Spectral and thermal characteristics of energy transferred polymeric solid dye mixtures

Ju Yong Cho, Won Kweon Jang*

Department of Aeronautic Electricity, Hanseo University, 46, Hanseo 1-ro, Seosan 31962, South Korea

ABSTRACT

We synthesized two solid dye mixtures with Coumarin-545 and Rhodamine-6G without a drying step, but it showed the comparable spectral and material properties with other reported solid dyes, despite a simplified synthesizing process. Coumarin-545 was selected as donor dye, because its fluorescence spectrum was well coincided to the absorption spectrum of Rhodamine-6G, for efficient energy transfer mechanism. We investigated the spectral characteristics with two molarities of 0.1 mM and 0.3 mM of Coumarin-545, at fixed molarity of 0.1 mM of Rhodamine-6G. The fluorescence peak and spectral width of the first one, 0.1 mM molarity for both dyes, appeared at 556 nm and 63 nm, which were 4 nm shorter and 16 nm wider than those of Rhodamine-6G only, respectively. On the other hand, the second one, 0.3 mM molarity for donor, showed 555 nm and 61 nm in their fluorescence peak and spectral width, respectively, which were also 5 nm shorter and 14 nm broader than those of Rhodamine-6G only. The second solid dye mixture showed a little shorter fluorescence peak and a narrower spectral width, compared to the first one. Maximum temperature at the spot where the sample is irradiated by a pumping laser source is investigated. The first one showed the maximum temperature raised from 30°C to 38°C, when a pumping laser power increases from 50 mW to 200 mW. On the other hand, the maximum temperature of the second one raised from 34°C to 53°C, when an output power of the source increases from 50 mW to 200 mW, due to larger absorption of pumping power than the first one.

Keywords: Solid dye mixture, C-545, Rh-6G, Energy transfer, MMA.

1. INTRODUCTION

Dye lasers have been applied in fields of scientific research, and spectroscopy, due to wide tunability and high gain (Costela et al., 2013; Jiang et al., 2011; Jiang et al., 2020). However, there are several disadvantages to be overcome, such as toxicity of solvent dyes and photodissociation. A fluid circulation system is required to lessen a problem of the photodissociation. But the sophisticated system of bulky and costly is required (Boremann and Lemmer, 2006; Oki et al., 2005). In addition, the toxicity of solvent dye is still a problem. A solid dye was reported to overcome the forementioned problems (Soffer and McFarland, 1967). The fluid circulation system and management of the toxic solvent were no longer required, and a laser system using the solid dye could be compact and low-cost. Many researches on the solid dye have been conducted with mainly using Rhodamine dyes, due to its excellent spectral characteristics in lasing (Costela et al., 1998; Maslyukov et al., 1995). Poly-methyl methacrylate has been widely used as a host material in many solid dyes, due to its outstanding properties in transparency of absorption and emission wavelength regions of the dye, solubility, and damage resistance (Costela et al., 1998). Though a dye has a broad emission spectrum compared to other laser sources, it is not easy to have a tuning range over 50 nm with one dye medium. However, Solid dye mixtures using energy transfer mechanisms are attractive, because it can extend the tuning range and improve the easy usage.
Energy transfer between two different dyes has been studied to broaden spectral range (Geethu and Basheer, 2018; Vijayaraghavan and Basheer, 2016). Basically, energy transfer occurs when the emission of a donor and the absorption of an acceptor are substantially superimposed. The research on energy transfer has been interested, because the mixed dyes having different physical characteristics can improve its physical characteristics, due to their outstanding physical properties in conversion efficiency and damage threshold (Seth et al., 2005; Gangopadhyay et al., 1987; Vijayaraghavan and Basheer, 2016). Since the broadened spectral property can be obtained by the energy transfer, some different types of dyes or pumping sources are not required. Therefore, the solid dye mixtures make the system compact and simplified. It does not require a circulation system, but the photodissociation is a problem because it induces the gain decrease, even though the physical properties of dyes can be improved by the energy transfer. Though some solid dye laser systems rotate a solid dye disc to avoid the heat accumulation and lessen the effect of photodissociation, it is not enough. Since the host material of methyl methacrylate has a poor thermal property, the evaluation of thermal profile on the surface of solid dye is necessary to improve heat dissipation.

In this paper, we synthesized the polymeric solid dye that Coumarin-545 (C-545) is added to Rhodamine-6G (Rh-6G). Spectral properties of solid dye mixtures were investigated in different molarities. And the synthesis process of solid dye mixtures is discussed in detail. In addition, thermal profiles on the surface of the solid dyes for different molarities are discussed in terms of the pumping laser power.

