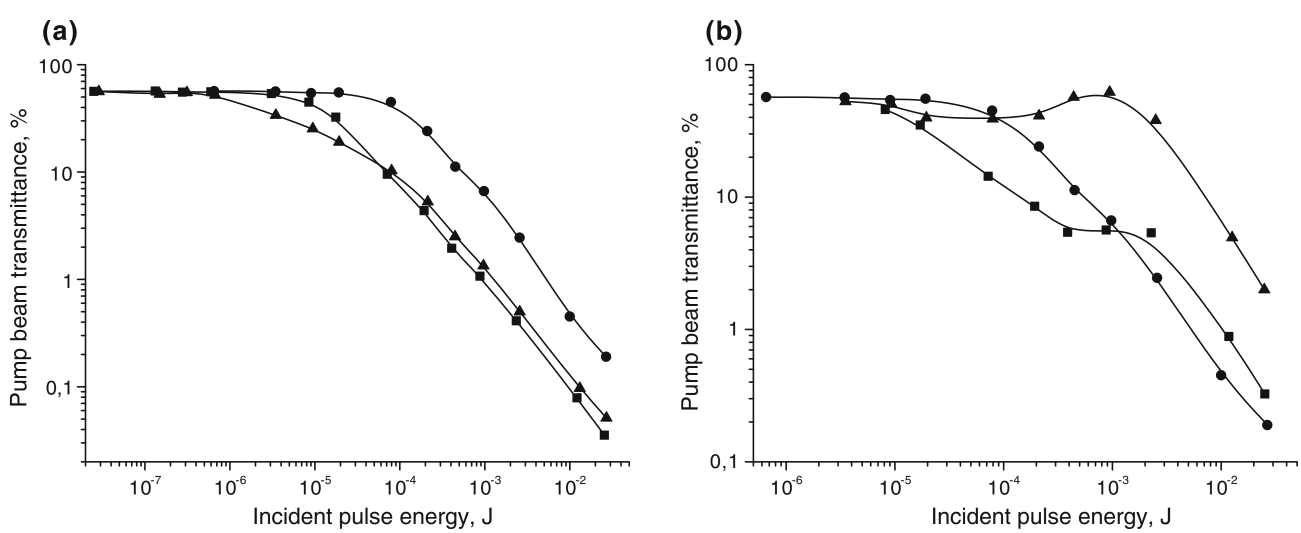

Fig. 2 Nonlinear transmittance of the three suspensions: aqueous PMFN suspension—*line with triangles*; aqueous CNF suspension—*line with squares*; suspension of CNF in PDMS—*line with circles* in single-shot regime of laser irradiation (**a**) and in pulse-periodic regime (at 10 Hz) of laser irradiation (**b**)

Table 1 Obtained OL characteristics

Medium	Rep. rate, Hz	E_{th}, μJ	FOM, times
PMFNs in H_2O	Single-shot	7	1,100
	10	3,000	30
CNFs in H_2O	Single-shot	20	1,600
	10	20	170
CNFs in PDMS	Single-shot	150	300
	10	150	300

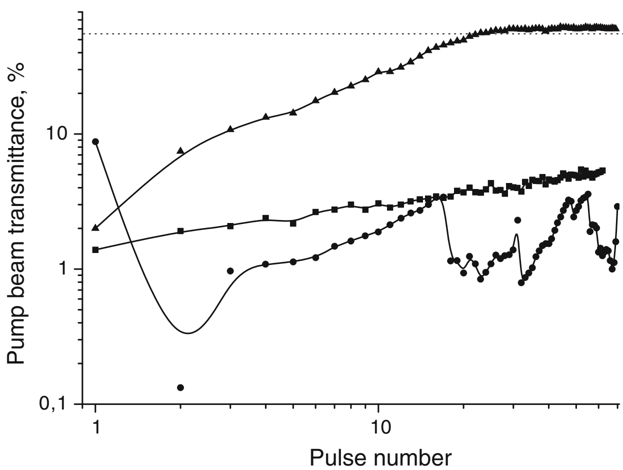

Fig. 3 Pulse number dependence of nonlinear transmittance at an incident energy level of 0.9 mJ and a repetition rate of 10 Hz for three suspensions: aqueous PMFN suspension—*line with triangles*; aqueous CNF suspension—*line with squares*; suspension of CNF in PDMS—*line with circles*. The *dotted line* designates the linear transmittance of the materials

