



Performance evaluation of thin-film solar concentrators for greenhouse applications

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Abstract

Fluorescent Poly (methylmethacrylate) films embedded with a commercial coumarin dyestuff (MACROLEX Fluorescent Red G) were prepared by flow-spin coating technique. The absorption and emission spectra were recorded in order to determine the dye concentrations corresponding to the maximum fluorescence intensity and red shift. The emission band was optimized to match to the absorption band of chlorophylls (650–680 nm), which is the most important wavelength band for the photosynthesis process in plants. These films showed a remarkable stability against both photo and thermal degradation, pointing to their excellent weathering durability for using as photosensitive films in greenhouse applications.

Keywords: Solar concentrators; Greenhouse; Polymethylmethacrylate; Photosensitive films for photosynthesis applications

1. Introduction

The plant growth is a matter of primary importance for maintenance of life. A great deal of interest and research are directed towards improvement in agricultural crops by modification of environmental factors surrounding the plant. Light, as an important factor, has long been recognized as a crucial element in plant growth [1]. Fluorescent solar concentrators

(FSCs) have attracted the attention of a large number of scientists and engineers since the first proposal by Weber and Lambe [2]. The operation of the FSC, which can be considered as a peculiar kind of light guide, is based on the following principles. One or more high quantum yield species are dissolved in a rigid highly transparent medium of high refractive index. Solar photons entering the plate are absorbed by the luminescent species and reemitted in random directions. Following Snell's law, a large fraction of the emitted photons will be trapped

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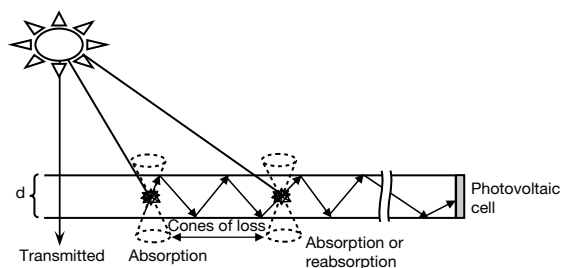


Fig. 1. Schematic representation of fluorescent solar concentrator.

within the plate and transported by total internal reflections to the edge of the plate, as illustrated in Fig. 1, where they will be converted by appropriate photovoltaic cells [3,4]. Recently, it has been reported that thin luminescent concentrator films could be implemented in the form of integrated devices or as sensitive elements in the traditional four-detector differential position sensors [5,6].

In this article we introduce a promising line of application of thin film FSCs in greenhouses. Transparent Polymethylmethacrylate (PMMA) films impregnated by a fluorescent organic laser dye of red emission spectra were prepared. As a result of small film thickness, a large fraction of the emitted photons is transmitted. The dye concentration could be optimized to match the spectral sensitivity for photosynthesis in red algae and higher plants [7].

2. Experimental

2.1. Material processing

Methylmethacrylate (MMA) monomer (Merck, Darmstadt, Germany) was freed from inhibitors by distillation at 50°C under reduced pressure using rotary evaporator ROTAVAPOR® R-114 (BUCHI, Switzerland). The polymer syrup (PMMA–MMA) was prepared by adding 0.1 wt.% AIBN initiator (Dupont, USA), to MMA. The solution was heated under reflux at 100°C for 1 h. The viscosity of the resulting

syrup was determined using BROOK FIELD DV-II+ viscometer (USA); which is equal to 20 cP. After cooling the syrup to room temperature, a coumarin dyestuff MACROLEX Fluorescent Red G (Bayer, Germany) was added in different concentrations (10, 20, ..., 100 ppm). The fluorescent PMMA films were prepared by flow coating of the solution on a polyethylene substrate which inclined vertically, then the substrate was spinned in a centrifuge at 2000 rpm for 20 s to obtain uniform film thickness [8]. In order to complete the polymerization of the residual monomer the substrates were kept in an electrical furnace at 50°C for 3 h, after that the films were removed carefully and cut into the desired area. The film thickness, determined using Fizeau fringe experiment [9] was found to be of the order of 0.5–1.5 μm .

