Chapter 3

Performance of dye-doped PVA films

3.1   *Spectral Characteristics*

The absorption, fluorescence and emission characteristics of C460, DF and R640 in PVA are shown in Figure 3.1. The fluorescence and lasing peaks are shifted to longer wavelengths with increasing concentration but the absorption peaks remain unchanged; the shifts indicate a re-absorption effect, which is in agreement with similar shifts noted in previous reports (Law *et al.*, 1998; Yee *et al.*, 1998). The wavelengths (C460 454-457 nm; DF 530-566 nm; R640 654-664 nm) increase as the concentrations increase (Figure 3.2) within the concentration ranges of 1×10^{-4} - 3×10^{-3} M for C460, 1×10^{-4} - 5×10^{-3} M for DF and 8×10^{-4} - 2.2×10^{-3} M for R640. Longer wavelengths for the R640/PVA films were not investigated as R640 is only sparingly soluble in ethanol.
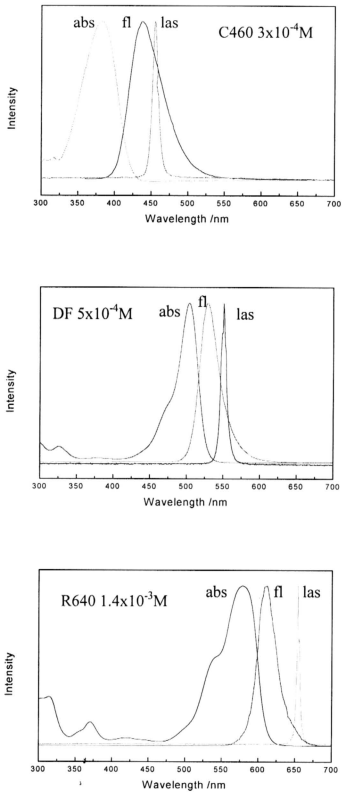
Figure 3.1 Spectral characteristic of C460, DF and R640
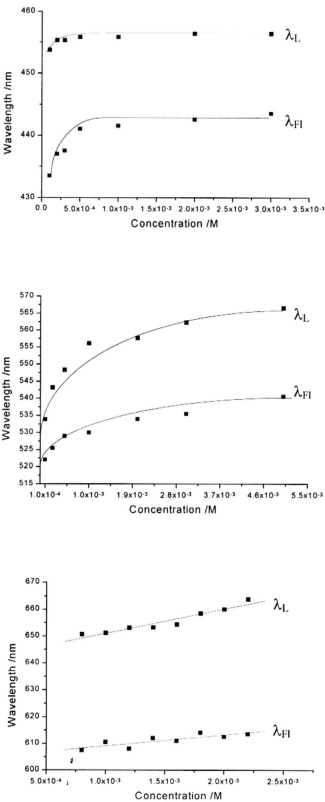(abs: absorption, fl: fluorescence, las: laser).

Figure 3.2   Shifts of the fluorescence (λ_{Fl}) peaks and lasing (λ_L) wavelengths with respect to concentration for C460 (a), DF (b) and R640 (c).

3.2   Laser performance

In the study, the laser efficiency is defined as the absorbed input conversion percentage based on the output energy/absorbed energy ratio. This definition differs from those used previously where the incident energy was assumed to be the energy absorbed (as by the slab) because the films will transmit up to 70% of the incident energy. This definition also takes into account variations in thickness among the samples, so that the calculated rate should give a more accurate measure of the compatibility of the dye/polymer system.

The three dye/PVA systems show of an optimum concentration for laser efficiency (8% for 2.0×10^{-3} M C460, 11% for 3.0×10^{-3} M DF and 9% for 1.0×10^{-3} M R640) as illustrated in Figure 3.3. Upon exceeding the optimum concentration, the dye molecules cannot be accommodated by the free volume of the polymer, so that these aggregate into oligomers, and the laser efficiency is reduced (Dyumaev *et al.*, 1992). When a concentrated dye/PVA solution was left undisturbed for several days, particles were observed for DF/PVA, whereas C460 separated from the mixture. In Figure 3.4, the particles in DF are clearly visible. The influences of the thickness of the films on output energy as well as the waveguiding feature of the dye-doped films are discussed in section 4.2.

