Viscosity dependence of optical limiting in carbon black suspensions

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We measure the optical limiting behavior of carbon black suspensions in various viscosity solvents by using a 10-Hz repetition rate, 532-nm, 5-ns pulsed laser. We found that, for common solvents used in the past such as water and ethanol, the limiting behavior ceases after a few laser firings and a turnover in the limiting curve appears. This can be explained by depletion of the carbon black within the focal volume. This turnover shifts to lower energies as the viscosity of the solvent becomes greater. However, for low viscosity liquids, such as carbon disulfide or pentane, the limiting is unaffected by the repetition rate, at least for frequencies up to 10 Hz, because of diffusion of the carbon black particles. This diffusion allows fresh material to replace the irradiated volume within the time between pulses.

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1. Introduction

Significant effort has been made to design optical limiting devices that have a low maximum output energy, while maintaining high linear transmittance.[1,2] Carbon black suspension (CBS), diluted India ink, has proved to be an excellent optical limiter material having a broadband response and a relatively low limiting threshold (~1 μJ), while maintaining high linear transmittance of >50%.[3–5] However, as reported in these studies, after repeated irradiation, the limiting ceases. This is to be expected, as the limiting mechanism vaporizes the carbon particles, and, at high laser repetition rates, the carbon black becomes depleted in the focal volume. In the typical solvents used including water and ethanol, with tightly focused beams, the repetition frequency at which the material ceases to limit is restricted to approximately 1 Hz, unless the liquid suspension flows rapidly. In general, thermal diffusion replenishes the CBS after a period of time that is determined by the material viscosity. Here we present a study of the viscosity dependence of the optical limiting behavior of CBS. We found that low viscosity solvents such as CS_2 and pentane allow replenishment of the focal volume faster than the 1/10th second between pulses up to energies much higher than the limiting threshold, as high as 35 mJ. This should allow effective optical limiting devices for 10-Hz repetition rates based on CBS by use of these solvents.

Considerable effort has been applied to determine the responsible mechanisms for transmission losses in CBS by use of different pulse widths and solvents.[6–10] Nonlinear scattering by microplasma generation and, on longer time scales, bubble formation appear to be the main limiting processes for picosecond, nanosecond, and microsecond pulses.[10] These mechanisms are fluence (rather than irradiance) dependent in that the energy per unit area needed to induce the limiting effect in thin samples remains nearly constant from 30 ps to hundreds of nanoseconds while the irradiance drastically increases for the shorter pulses. Because of the fluence dependence and because of a turn-on of hundreds of picoseconds for the limiting, picosecond pulses are not limited well by CBS.[10]

In Ref. 7 Nashold and Walter performed a comparison between CBS and fullerenes by measuring the total scattered energy and its angular distribution versus absorbed energy in these two media. The authors concluded that different mechanisms domi-

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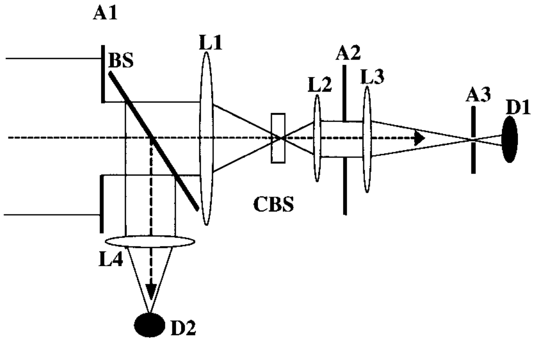

Fig. 1. Optical limiting setup.

nate the limiting processes in each. In particular, they concluded that reverse saturable absorption is dominant in the fullerenes.[7] McEwan *et al.* studied the influence of the thermodynamic properties of 14 solvents on the limiting behavior of CBS for microsecond and nanosecond pulses.[11] They showed that, for microsecond pulses, the surface tension and viscosity of the solvent were the determinants for optical limiting of individual pulses, whereas for nanosecond pulses the thermal conductivity and heat of vaporization were the most important parameters.

Here we demonstrate that the solvent viscosity is one of the most crucial factors in the limiting performance of CBS at repetition rates above 1 Hz. We compare the optical limiting response of CBS in different solvents with different viscosities by using 10-Hz and single-shot laser pulses. We found that, as the viscosity of the solvent decreases, the optical limiter performance improves for the 10-Hz repetition rate.