31]. The diminishing particle size leads to the so-called bleaching effect. This bleaching is a transient growth of the linear transmittance of the material to a higher value than its initial value after the action of the powerful laser pulse [17, 26]. After the action of the laser pulse, new particles replace the old ones by diffusion and solvent convection. But the time needed for this process is rather long so that at higher repetition rates, the bleaching effect accumulates and leads to the degradation of OL behavior.

From our point of view, the particle-size-diminishing mechanism of bleaching can be accompanied by the expulsion of particles out of the irradiated volume as well. Local heating leads to a rapid local increase in temperature and pressure, material expansion and generation of an acoustic shock wave [32–35]. While propagating, this wave interacts with suspended particles and transfers part its momentum to them. As the direction of the propagation of the wave is outside the focal volume, the particles are pushed out of the focal and neighboring volume. Although this concept needs to be theoretically and experimentally supported, it does not contradict common sense and even helps in the explanation of the observed differences of bleaching phenomena in aqueous suspensions of PMFNs and CNFs.

By pump-probe technique, we retraced the behavior of the linear transmittance of the three studied suspensions upon the action of the powerful laser pulse; these results are presented in Fig. 4. Zero on the time axis corresponds to the time when a single pumping pulse with an energy level of 0.9 mJ was shot. One can see that bleaching effect was registered in the aqueous suspensions of PMFNs and CNFs (see Fig. 4a) and did not appear in the CNF suspension in PDMS (see Fig. 4b). In Fig. 4a, one can see that after the pumping pulse action, the transmittance, at first, drops for about 10 ms. It happens as the pumping pulse leads to the formation of nonhomogeneities such as microplasma, bubbles and shock waves. All together, these phenomena lead to the observed limiting of the pumping pulse and attenuation of the probe beam. Then, the bleaching phenomena manifest themselves by the growth of the transmittance above its initial value. Here, one can note that the bleaching effect in the PMFN aqueous suspension (solid line) is stronger than in the CNF aqueous suspension (dashed line). This can be due to the difference in particles size and geometry. Firstly, the CNFs are initially bigger particles than the PMFNs, so they need more energy to be destroyed. That is why, when subjected to powerful laser pulse of the same energy, the CNFs would be destroyed less than PMFNs. Secondly, due to the geometry of the particles (PMFNs—quasi-spheres; CNFs—thread-like clusters), the PMFNs will be moved out of the beam path and its vicinity by the generated shock wave more easily and farther than the CNFs.

The behavior of the linear transmittance of the CNF suspension in a viscous PDMS upon the action of the powerful laser pulse (see Fig. 4b) is different. The long-term (seconds) darkening can be seen in the oscillograms for different pumping pulse energy levels. Zelensky et al. [36] studied OL and the bleaching effect in a suspension of carbon particles in epoxy resin. It was evidenced that there is also no bleaching effect in it. The explanation given in [36] seems reasonable: An overheated carbon particle produces stable entities of the pyrolytic products—long-lived bubbles (filled with poorly soluble gases) and carbonized products. As a result, persistent changes in the optical transmittance were observed in epoxy suspensions. As to our observations, after excitation by pumping pulse, the bubble together with a slight darkening of the suspension (carbonized products) was observed by the naked eye. These products were slowly (due to the high viscosity of the PDMS) moving upwards. The bubbles formed are effective light scatterers and the carbonized products bring additional absorption, so we observe a long-term darkening (transmittance loss) of the probe beam. Moreover, these

