Optical Limiting Properties of Double-C_{60}-End-Capped Poly(ethylene oxide), Double-C_{60}-End-Capped Poly(ethylene oxide)/Poly(ethylene oxide) Blend, and Double-C_{60}-End-Capped Poly(ethylene oxide)/Multiwalled Carbon Nanotube Composite

H. W. Goh,[†] S. H. Goh,*[,†] G. Q. Xu,[†] K. Y. Lee,[‡] G. Y. Yang,[‡] Y. W. Lee,[‡] and W.-D. Zhang[§]

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore, DSO National Laboratories, 20 Science Park Drive, Singapore 118230, Singapore, and Institute of Material Research and Engineering, National University of Singapore, Research Link, Singapore 117602, Singapore

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Double-C_{60}-end-capped poly(ethylene oxide) (FPEOF) exhibited concentration-dependent optical limiting behavior in toluene, THF, and water. Its performance was not only inferior to C_{60}−toluene solution with similar C_{60} concentration, but its linear transmittance was also remarkably lowered by the aggregation of C_{60} in the solutions. Optical limiting studies with poly(ethylene oxide)/FPEOF blends suggested the significance of bimolecular excited-state processes (such as the formation of C_{60} excimers) to the optical limiting performance of FPEOF at 532 nm. Although an aqueous multiwalled nanotube (MWNT) suspension showed only weak optical limiting actions toward laser at 532 nm operating at 20 Hz, its mixing with FPEOF solution resulted in enhanced optical limiting responses. FPEOF/MWNT composites also exhibited optical limiting responses at 1064 nm.

Introduction

Development of photonic devices requires the control of light (frequency and intensity) in a predictable manner. This has been one of the main motivations for the studies and search for new materials with nonlinear optical properties, which can inherently act as smart optical switching and limiting devices without the need of external control. In particular, there has been a great interest in the development of effective optical limiters as devices for the protection of optical sensors over the past two decades. Early works have established that reverse saturable absorption (RSA), two-photon absorption, free-carrier absorption, nonlinear refraction, induced nonlinear scattering, and photorefraction can be effective optical limiting mechanisms.[1] Various classes of materials including carbon black suspensions, organometallics, fullerenes, semiconductors, and liquid crystals were reported to be promising optical materials.[1] Among these materials, organometallic dyes such as heavy atom substituted phthalocyanines exhibit excellent optical limiting performance toward 532 nm Nd:YAG laser.[2−4] However, these are narrow band optical limiting materials.

On the other hand, [60]fullerene (C_{60}) in toluene solution was reported by Tutt and Kost[5] to be potentially an ideal broadband optical limiter from 400 to 700 nm. Following the discovery, there have been extensive investigations on the optical limiting responses of C_{60}−organometallic complexes,[6,7] C_{60} derivatives,[8−14] C_{60}-containing polymers (in solutions or solid state),[15−27] and C_{60}-containing sol−gel materials[28−33] with the aim to develop a solid-state optical limiter based on C_{60} materials. It is now well accepted that the primary mechanism of optical limiting for solid-state C_{60} materials is RSA. RSA involves the formation of excited states with absorption cross sectional areas much larger than the ground-state absorption cross sectional areas under photoexcitation, therefore leading to nonlinear absorption. Sun et al. have further proposed a bimolecular RSA mechanism to account for the concentration dependence of optical limiting in solutions of C_{60} and its derivatives.[12,13] However, the possibility of nonlinear scattering in C_{60} solutions, proposed by Tutt, Kost, and co-workers[15] cannot be entirely ruled out.

More recent studies have shown that suspensions of carbon nanotubes (CNTs), which also belong to the fullerene family, can be potentially employed as a broadband optical limiting device from 430 to 1064 nm.[34−40] Aqueous suspensions of multiwalled carbon nanotubes (MWNTs) synthesized by arc discharge method were reported to show excellent optical limiting behavior not only at 532 and 700 nm but also at 1064 nm.[34] MWNTs prepared by catalytic CO disproportionation and dispersed in ethanol[35] and single-walled carbon nanotubes (SWNTs)[36] or MWNTs[37] produced by arc discharge in a water/surfactant suspension also exhibited broadband optical limiting behavior with efficiencies comparable or superior to carbon black and C_{60}. Apparently, the synthetic methods of the CNTs and whether they are multiwalled or single-walled do not have an effect on the optical limiting properties of their suspensions.[37] The influence of MWNT diameter was previously reported to be minimal too.[35] In contrast, the effects of the laser beam diameter,[34] the laser pulse duration, and wavelength,[39] as well as the solvent used,[38−40] on the optical limiting performance are more dramatic. Such observations form a strong basis that the optical limiting mechanisms involved in the CNT suspensions are of thermal origin.