2. METHODOLOGY

2.1 Sample Preparation

Methyl methacrylate (MMA) of 20 mL was prepared as a host material. Solubilities of Rh-6G and C-545 in MMA are not high. Therefore, Rh-6G and C-545 were dissolved in methanol before they are added into MMA. Two solid dye mixtures of different C-545 molarity were prepared. Molarity of C-545 was 0.1 mM and 0.3 mM for a fixed molarity of 0.1 mM of Rh-6G, respectively.

1,1′-Azobis (cyclohexancarbonitrile) was used as an initiator for polymerization, and the initiator was prepared to be 1 wt% about MMA. And molecular sieves of 40 mg were added into the prepared solution. In the polymerization process, the solution should be kept in constant temperature. Therefore, a water tank of 100 mL was prepared and boiled with stirring. A dye solution container was inserted into the water tank. The temperature of water was kept to 90 °C until the prepared solution becomes viscous. This process took 2 hours. Then, the temperature of the water was adjusted to 70 °C, and kept for 5 hours. Small bubbles were observed in the solution before the temperature of the water was adjusted. However, these bubbles were removed 5 hours after the temperature was adjusted. In order to make the sample to be robust, the temperature of the water was adjusted to 80°C and kept for 5 hours. This process does not require any drying step to harden a sample. The solid dyes were successfully synthesized in absent of bubbles. Fig. 1(a) shows the synthesized solid dyes. In the figure, a represents the solid dye mixture with molarity of 0.1 mM for both C-545 and Rh-6G, and b represents the solid dye mixture of C-545 and Rh-6G of 0.3 mM and 0.1 mM, respectively. In order to reduce the scattering at the surface, both sides of the solid dye were polished. Fig. 1(b) shows the polished solid dye mixtures of C-545 and Rh-6G, and solid dye of only Rh-6G. And c represents the solid dye with only Rh-6G of 0.1 mM.

2.2 Experimental Setup

The spectral properties of two solid dye mixtures were investigated by a spatially modulated Fourier transform spectrometer based on a modified Sagnac interferometer that we fabricated. Compared to other spectrometers, this spectrometer has advantages of fast measurement and remote sensing in real time (Cho et al., 2019; Watanabe and Furukawa, 2018). Fig. 2 shows an experimental setup to investigate the spectral and thermal properties of the synthesized solid dye mixtures. A He-Ne laser with a central wavelength of 543 nm and a diode laser with a central wavelength of 450 nm were used to excite the acceptor, Rh-6G, and the donor, C-545, in solid dye mixtures samples.
The energy of the excited donor could be transferred to the acceptor, because the fluorescence spectrum of C-545 is well coincided to the absorption spectrum of Rh-6G. Two convex lenses, 2 inches in diameter and focal lengths of 100 mm and 300 mm, were used to collect the fluorescence from the solid dye to the interferometer, and send the optical signal to the detector.

In the spectrometer, the surfaces of constituent 2 inches square mirrors, M1 and M2, were silver coated. The beam splitter has a transmittance of 50% at 45° in a wavelength region from 488 nm to 694 nm. The beam splitter is inclined by 45° about the optical axis, and M1 and M2 are inclined by 22.5° about each incident surface, respectively. In order to generate the optical path difference, M2 was fixed after moved by 0.5 mm from the symmetrical position. A linear array detector, a measurement range from 200 nm to 1100 nm and effective pixels of 2048, was used to detect a spatially modulated interferogram. The line width of the detector is 28.7 mm, and the width per pixel is 14 μm.

Thermal profile variation of the solid dye mixture in time was investigated with a diode laser with a central wavelength of 450 nm. The optical power was adjusted from 50 mW to 200 mW in interval of 50 mW. The sample was irradiated by the laser beam for 5 min. Thermal profile was recorded by a thermal imager with pixels of 320 and 240 horizontally and vertically, respectively. Frame rate was set to 30 Hz. Emissivity of the solid dye was assumed to be 0.93 (Rühl et al., 2016).

3. RESULTS AND DISCUSSION

Fig. 3 shows the fluorescence and absorption spectra for C-545 and Rh-6G, respectively. In C-545, an absorption peak appears at 480 nm and an emission peak appears at 520 nm, while Rh-6G showed an absorption peak appears at 530 nm and an emission peak appears at 560 nm. The absorbed energy by C-545 is transferred to Rh-6G, then the fluorescence of Rh-6G will be appeared despite it does not have an absorption at pumping wavelength of 450 nm. We investigated the relation between the intensity of Rh-6G fluorescence and the molarity of C-545, at the same pumping conditions. And the thermal properties of the synthesized solid dye mixtures are also investigated in term of the molarity of C-545. Compared to other research, reported by Maslyukov et al. (1995) and Geethu and Basheer (2019), we could synthesize the solid dye mixtures by modifying the curing process without a drying step. Nevertheless, the synthesized solid dye mixture showed the excellent hardness and optical characteristics. Once, solid dye had been interested as a strong candidate to replace the dye solution, but rapidly forced to be expelled by other solid-state lasers. However, there is still a strong demand for the laser source around 590 nm, and no solid-state laser including a diode laser has been developed at this wavelength range.