2. Experimental Setup

Figure 1 shows the experimental setup used for this study. We used a frequency-doubled, *Q*-switched, 5-ns (FWHM), single-mode (injection-seeded), Nd:YAG laser, operating at a 10-Hz repetition rate and/or single shot. Single shot means that many seconds pass (>10 s) between each laser firing. We produced a top-hat spatial irradiance distribution at the entrance of the system by expanding the beam at the input to overfill a 2-cm-diameter aperture, A1. Lens L1 (f = 10 cm) focused the beam into a 10-mm cell containing CBS in different solvents (carbon disulfide, pentane, ethanol, water, or different mixtures of undecane/CS_2). The beam was focused approximately 2 mm from the back window of the cell. The low irradiance spot size, measured by the thin-sample Z-scan technique,[12,13] was 3.4 μm (HW1/e^2M). Aperture A2 (8-mm diameter) defined the collection aperture through the limiter. L2 (f = 3 cm) recollimated the beam after the cell (left to right) and L3 (f = 1.0 m) collected the beam into detector D1. We measured the encircled transmitted energy, which is important for applications of optical limiters to eye protection,[2] by placing aperture A3 (1.5-mm diameter) on axis in the focal plane of L3.

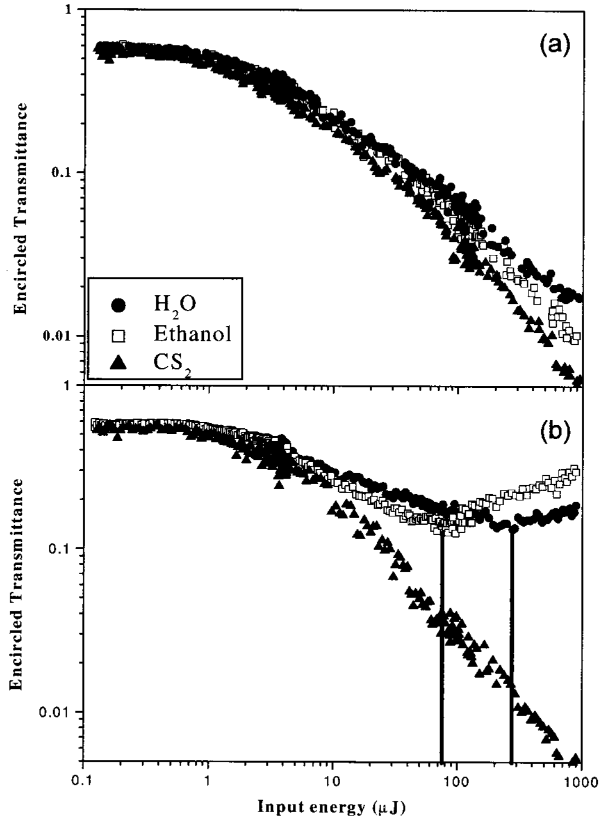

Fig. 2. Encircled energy transmittance versus input energy for CBS for three solvents by use of (a) single shot and (b) 10-Hz repetition rate for CS2 (▲), ethanol (□), and water (●). The linear transmittance of the samples was approximately 60%.

Thus, detector D1 measures the light transmitted through a 1.5-mrad aperture. A beam splitter (BS) was used to reflect a portion of the incident beam into detector D2 as an incident energy reference with the help of L4 (f = 10 cm). A half-wave plate (λ/2) and a polarizer were used in combination to control the input energy (not shown in Fig. 1).

We prepared samples by mixing amorphous carbon particles with all the previously mentioned solvents. The suspensions were sonicated for approximately 1 h before being filtered with 0.45-μm nylon filters. Attempts to filter the suspensions with a 0.22-μm filter failed, which suggests that the particle sizes are between 0.22 and 0.45 μm. However, the hydrodynamic average particle diameter, measured by use of dynamic light scattering,[14] was 0.155 μm.

3. Results and Discussions

Three CBS samples in three different solvents were tested to compare the response at different pulse repetition rates for different solvent viscosities. In Fig. 2 we show the encircled energy transmittance versus input energy for CBS in CS_2 (▲), ethanol (□), and water (●), using single shot [Fig. 2(a)] and with the laser working at 10 Hz [Fig. 2(b)]. The linear transmittance was $T_L \approx 60\%$ for all three suspensions.