Optical limiting mechanisms in CNT suspensions are believed to be very different from that in C_{60} solutions or C_{60}-based devices but very similar to that of carbon-black suspensions. Absorption-induced nonlinear scattering, in addition to (self-focusing) nonlinear refraction, has been found to be the dominant optical limiting mechanism.[37−40] Furthermore, de-

* To whom correspondence should be addressed. E-mail: chmgohsh@nus.edu.sg.
[†] Department of Chemistry, National University of Singapore.
[‡] DSO National Laboratories.
[§] Institute of Material Research and Engineering, National University of Singapore.

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pending on the laser wavelength, the pulse duration, and the solvent used, nonlinear scattering due to solvent microbubble growth can contribute very efficiently to optical limiting at lower fluences.[38−40] At higher fluences, nonlinear scattering due to the sublimation of CNTs dominates.[35,39,40] Hence, the superior performance of CNT compared to carbon black lies in its larger surface area, which can absorb more heat and transfer it more efficiently to the solvent, and if the solvent has low boiling point or viscosity to form microbubbles more effectively, the optical limiting performance of the CNT suspensions will be further enhanced.[40]

One main concern about the CNT suspensions, like the carbon black suspensions, is their stability over a prolonged period. Therefore, attempts were made to produce polymer-coated and polymer-grafted MWNTs that could be better stabilized in suspensions. These suspensions were found to retain good nonlinear optical properties of the pristine MWNTs suspensions.[41] Advances in the functionalization of CNTs have also led to the investigations of the nonlinear optical properties of solubilized CNTs.[42−44] While solubilized MWNTs were reported to show comparable optical limiting performance to C_{60}−toluene solution at 50% linear transmittance,[44] solubilized shortened SWNTs exhibited significantly weaker optical limiting responses when compared to shortened SWNTs and as-prepared SWNTs suspension, as well as C_{60} solution, toward 532 nm laser pulses.[43] It has been proposed that functionalization had led to the debundling of the SWNT and the individual SWNTs have nonlinear RSA, similar to that of C_{60}. Our recent report on the size-dependent optical limiting behavior of MWNTs is in line with this finding.[45]

Our group has recently synthesized a telechelic poly(ethylene oxide) end-capped with two C_{60} cages (FPEOF).[46] This polymer shows excellent mechanical properties with shape memory effect.[47] We are interested to further investigate its optical limiting properties. Its excellent solubility in water also enables us to blend it with an aqueous MWNT suspension and study the optical limiting performance of the resultant stabilized suspension. It would be interesting to examine whether the RSA of C_{60} and the nonlinear scattering of MWNT working together can produce enhanced optical limiting behavior. Moreover, the combination of C_{60} and MWNT might offer a possibility to develop a supramolecular RSA system, as proposed by Sun and Riggs. The results are reported herein.

Experimental Section

Poly(ethylene oxide) (PEO) (M_w = 4600) was purchased from Aldrich and used as received. FPEOF was synthesized as previously reported.[46] MWNTs were synthesized by chemical vapor deposition and purified by treating with 2.6 M nitric acid for 2 days before dispersing in water by means of sonication. Optical limiting experiments were conducted at 532 nm using laser pulses generated by a frequency-doubled Q-switch Nd:YAG laser. The laser pulse width is 5 ns, and the repetition rate used is 20 Hz. (Repetition rates of 10 and 1 Hz have been employed only for a C_{60} solution and a MWNT suspension.) A small part of the input beam was split using a glass plate to monitor the energy (or the input fluence). The major part of the laser beam was focused with a 250 mm focal length lens and the sample was placed near the focal point such that the beam diameter was ∼100 μm. A photodiode was placed at the other end of the sample to monitor the output fluence. All of the data points were obtained by averaging the measurements of 40 shots. No aperture was used in the laser setup.

Optical limiting experiments at 1064 nm were run with the same laser source and repetition rate. The focal length of the lens used to focus the laser beam was 300 mm. The rest of the experimental conditions remain. All measurements were made in 1 or 10 mm quartz cells.