Energy output was measured at one of the two short sides of the as-cut glass slide. In an attempt to measure the total emission energy from both sides, the other side was coated with aluminium (by vacuum evaporation). The emissions leaving the slide was found to be approximately doubled, which gives an absorbed input conversion efficiency to be twice the earlier value. These values are much higher than those of dye doped silica-PMMA films (Reisfeld & Shamrakov, 1993).

Elevated absorption of the incident energy, which depended linearly on the dye concentration, increased with output energy value; this dependence for a specific concentration (C460 1.0×10^{-3} M, DF 2.0×10^{-3} M and R640 2.0×10^{-3} M) is shown in Figure 3.5(a). The ratio of absorbed energy/incident energy is almost the same for the three systems. The absorbed energy increased with respect to concentration at a similar rate for the three dye/PVA systems (Figure 3.5(b)).
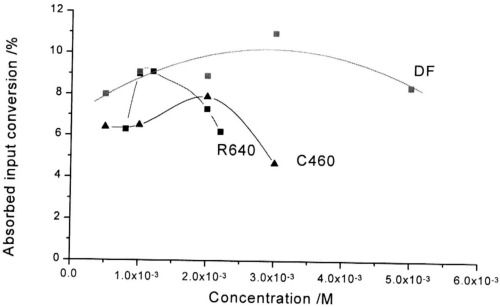
Figure 3.3   Absorbed input conversion for the dye films.
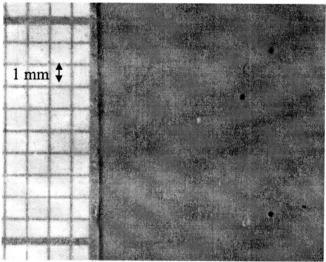
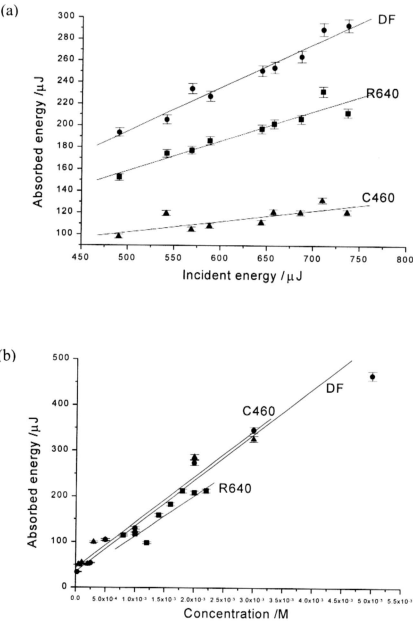Figure 3.4   Dye aggregation in DF/PVA mixture.

Figure 3.5   Absorbed energy as a function of incident energy (a) and its relation to dye/PVA concentration (b).