Around 590 nm, Rh-6G dye laser is still collecting wide interests due to its high potential in scientific application. However, the toxicity of dye and inconvenience in management is still an obstacle hard to solve. And the flashlamp pumping has been replaced by diode pumping structure in many solid-state laser systems, but it seems to be difficult for Rh-6G dye laser to have a same system, because of high price and bulky pumping system at 530 nm of the absorption peak wavelength.

Therefore, the dye mixture to use the energy transfer mechanism can be a solution for it, because the diode laser at the wavelength of coumarin dye is easier than that of rhodamine dye. We synthesized the dye mixture of Rh-6G and C-545 to investigate the availability of the energy transferred solid dye laser system.

Fig. 4 shows the fluorescence spectrum of the mixture of C-545 and Rh-6G. Fig. 4(a) shows the fluorescence spectrum of the mixture that molarity was 0.1 mM for both of C-545 and Rh-6G, and compared it to that of Rh-6G of 0.1 mM. A dot line is the fluorescence spectrum of solid Rh-6G only, when it is pumped by a 543 nm laser. And the spectral width of solid Rh-6G only was 47 nm, but it was narrowed to 44 nm when it is mixed with C-545 in the solid dye mixture, as depicted in a dashed line. The narrower spectral width results from partly overlapping absorption

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spectrum of C-545. However, the fluorescence spectrum of the solid dye mixture showed a broadened spectral width of 63 nm when it was pumped by the 450 nm laser, depicted by a solid line. It was 16 nm broader than the fluorescence spectral width of only Rh-6G when it was pumped by the 543 nm laser. The fluorescence peak of dye mixture appeared at 556 nm, which is 4 nm shorter than that of only Rh-6G.

Fig. 4(b) shows the fluorescence spectrum of the mixture that molarity was 0.3 mM and 0.1 mM for C-545 and Rh-6G, respectively. A dashed line indicates the fluorescence spectrum of the solid dye mixture of C-545 and Rh-6G, when it was pumped by the 543 nm laser. And the spectral width of dye mixture was 50 nm. Dashed line indicates the fluorescence spectrum of same solid dye mixture when it was pumped by the 450 nm laser, and the spectral width was broadened to 61 nm. And the fluorescence peak of solid dye mixture moved to 5 nm shorter wavelength from 555 nm, that is the fluorescence peak of Rh-6G only.

Fig. 4 shows the temperature distribution of the surface of the solid dye mixture, C-545 is added to Rh-6G, along with the output power of the laser and the molarities of dyes. The thermal profile on the surface is obtained after the sample is irradiated by the laser with the central wavelength of 450 nm for 5 min. The shape of the laser beam is rectangular. Fig. 5(a) shows the temperature distribution on the surface of the solid dye mixture, of which the molarity is 0.1 mM for both of C-545 and Rh-6G, when the irradiated laser power is 50 mW. The surface temperature of solid dye mixture increased to 30 °C, and then saturated. The temperature at the edge was about 28 °C on average. Fig. 5(b) shows the temperature distribution on the surface of the solid dye mixture, of which molarities are 0.3 mM and 0.1 mM for C-545 and Rh-6G, respectively, when the irradiated laser power was 50 mW. The surface temperature reached to 34 °C, but the temperature at the edge was about 28 °C on average, nearly same as that of Fig. 5(a). The surface temperature of Fig. 5(b) was 4 °C higher than that of Fig. 5(a), it was due to three times higher molarity of C-545 in Fig. 5(b) than that of Fig. 5(a). On the other hand, the temperature at the edge was remained about 28 °C on average in both cases. It was because of poor thermal conductivity of MMA host material.