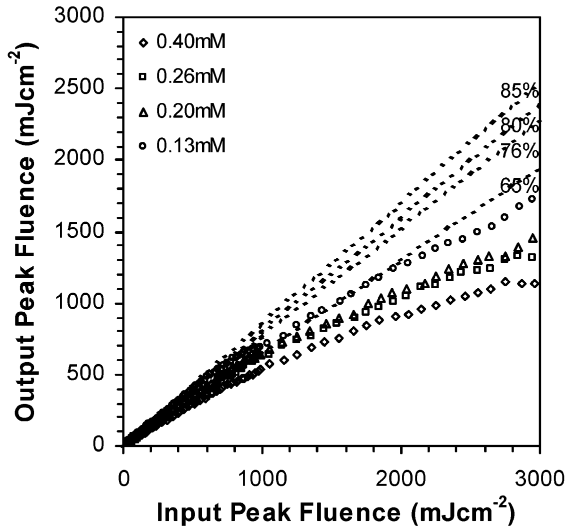


Figure 1. Optical limiting responses toward 532 nm laser of aqueous solutions of FPEOF at different concentrations.

Results and Discussion

Optical Limiting Behavior of FPEOF. The incorporation of C_{60} into poly(ethylene oxide) (PEO) has imparted not only novel mechanical properties[47] but also nonlinear optical properties, as shown in Figure 1. An aqueous solution of FPEOF exhibited optical limiting responses that depended not only on its amount in the laser beam[48] but also on its concentration, which is a phenomenon characteristic of C_{60} solutions[12,13] (see Figure 2).

The excellent solubility of FPEOF also allows its optical limiting properties to be studied in a wide range of solvents. In the study, the molar concentration of FPEOF and the optical path length of the laser beam were kept constant at 0.40 mM and 1 mm, respectively. Taking into consideration that each FPEOF chain has two C_{60} cages, a C_{60} solution in toluene with an equivalent concentration (0.83 mM) has been prepared for use as a reference. The ultraviolet/visible (UV/vis) spectra of all FPEOF solutions were featureless (as shown in Figure 3), in comparison with those of C_{60} and C_{60}-derivatives.[8−13] Such UV spectra have been observed in several C_{60}-containing polymeric systems. They have been attributed to the (linear) scattering by C_{60} clusters in the solutions.[49−51] C_{60} derivatives[52,53] and C_{60}-containing polymers[54−57] are also known to form aggregates in solutions. Hence, it may be followed that there are some forms of aggregation present in the FPEOF solutions, and the degree of aggregation is the least in toluene, followed by THF and water. As a result of more extensive aggregation, the linear transmittance of FPEOF in water (72%) was found to be lower than that in THF (76%) or toluene (76%), even though the FPEOF solutions have the same concentration of C_{60}. A 0.83 mM C_{60} solution had a linear transmittance of 83%. Interestingly, the optical limiting properties of FPEOF appear to be less affected by the solvent (Figure 4). The transmitted laser fluence is apparently still primarily decided by the amount of C_{60} in the laser beam path. The optical limiting responses of FPEOF in water and toluene at 532 nm were very similar, while that of FPEOF in THF was slightly weaker. The optical limiting performance of FPEOF was also poorer than pristine C_{60} in toluene. This can be attributed to a lower quantum

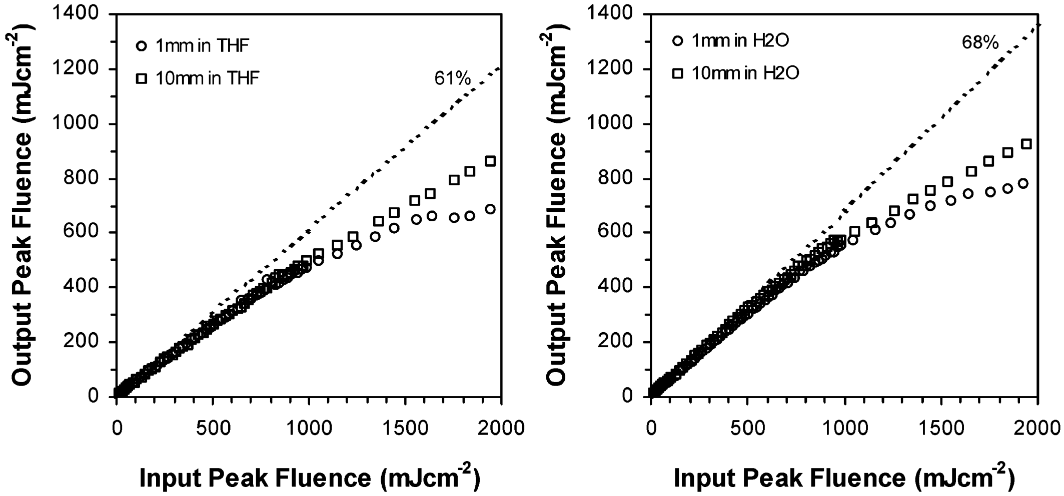


Figure 2. Optical limiting responses toward 532 nm laser of FPEOF in THF (left) and water (right).