As seen in Fig. 2(a), the onset of limiting for CS_2

Table 1. Solvent Viscosities and Thermodynamic Parameters Reported at 25 °C[a]

Solvent	Viscosity (mPa s)	Surface Tension (mN/m)	T_b (°C)	ΔH_{vap} (KJ/mol)	n (at 20 °C)	Thermal Conductivity (W/mK)	C_p (J/mol K)
Pentane	0.224	15.49	36	26.43	1.3575	0.113	167.2
CS_2	0.352	31.58	46	27.51	1.6319	0.149	76.4
H_2O	0.89	71.99	100	43.98	1.3328	0.607	75.3
Ethanol	1.071	21.97	78	42.32	1.3611	0.169	112.3
Undecane	1.098	24.21	196	56.43	1.4398	0.14	344.9

[a]Ref. 16.

and ethanol suspensions occurs at approximately the same input energy ($E_{in} \approx 0.76$ μJ), whereas for water it is achieved at a higher energy ($E_{in} \approx 0.9$ μJ). We also observed a slight difference in slopes among all three curves. These results were as expected according to McEwan *et al.*,[11] who reported that, for nanosecond pulses, the lower the thermal conductivity of the solvent (see Table 1),[15] the lower the limiting onset, and the steeper the slope of the limiting curve. It is clear from Fig. 2(a) that, by use of single shot, all three samples provide adequate limitation of the output over the entire range of input energies. This result was anticipated because, by use of single shot (<0.1 Hz), there is enough time between laser firings for the CBS to diffuse back into the focal volume. On the other hand, using a 10-Hz repetition rate we observed a large difference in limiting among the three suspensions as shown in Fig. 2(b). CBS/CS_2 (▲) limits well at 10 Hz, exactly the same as for single-shot irradiation. For CBS/ethanol (□) and CBS/water (●), we observed a reduction in limiting and a turnover at inputs of approximately 75 and 280 μJ, respectively. This result is consistent with the different diffusion coefficients for carbon particles in each of the different solvents. Once the suspension was irradiated with a strong laser pulse, we destroyed carbon particles within the focal volume and created a concentration gradient. Therefore, fresh carbon particles diffuse into the irradiated region. According to the Stokes law for the resistance of a sphere moving in a liquid, the displacement speed v is inversely proportional to particle radius r_a and solvent viscosity η.[16] Thus, using the Stokes–Einstein relation, which connects the particle diffusion coefficient (D_s) with the viscosity of the solvent, yields

$$\frac{D_s}{T} = \frac{k}{6\pi\eta r_a}, \tag{1}$$

where k is the Boltzmann constant and T is the solvent temperature.[17] If we assume that the amorphous carbon particles are spherical and that r_a is the same ($r_a \approx 80$ nm) in all three suspensions, the solvent viscosity is the only relevant parameter to take into account for our qualitative analysis. In Table 1 we show the viscosity for all three solvents.[15] We observed that CS_2 has the lowest viscosity of the tested suspensions. According to the experimental results, the viscosity of CS_2 should be low enough for fresh particles to replenish the focusing volume effectively in less than 100 ms. However, because of the complexity of the system, we could not estimate the real time for carbon black particles to travel across the beam just by solving the diffusion equation. In fact, we need to know the local temperature changes, the real limiting mechanisms, the depletion factor, etc.

For a higher viscosity solvent such as water, the time to replace all the atomized particles within the focal volume completely becomes greater than the interval between pulses. This is manifested by a turnover in the transmittance at $E_{in} \approx 280$ μJ. In CBS/ethanol we observe the same behavior as in CBS/water, however, the turnover appears at lower input energy ($E_{in} \approx 75$ μJ). This result is consistent with Eq. (1), where, as the viscosity of the liquid increases, the diffusion of spherical particles decreases. Other solvent thermodynamic parameters such as thermal conductivity and heat capacity, which would be indicative of recovery mechanisms other than diffusion, do not show any correlation with the observed behavior. This can be seen from the list of thermodynamic properties given for each solvent in Table 1. Hence we conclude that diffusion is the dominant mechanism for recovery of carbon particles between pulses.

To gain a better understanding of the previous results we measured the limiting curves of CBS in five distinct mixtures of undecane ($C_{11}H_{24}$) and CS_2 in different ratios. These two solvents are miscible and have different viscosities (see Table 1). All suspensions had approximately the same linear transmittance ($T_L \approx 70\%$). In Fig. 3 we show the normalized encircled transmittance versus input energy for $C_{11}H_{24}/CS_2$ = 1/0 (■), 3/1 (△), 1/1 (●), 1/3 (□), and 0/1 (▲). Once the concentration of undecane increases in the suspension, the turnover moves to lower energies because of the larger viscosity (see Table 2). This result is consistent with the larger viscosity of undecane than that of CS_2. The relatively large noise observed in Fig. 3 is possibly due to some turbulence as a consequence of solvent convection related to the large difference in solvent densities.[15] However, the reproducibility of the experimental data shown in Fig. 3 proves that this does not affect the overall results.