3.3   Effect of pH on performance of DF/PVA films

Hydrochloric acid (0.1 M, approx. 30 - 150 μl) when added to the host material gave rise to changes in the emission properties and the output characteristics of DF-doped PVA films. The absorption spectra are shown in Figure 3.6. When the acid concentration in the DF/PVA mixture exceeded 1.0×10^{-8} M, the intensity of dominant peak decreased, but there was a small peak at 450 nm-460 nm. This feature parallels that reported for Rhodamine B dissolved in polar and non-polar solvents (Fujii *et al.,* 1995). The emission wavelengths were also shifted to the blue (Figure 3.7(a)). Little changes were noted when sodium hydroxide is used in place of hydrochloric acid. The absorbed input conversion of the DF/PVA was reduced as the acidity increased whereas increasing the alkalinity showed little difference in the efficiency (Figure 3.7(b)).
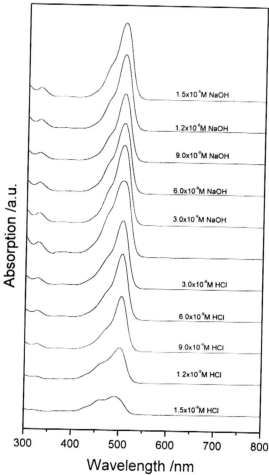
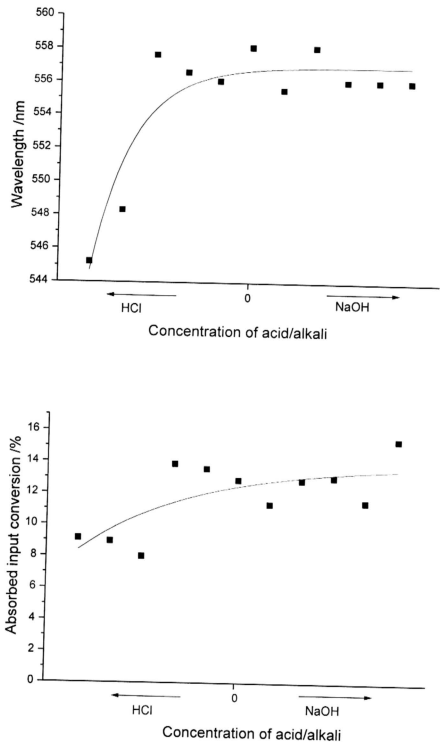Figure 3.6   Absorption spectra of DF/ PVA with addition of HCl and NaOH.

Figure 3.7   Emission wavelength (a) and the absorbed input conversion (b) of DF/PVA with the addition of HCl and NaOH.

3.4   Photostability

The presence of entrained liquid in the film which would increase the photostability (Costela *et al.*, 1998), was investigated by measuring the output energy of two films, one of which was air dried and the other dried at 60° C for 2 hours. Each output energy was found to be constant within the first 200 pulses (Figure 3.8), with that of the oven-dried film being about 10% greater than that of the air-dried film. The difference in output energies corresponded with a difference in emission wavelengths of 1.0 nm. As noted earlier (in section 3.1), wavelengths increase with increasing concentration, so that this difference is possibly attributed to a difference in the concentration of the dye in the dried PVA.
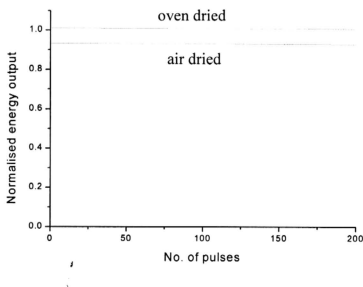

Figure 3.8 Photostability of air-dried and oven-dried films.

The photostability of the films was further examined under UV irradiation at ~0.75 Hz. The PVA films were found to have longer lifetimes with respect to pump pulses compared with the PMMA films (Figure 3.9). In particular, DF/PVA showed the best performance, and only less than 15% decrease in output energy after 1000 pulses was noted (Figure 3.10). On the other hand, the DF/PMMA film could not be examined as the dye decomposed when doped in PMMA; the same problem was also noted elsewhere (Yap, 1995).

Figure 3.9 shows the plot of absorption energy of each film versus the number pulses. At constant absorption energy, the R640/PVA and DF/PVA systems showed emission energy that did not change with respect to the number of pulses. On the other hand, the C460/PVA system showed decreasing emission energy decrease with increasing pulses, which is attributed to energy being converted for other non-radiative processes. However, inter-system crossing of the dye molecules to the triplet state would be negligible because of the rapid risetime of the pumping source compared with a typical inter-system crossing rate of 10^7 s^{-1} (Schäfer, 1990). The rates being unchanged for the other two systems imply stable solid-state dye lasers.

With C460/PMMA, the absorption energy decreased with the number of pulses, and the material became more transparent to UV after being pumped. With R640/PMMA, this increased, and a dark line was seen at the pumped region of the film (Figure 3.11). A similar result has been reported on R6G doped PMMA, and the formation of the line was explained as the local increase of dye molecules. The higher concentration led to the formation of dimers, which absorbed energy without radiative emission (Popov, 1998). Figure 3.12 verifies a positive wavelength shift with respect

to pump pulses that was caused by the concentration change for the R640/PMMA films at the localised region. The values found for other films are listed in Table 3.13.