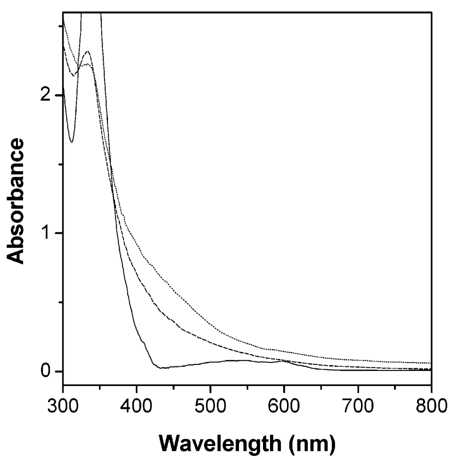


Figure 3. UV spectra of 0.80 mM C_{60} in toluene (—) and 0.45 mM FPEOF in toluene (– – –) and in water (···).

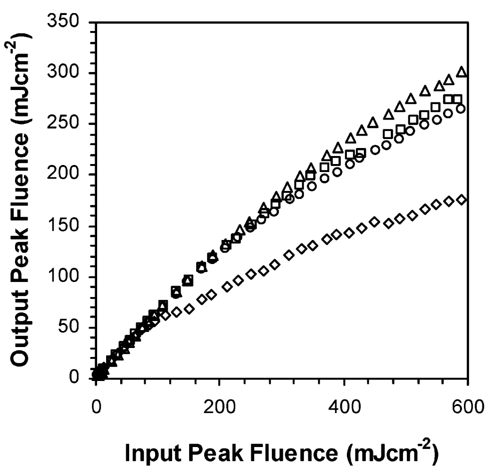
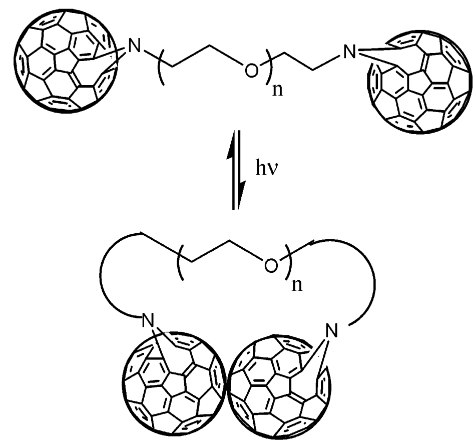


Figure 4. Optical limiting responses toward 532 nm laser of 0.40 mM FPEOF in toluene (□), tetrahydrofuran (△), water (○) and 0.83 mM C_{60} in toluene (◇).

yield for the intersystem crossing of C_{60} from its excited singlet to triplet state, as a result of aggregation.[21,58] Functionalization of the C_{60} cage may also have contributed to the poorer performance of FPEOF.

Optical Limiting Properties of PEO/FPEOF Blends. Sun and Riggs have previously reported a modified reverse saturable absorption model that includes both unimolecular and bimolecular excited-state processes to account for the concentration-dependent optical limiting responses of C_{60} and its derivatives solutions.[12,13] They have proposed that the formation of excimer states, through C_{60} triplet−triplet annihilation or self-quenching (both being bimolecular processes), with greater absorption cross sections could be responsible for the enhanced optical limiting responses of C_{60} in solution, in comparison to C_{60} in solid-state devices. FPEOF possesses a unique telechilic structure, which allows the formation of intramolecular excimers (Scheme 1). Unfortunately, the aggregation in FPEOF, shown by the above studies, adversely affects its optical limiting performance, partly by hindering the formation of intermolecular and intramolecular excimers.

SCHEME 1



Frank and co-workers have previously demonstrated that individual PEO chains tagged with pyrene on both ends could be molecularly isolated from one another when PEO is added in great excess.[59−61] Hence, it would be interesting to investigate what effect this will have on the nonlinear optical behavior of PEO/FPEOF blends. The blends were prepared in such a way that the concentration of FPEOF was the same throughout the series while the relative concentration of PEO was progressively increased.