As further evidence of the low viscosity require-

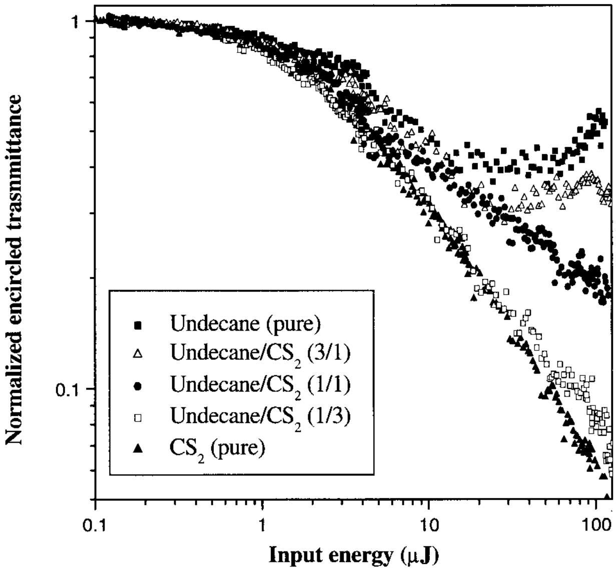

Fig. 3. Limiting curves of CBS for five mixtures of undecane/CS_2 with the laser operating at 10 Hz: 1/0 (■), 3/1 (△), 1/1 (●), 1/3 (□), and 0/1 (▲). The linear transmittance of the samples was approximately 70%.

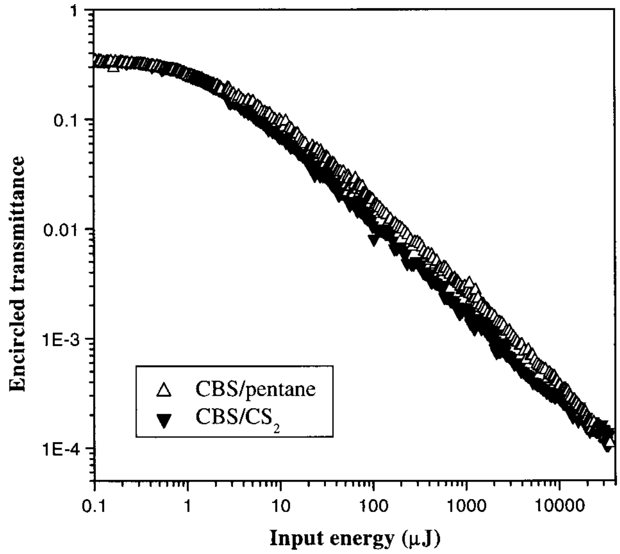

Fig. 4. Encircled energy transmittance versus input energy for CBS/CS_2 (▼) and CBS/pentane (△). The linear transmittance for both samples was approximately 35%.

ment for higher repetition rate CBS optical limiters, we performed measurements on pentane (C_5H_{12}) and CS_2 ($T_L \approx 35\%$) up to 35-mJ input energy (see Fig. 4). As seen in Table 1 pentane presents a slightly lower viscosity than CS_2. In Fig. 4 we show that, as anticipated, both suspensions have a similar limiting response for the entire range of input energies by use of the 10-Hz repetition rate.

4. Conclusion

In summary, we have demonstrated that the viscosity of the host solvent for carbon black suspensions is crucial for determination of the optical limiter performance for repetitively pulsed lasers. The optical limiting performance of CBS in a high viscosity solvent at high repetition rate is manifested by a turnover of the energy-dependent transmittance curve. However, for CBS suspended in low viscosity solvents such as CS_2 and pentane, we did not observe a degradation of the limiting performance at 10 Hz for input energies up to 35 mJ. These results might allow wavelength-independent optical limiters to be designed by use of CBS for higher repetition rates than have been previously reported.

Table 2. Undecane/CS_2 Mixture Viscosities at 25 °C

Mixtures	Viscosity (mPa s)
100% Undecane/0% CS_2	1.098
75% Undecane/25% CS_2	0.912
50% Undecane/50% CS_2	0.716
25% Undecane/75% CS_2	0.539
0% Undecane/100% CS_2	0.352

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