As the films displaying the type of photodegradation that is accompanied by no change or an increase in absorption energy would severely damaged at the end of the measurements, a slab of such a dye laser would be expected to have a short operational lifetime as any lines would prevent passage of pumping radiation. In contrast, since C460/PMMA became more transparent, a dye-laser slab should maintain an output energy higher than that of the experimental film as the incident radiation could reach the layer below to excite the dye molecules at this level, at which the radiation does not deviate much from the focusing region.
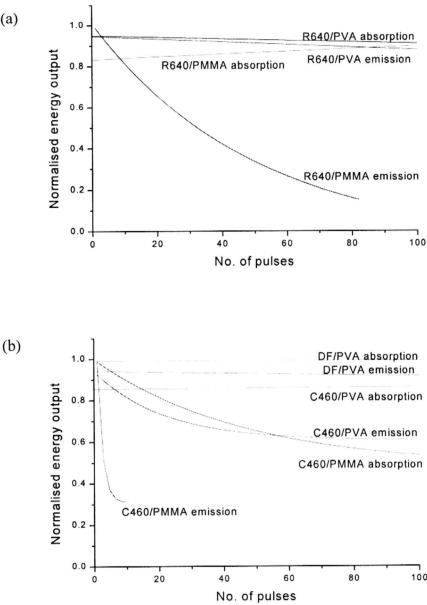
(a)

(b)

Figure 3.9 Output degradation characteristics of (a) DF/PVA and (b) C460/PVA, R640 /PVA compared with degradation characteristics of C460/PMMA and R640 /PMMA.
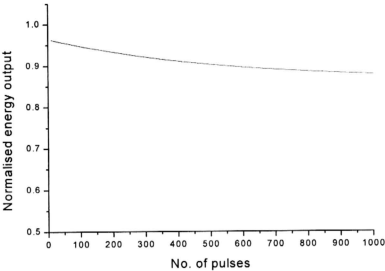
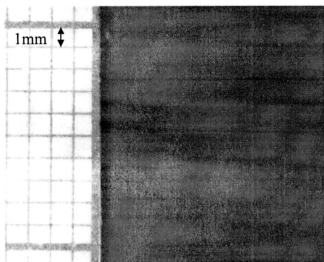Figure 3.10   Photostability of DF/PVA after large numbers of pulses.

Figure 3.11 Change in optical density after irradiation of R640/PMMA film (after 80
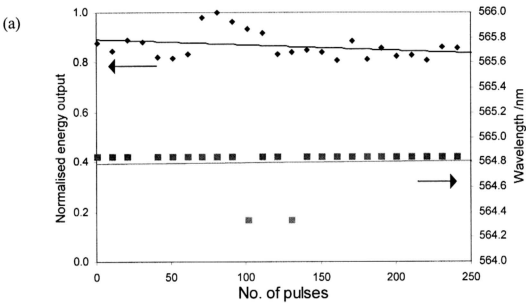   shots).

(a)

Figure 3.12   (a) Laser wavelength shift and the degradation versus pump pulses for
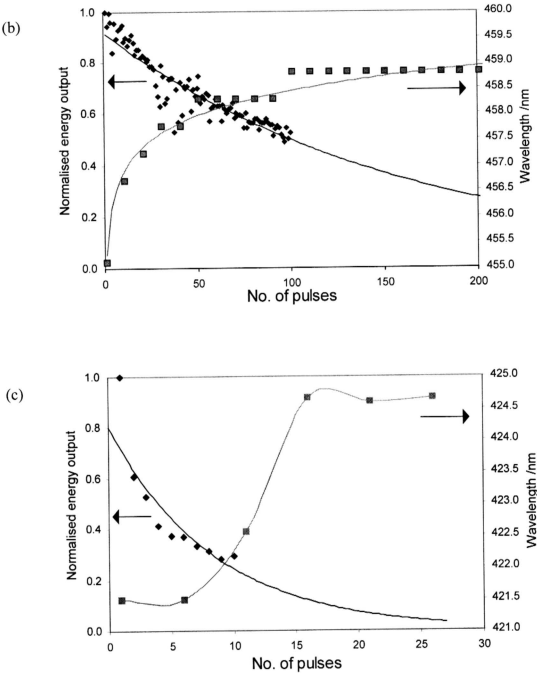DF/PVA.