Figure 5 shows the optical limiting responses of PEO/FPEOF in THF and toluene. Apparently, blending 6 or 12 equiv of PEO with FPEOF had a negative effect on the optical limiting performance of FPEOF, presumably due to the hindrance of bimolecular interactions by the increased viscosity in the medium. However, the PEO/FPEOF blend in THF with a PEO/

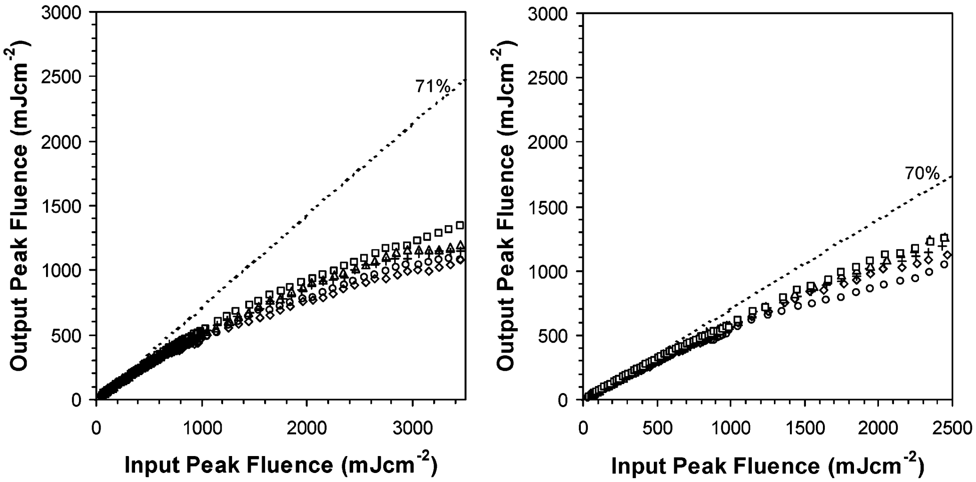


Figure 5. Optical limiting responses toward 532 nm laser of FPEOF (◇) and PEO/FPEOF blends in toluene (left) and THF (right) with PEO/FPEOF molar ratio of 6 (+), 12 (△), 50 (○), and 100 (□). Optical path = 1 mm.

FPEOF molar ratio of 50 was found to have better optical limiting performance than FPEOF itself. Such an anomaly was similarly observed in PEO/FPEOF blends in toluene or water, although the extent is more moderate. Apparently, when the PEO/FPEOF molar ratio was 50, FPEOF was molecularly isolated, and the formation of intramolecular excimer was contributing to the optical limiting responses. However, when the molar ratio was further increased to 100, the formation of intramolecular excimer was hindered by the presence of excessive PEO. The above results thus provide an additional experimental support to the bimolecular processes, proposed by Sun and Riggs, to explain the concentration-dependent optical limiting properties of C_{60} derivatives in solutions.

Optical Limiting of FPEOF/MWNT Composite Solutions. Preliminary results have shown that increasing amounts of MWNTs dispersed in FPEOF can bring about stiffer FPEOF/MWNT composites.[62] Although these films possess too low transparency for meaningful optical limiting applications, it is still interesting to observe the optical limiting properties of these composites in solutions, in view that the RSA of FPEOF may complement the nonlinear scattering of MWNT and lead to enhanced optical limiting performance.

The composites are very stable in the solutions, and they exhibit stronger optical limiting responses with increasing MWNT content (Figure 6). Nevertheless, the addition of MWNT to FPEOF led to scattering and resulted in a remarkable decrease in the linear transmittance. Interestingly, the corresponding MWNT suspensions, with the same concentrations but without any FPEOF, showed no optical limiting responses at all in a 1 mm cell. In fact, transmittance has been found to increase at higher laser fluences (Figure 7). The MWNT suspensions, nonetheless, exhibited weak optical limiting responses in 10 mm cells (Figure 8). In a 10 mm cell, a MWNT suspension showed poorer optical limiting responses when the input fluence was higher than 2 J/cm^2, despite better performances at lower fluences. This observation is in contrast with the reports in the literature, in which the optical limiting measurements have been performed using single laser shots or at a repetition rate of 10 Hz.[34−36,37,43,44]