2.2. Spectroscopic measurements

The absorbance spectra of the as prepared films were recorded in the wavelength range 190–1100 nm using UV–VIS spectrophotometer UNICAM (Helios Co., Germany). The fluorescence spectra were recorded in the range 200–900 nm using spectrofluorometer (SCHIMADZU RF-5301 PC, Japan); the spectrofluorometer is equipped with a temperature regulator. The photoreponse of the optimized film (100 ppm) towards UV–VIS light was performed using Xenon-arc lamp with the aid of photodegradation accelerator (SUNTEST XLS+, Germany); the film was irradiated at 1800 kJ/m² min for 24 h which corresponds to the irradiance for about 1 year exposure to sunlight.

3. Results and discussion

3.1. Absorption

The absorption spectra for all the as prepared PMMA films are shown in Fig. 2. Two major bands are observed. The first one lies in the UV region around ≈ 214 nm characterizing π – π^*

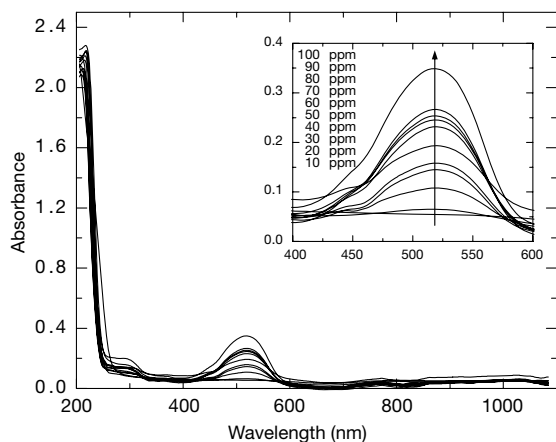


Fig. 2. Concentration effect on the absorption spectra of MACR Fluorescent Red G (inset), and PMMA/MACROLEX Fluorescent Red G films.

transition in the carbonyl group of PMMA. The second one appears around ≈ 520 nm corresponding to the vibrational transition to the first excited singlet state ($s_0 \rightarrow s_1$) of the dye [10]. It is noted that the dye absorbs the green–yellow band which is not utilized by chlorophylls (Fig. 3).

3.2. Fluorescence

The effect of dye concentration on the fluorescence spectra of the investigated films is illustrated in Fig. 4. It is observed that a maximum

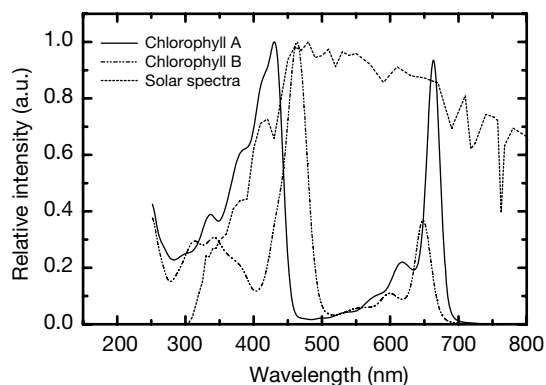


Fig. 3. The action spectra of photosynthesis [7].

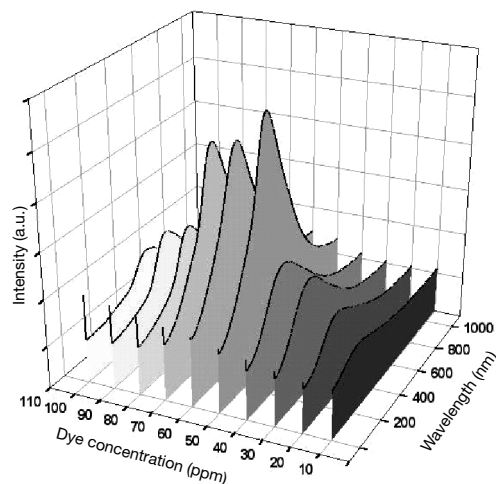


Fig. 4. Effect of MACROLEX Fluorescent Red G concentration on the fluorescence spectra of PMMA films.

in the intensity is obtained for the concentration 50 ppm and the maximum red shift (623 nm) for 100 ppm.