Figure 3.12 Laser wavelength shift and the degradation versus pump pulses for (b) C460/PVA and (c) C460/PMMA.
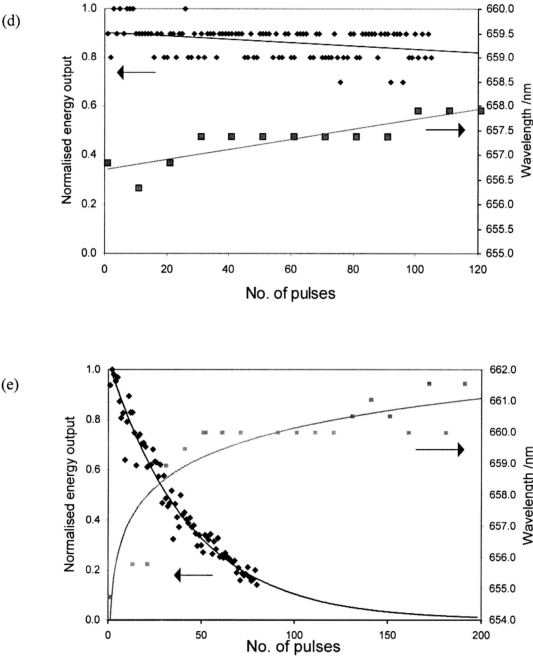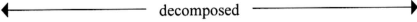
(d)

(e)

Figure 3.12 Laser wavelength shift and the degradation versus pump pulses for (d)
R640/PVA and (e) R640/PMMA.

Dye/polymer	Absorption energy	Emission energy	Wavelength change	Observable optical density change
C460/PVA	unchanged	decreased	~4 nm/150 pulses	none
DF/PVA	unchanged	unchanged	~1 nm/200 pulses	none
R640/PVA	unchanged	unchanged	~1 nm/120 pulses	none
C460/PMMA	decreased	decreased	~4 nm/15 pulses	none
DF/PMMA	←		decomposed	→
R640/PMMA	increased slightly	decreased	~6 nm/120 pulses	increased

* Refer to Figure 3.12 for number of pump pulses.

Table 3.1 Summary of changes for dye doped PVA and PMMA films with increasing number of pump pulses.

As reviewed in section 1.3, degradation of dyes has often been attributed to the formation of dye radicals and higher aggregates that causes the degree of absorption to change. Under high power pumping, dimers can form when excited dyes react with chemically active species; this process is enhanced, particularly when the matrix is heated at a localised area. With PVA as the host matrix, only a minor difference in the absorption value was found with the two Xanthene dyes, DF and R640 when excited at a power density that exceeded 1×10^6 Watt cm^{-2}. This observation implies stabilisation of the dye by the host matrix.

In a study on holographic processes, PVA containing DF was found to undergo crosslinking reactions when irradiated by high-power lasers (Bloom & Burke, 1977,

Manivannan *et al.*, 1994). The crosslinking process can reduce the formation of both of the harmful species that induce photodegradation. Firstly, the crosslinking process itself increases the rigidity of the dyes incorporated in the polymer, so that dimers and higher aggregates are not easily formed. The addition of a specific amount of crosslinking monomer was found to increase the output stability (Amat-Guerri *et al.*, 1993). The crosslinking reactions consume the dye radicals but the concentration of the dye is not altered. This termination of dye radicals has been documented by ESR measurements on Xanthene-doped PVA (Manivannan *et al.*, 1994).