Therefore, measurements were also made for a C_{60} solution and a MWNT suspension using repetition rates of 1 and 10 Hz. While no repetition rate dependence was observed for the optical limiting performance of a C_{60} solution, the use of laser operating at a higher repetition rate seriously impaired the optical limiting properties of MWNT suspensions (Figure 9). Similar phenomenon has previously been observed in carbon black suspensions under fast repetitive pulse limiting because much of the active material leaves the interaction volume in the early pulses, causing a reduction in limiting for later pulses.[1]

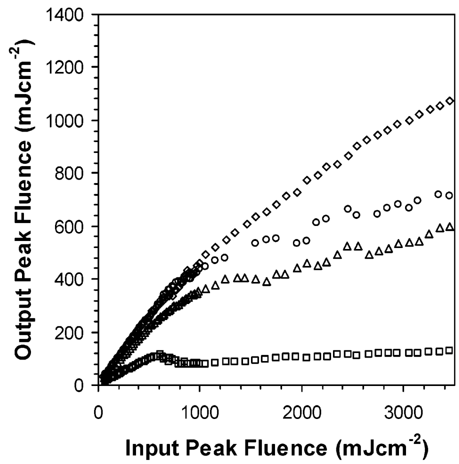


Figure 6. Optical limiting responses toward 532 nm laser of FPEOF/MWNT composites in water with 0 (◇), 1.1 (○), 2.2 (△), and 8.4 (□) wt % MWNT.

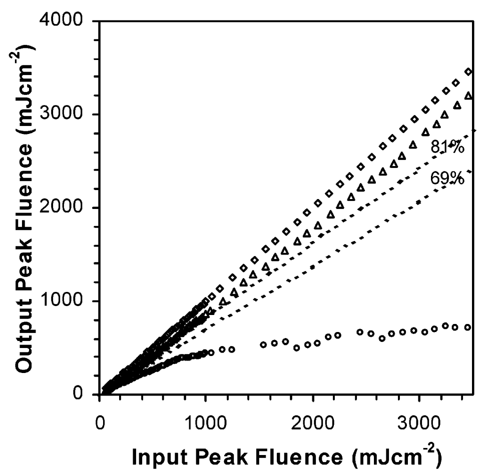


Figure 7. Optical limiting responses toward 532 nm laser of 0.03 g L^{-1} (◇) and 0.06 g L^{-1} (△) MWNT suspensions in water compared to that of FPEOF/MWNT composite (○) in water with 1.1 wt % MWNT and FPEOF concentration at 2.7 g L^{-1}.

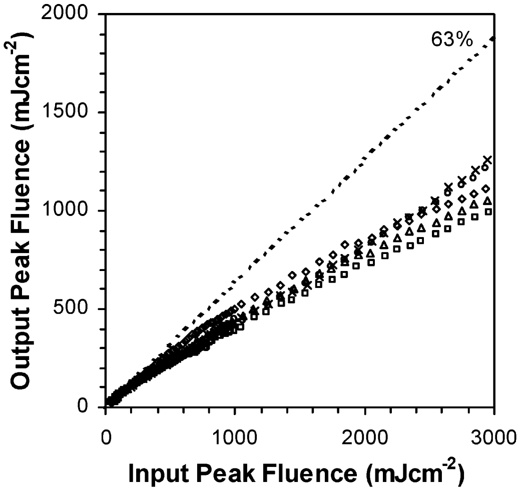


Figure 8. Optical limiting responses toward 532 nm laser of FPEOF/MWNT composites in water with 0 (◇), 2.8 (△), and 5.4 (□) wt % MWNT compared to PEO/MWNT (×) and MWNT (○) suspensions at 63% linear transmittance.

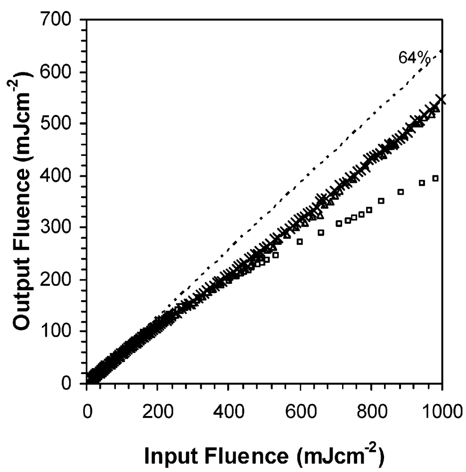


Figure 9. Optical limiting responses toward 532 nm laser of MWNT aqueous suspensions recorded at a repetition rate of 20 (×), 10 (△) and 1 Hz (□) at 64% linear transmittance. Optical path = 10 mm.