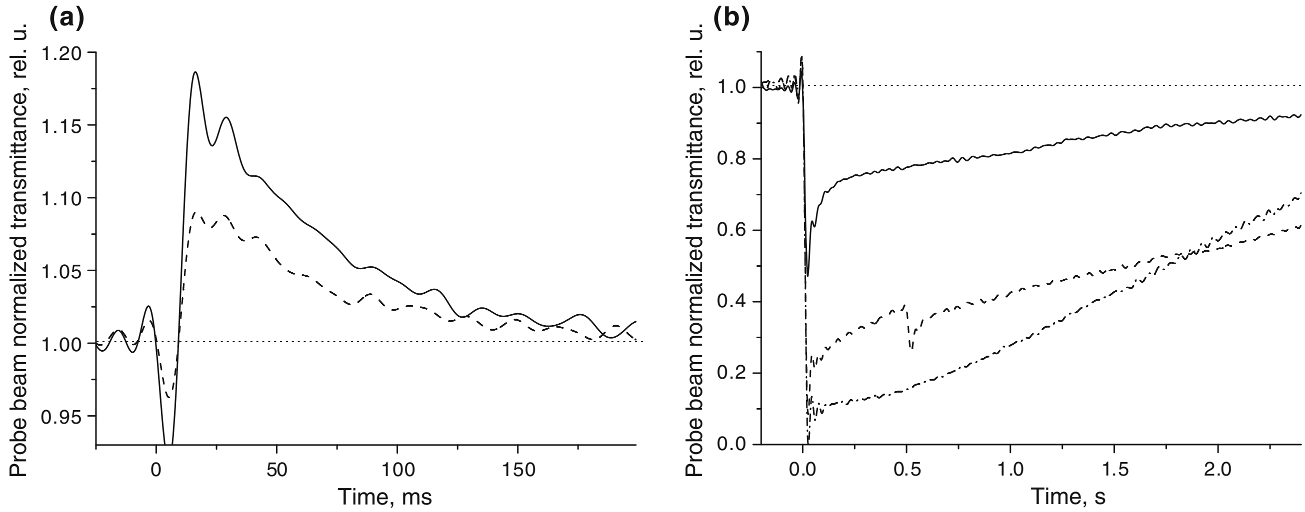

Fig. 4 Oscillograms of probe beam transmittance upon a single-shot excitation by pumping pulse with an energy level of 0.9 mJ for aqueous suspension of PMFNs (*solid line*) and CNFs (*dashed line*) (**a**). Oscillograms of probe beam transmittance of CNF suspension in PDMS upon a single-shot excitation by pumping pulses with energy levels 0.2 mJ—*solid line*, 0.4 mJ—*dashed line*, 0.9 mJ—*dash dotted line* (**b**). The *dotted line* designates the initial normalized transmittance of the materials

products together can explain the absence of the OL degradation in the CNFs in PDMS suspension as they will also strongly scatter and absorb powerful pulses coming at a high repetition rate.

4 Conclusion

In conclusion, we studied the OL behavior of the CNF in PDMS suspension and compared it with that of the CNF in water and the PMFN in water. The absence of degradation of OL characteristics in the CNF in PDMS suspension was shown in contrast to the aqueous suspensions. The aqueous CNF suspension showed a better performance in the pulse-periodic mode of laser irradiation when compared with the aqueous PMFN suspension. This was probably due to the difference in size and geometry of particles.

Pump-probe measurements showed bleaching effects of different magnitudes in the aqueous CNF suspension (weaker) and the aqueous PMFN suspension (stronger). On the other hand, long-term darkening was registered in the CNF in PDMS suspension. This was due to the observed long-lived products of the pyrolysis of the PDMS, namely poorly soluble gases and carbonized products, which can explain the absence of degradation of OL in the CNF in PDMS in pulse-periodic regime (at 10 Hz) of laser irradiation.

Acknowledgments The authors acknowledge the support of Russian Foundation for Basic Research (Grant Nos. 110301106a and 130301111-a) and The Ministry of Education and Science of The Russian Federation (Contract No. 14.513.12.0003) for financial support. The authors thank Eduard G. Rakov for synthesizing and granting of CNFs and Valery M. Volynkin and Anastasiya V. Venediktova for the preparation of suspensions. This work has benefited from fruitful interactions with Ivan M. Kislyakov, Anton A. Ryzhov, and Andrey Yu. Vlasov and Marcus Godwin.

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