The experiments repeated for two dye mixtures when the irradiated laser power raised to 200 mW. Fig. 5(c) shows the temperature distribution on the surface of solid dye mixture, of which molarity is 0.1 mM for both of C-545 and Rh-6G, when the irradiated laser power was 200 mW. The surface temperature reached to 38 °C. And the temperature at the edge was about 29 °C on average. Fig. 5(d) shows the temperature distribution on the surface of solid dye mixture, of which molarities are 0.3 mM and 0.1 mM for C-545 and Rh-6G, respectively, when the irradiated laser power was 200 mW. The surface temperature raised up to 53 °C, and the temperature at the edge was about 31 °C on average. The temperature was increased by the pump energy absorption by C-545, that has an absorption at a pumping laser wavelength of 450 nm. Higher molarity of C-545 could absorb larger pumping energy, but induced a temperature increase on the surface of solid dye mixtures. It can provoke the photodissociation that is the fatal to solid dye mixtures. Moreover, a large temperature gradient between center and edge of solid dye mixtures indicates that the thermal conductivity of host material, MMA, is poor. Though a solid dye mixture can provide wider tunability, higher molarity of C-545 is requested for more efficient energy transfer. Its operation condition should be limited by the pumping power level lower than damage threshold. Even if the mixture of two different dyes may have an improved property of the damage threshold, the photodissociation would occur due to accumulation of the heat. Changing the irradiated spot constantly, or introducing an additional cooling system may help reducing or delaying photodissociation.
Fig. 5. The temperature distribution on the surface of solid dye mixtures. (a) The solid dye mixture, of which molarity is 0.1 mM for both of C-545 and Rh-6G and (b) the solid dye mixture, of which molarities are 0.3 mM and 0.1 mM for C-545 and Rh-6G, respectively, when the irradiated laser power was 50 mW. (c) The solid dye mixture, of which molarity is 0.1 mM for both of C-545 and Rh-6G, and (d) The solid dye mixture, of which molarities are 0.3 mM and 0.1 mM for C-545 and Rh-6G, respectively, when the irradiated laser power was 200 mW.

Fig. 6 shows the temporal temperature variation for the center spot of the surface of solid dye mixtures. The measured temperature was obtained at highest temperature of the center spot where the sample absorbs the light. The sample surface was irradiated for 5 min by a laser diode of 450 nm. The temporal temperature variation was measured every 50 mW increment in the range from 50 mW to 200 mW of the irradiated laser power. Fig. 6(a) shows the temporal temperature variation for the solid dye mixture, of which molarity was 0.1 mM for both of C-545 and Rh-6G. The temperature was 30.7 °C after 5 min, when it is irradiated at 50 mW of the pumping laser power. It was increased to 39.0 °C when the irradiated laser power was 200 mW. Fig. 6(b) shows the temporal temperature variation for the solid dye mixture, of which molarity is 0.1 mM for both of C-545 and Rh-6G. The temperature was 34.4 °C after 5 min, when it was irradiated at 50 mW of the pumping laser power. And it was increased to 53.3 °C when the irradiated laser power was 200 mW.

Fig. 7 shows a temperature difference between two solid dye mixtures, after they are irradiated for 5 min by a 450 nm laser. When the pumping laser power was 50 mW, the temperature difference between two solid dye mixtures was 3.8 °C. However, the temperature difference increased to 14.3 °C, when the irradiated laser power was 200 mW. It is assumed that the host material of MMA has a low thermal conductivity. As increasing the irradiated laser power, the absorbed energy will be accumulated and changed into thermal effect to solid dye mixtures. The irradiated laser power must not exceed the damage threshold not to induce a photodissociation of the solid dye mixtures.
4. CONCLUSION

The solid dye mixtures of Rh-6G and C-545 were synthesized, and their optical and thermal properties were investigated. The synthesis process did not require the drying step to harden the solid dye mixtures.

In the fluorescent characteristics for the solid dye mixture, of which molarity was 0.1 mM for both of C-545 and Rh-6G, the emission peak appeared at 556 nm. And its spectral width was 63 nm, which is 16 nm wider than that of Rh-6G only. In case of the solid dye mixture, of which molarity was 0.3 mM and 0.1 mM for C-545 and Rh-6G, respectively, an emission peak appeared at 555 nm and its spectral width was 61 nm, which was 14 nm wider than that of Rh-6G only. The second solid dye mixture showed an emission peak at 1 nm shorter wavelength and a spectral width of 2 nm narrower than that of the first one. The second solid dye mixture has a higher molarity of C-545 for more efficient energy transfer than the first one. However, the stronger absorption of C-545 induced a narrower spectral width of the solid dye mixture. In thermal characteristics investigation, the higher molarity of C-545 could absorb more pump laser energy, but it provoked a local heat up that can cause a photodissociation. Therefore, we could get the information about the limitations of the solid dye mixture in molarity and pump laser power when it is applied to laser medium. The molarity of donor dye should not be excessive than that of acceptor, and the pumping laser power should be lower than the damage threshold of solid dye mixture, when C-545 and Rh-6G are synthesized for the solid dye mixture. The molarity and the pumping laser power are in a relationship of trade off each other. We showed the synthesizing a solid dye can be simplified than the former process by omitting the drying step.

Despite of these limitations, the solid dye mixture can have a broadened emission spectrum with extended selectivity of a pumping source. It can be applied to many fields, when it is used under certain pumping power level and molarity. Power level scale up is also expected to be possible when it is fabricated in a form of sophisticated power combining structure.

DISCLOSURE

The authors declare that there are no conflicts of interest related to this article.

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