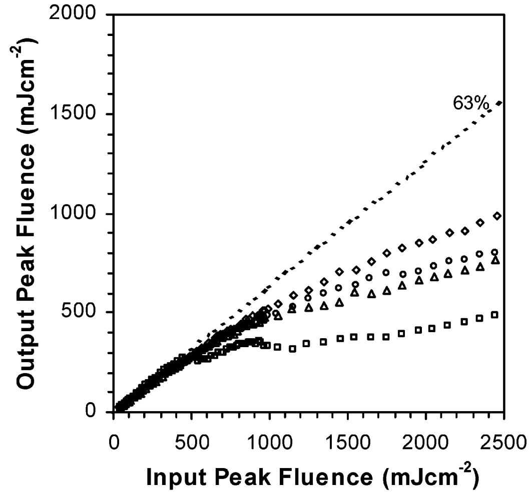


Figure 10. Optical limiting responses toward 532 nm laser of FPEOF/MWNT composites in water with 0 (◇), 1.1 (○), 2.2 (△), and 8.4 (□) wt % MWNT at 63% linear transmittance.

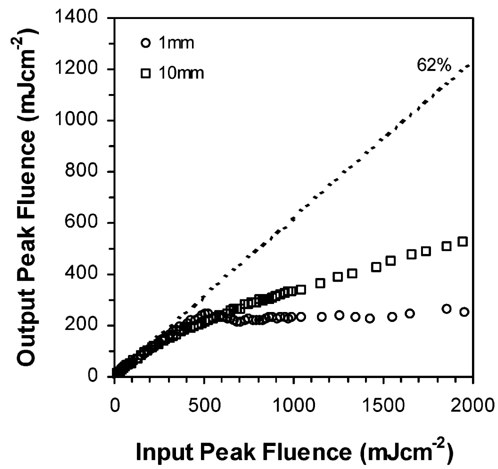


Figure 11. Optical limiting responses toward 532 nm laser of FPEOF/MWNT with 8.4 wt % MWNT in water.

It has also been noted that under the employed laser setup MWNT suspensions are not very effective optical limiters, even toward a laser operating at 1 Hz, contrary to reports in the literature. This is not entirely surprising because the optical limiting performance for a MWNT suspension is highly dependent on the laser diameter[34] and pulse duration.[39] The employed laser may not have been sufficiently tightly focused[34] to trigger rapid formation of microbubbles over a short pulse duration of 5 ns so as to effect strong optical limiting action. Moreover, the optical limiting results of different batches of MWNT suspensions have been found to vary, though not to a great extent. It may be due to the different sizes of suspended particles in the solvent.

On the other hand, it is interesting to note that mixing FPEOF with MWNT not only may have, to some extent, inhibited MWNT from leaving the interaction volume but also seems to have brought about some synergistic effect, leading to a good optical limiting performance toward 532 nm laser operating at 20 Hz (Figures 6 and 7). However, the optical limiting performances of the FPEOF/MWNT composite solutions can only be compared when their linear transmittance values have been adjusted to the same value.

Indeed, when the FPEOF/MWNT composite solutions with different MWNT contents were adjusted to the same linear transmittance at 63% at 532 nm, those with higher MWNT contents were observed to have stronger optical limiting performance than FPEOF or MWNT (Figures 8 and 10). In contrast, a PEO/MWNT composite solution with 64% linear transmittance only shows similar optical limiting responses as a MWNT suspension. This indicates that the presence of C_{60} (in FPEOF) is playing an important role in the enhancement of optical limiting performance in the FPEOF/MWNT composites. Given the weak nonlinear scattering exhibited by MWNT or PEO/MWNT under the given experimental condition at 532 nm and considering the lower concentration of C_{60} in the FPEOF/MWNT composite solution (adjusted to 63% linear transmittance), it is not very likely that the simple combined actions of the RSA of C_{60} and the nonlinear scattering of MWNT can bring about such a significant enhancement.

Whatever other mechanisms are at work, bimolecular processes are involved. As shown in Figure 11, the optical limiting responses of a FPEOF/MWNT composite solution containing 8.4 wt % MWNT were even more concentration-dependent than FPEOF solutions. In addition, we observed the formation of bubbles formed in the aforementioned composite at the end of the optical limiting measurements performed at 532 nm in a 1 mm cell. This, in contrast, had not been seen in a MWNT suspension. To sum up, C_{60} in FPEOF and the MWNTs, known to form microbubbles under strong laser photoexcitation, had

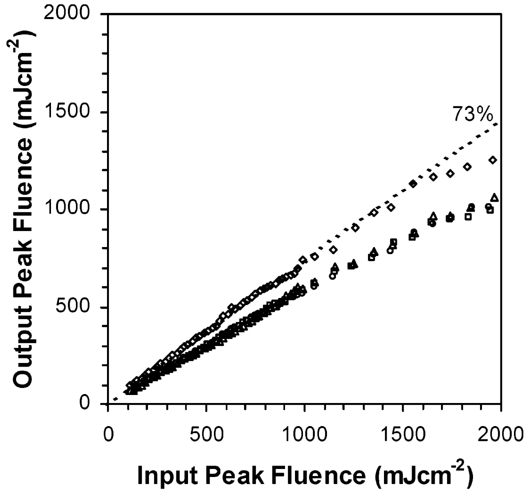


Figure 12. Optical limiting responses toward 1064 nm laser of FPEOF/MWNT composites in water with 0 (◇), 2.8 (△), and 5.4 (○) wt % MWNT compared to an MWNT aqueous suspension (□) at 73% linear transmittance.

to be involved in some bimolecular processes that result in optical limiting enhancement. It is thus reasonable to propose the following mechanism. Upon laser photoexcitation, C_{60} triplet states are formed in the FPEOF/MWNT composite solutions. Not only can these triplet states undergo triplet−triplet absorption or form C_{60} excimer states with much larger absorption cross sections, but they can also collide with MWNTs and transfer energy to them. Higher C_{60} excited states can also be quenched similarly (instead of only by solvent molecules).[48] Unlike the transfer of energy to solvent molecules, such a transfer of energy to MWNTs can lead to the generation of local hot spots and ultimately the formation of microbubbles, which can act as an additional optical limiting mechanism. From a reverse point of view, the presence of FPEOF assists the absorption of energy by the MWNTs through bimolecular processes and hence enhances the efficiency of microbubbles formation.

Nonetheless, other bimolecular processes cannot be totally ruled out. Sun and Riggs have previously proposed the possibility to employ supramolecular reverse saturable absorbers as strong optical limiters.[63] They have experimented with a C_{60}/β-carotene pair, in which C_{60} is the triplet energy donor while carotene is the triplet energy acceptor. However, the conditions for efficient electron transfer ultimately lead to competition between ground-state absorptions of both species, causing optical limiting responses to be hardly observed. The group has also recently pointed out the possibility of RSA being the primary optical limiting mechanism in solubilized SWNTs and MWNTs, suggesting that SWNTs or MWNTs may also have large excited-state absorption cross sections.[43] Given some structural resemblance between MWNT and carotene, MWNTs may likewise have very strong triplet−triplet absorption. It is possible that the action of C_{60} and MWNT as an effective pair of supramolecular reverse saturable absorber is bringing about the observed enhancement in the optical limiting responses at 532 nm. Alternatively, it is also likely for bimolecular processes involving C_{60} and the MWNTs to occur and result in the formation excimer states with very much larger absorption cross sections than that of C_{60}, hence bringing about the enhancement effect.

Optical limiting measurements of FPEOF and these FPEOF/MWNT composite solutions performed at 1064 nm also reveal optical limiting actions (Figure 12), demonstrating their potential as broadband optical limiters. It is interesting to find that FPEOF aqueous solution is also optical limiting at 1064 nm, though the responses are weak. However, the optical limiting performances of the composites are at best comparable to that of MWNT. The small ground-state absorption cross sectional area of FPEOF at 1064 nm implies a small population of excited (singlet or triplet) C_{60} that can interact with MWNT bimolecularly or transfer an electron to it. Therefore, no significant enhancement can be observed.

Conclusions

In conclusion, FPEOF in toluene, THF, and water shows optical limiting properties. The poorer performance of FPEOF compared to C_{60} can be partly ascribed to aggregations and partly to functionalization of the C_{60} cages. Optical limiting experiments involving the PEO/FPEOF blends suggest that formation of intramolecular and intermolecular excimers with large absorption cross sections contributes to the optical limiting responses of FPEOF. More excitingly, the addition of MWNT to FPEOF in solution has been found to enhance greatly the optical limiting performance of FPEOF, particularly at 532 nm, and the FPEOF/MWNT composite solutions show promise in potential application as broadband optical limiters. The reasons behind the enhancement remain unclear, and more photophysics experiments will be necessary for clarification of the optical limiting mechanism.

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