This remarkable red shift can be explained by the room temperature synchronous excitation spectra illustrated in Fig. 5. One distinct maximum can be observed at the coordinates (exc., ems.) = (520, 623 nm). The broadening of the contour lines indicates a wide distribution of the aggregated dye molecules which form excited dimers (excimers) at this concentration [11].

The absolute fluorescence quantum yield of the as prepared samples was calculated, relative to Rhodamine 101 doped in PMMA as a reference ($\phi_f \approx 100\%$), using the following equation [12].

$$\phi_f = \phi_{\text{ref}} (A_{\text{ref}} / A) (n / n_{\text{ref}}) (a / a_{\text{ref}}), \quad (1)$$

where ϕ_{ref} is the fluorescence quantum yield of the reference, A is the absorbance, n is the refractive index and “ a ” is the area under the fluorescence curve. The Stokes shift $\Delta\lambda_s$, which is a measure of self-absorption of the emitted light, was calculated from [13].

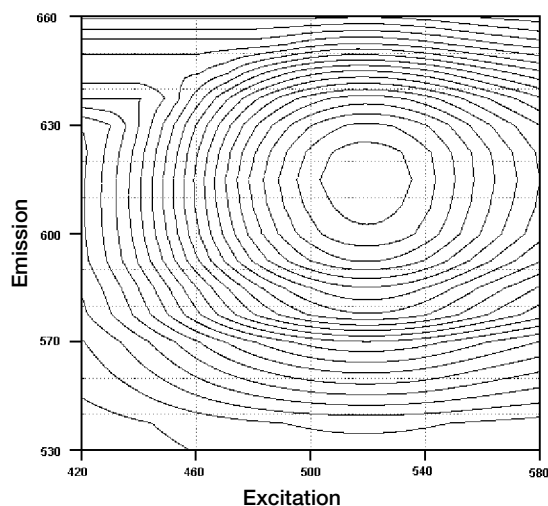


Fig. 5. Surface map representation of a synchronous excitation spectrum of PMMA/100 ppm MACROLEX Fluorescent Red G film.

$$\Delta\lambda_s = \lambda_{em} - \lambda_{abs}, \quad (2)$$

where λ_{em} and λ_{abs} are the wavelengths at the fluorescence and absorbance maxima respectively. The values of λ_{abs} , λ_{em} , $\Delta\lambda_s$ and ϕ_f are listed in Table 1. The observed decrease in ϕ_f accompanied with larger $\Delta\lambda_s$ values at concentrations

higher than 50 ppm can be attributed mainly to the formation of dimers and higher aggregates which have small values of ϕ_f . The strength of aggregation depends mainly on the dye nature, the host media and the other factors related to the preparation conditions. The decrease in the quantum yield at higher concentrations is caused by Förster-type energy transfer to dimers, the equilibrium between the monomer and dimer shifts to the side of the latter with increasing dye concentration [14]. The tabulated values of the transmittance at the emission wavelength T_{em} for different dye concentrations reveal that all the samples exhibit high transmission values with a maximum value around the concentration 50 ppm due to its excellent fluorescence properties, so most of the effective red light can be transmitted promoting the growth of the plants (Table 1).

3.3. Photostability

The accelerated photoresponse of the sample of 100 ppm towards UV–VIS radiation was studied. The film was irradiated with artificial sunlight from Xenon arc lamp for 24 h. The photodegradation $P\%$ which is the percentage change of optical

Table 1

The effect of concentration on the spectroscopic properties of the as prepared PMMA/MACROLEX Fluorescent Red G films

Concentration (ppm)	λ_{abs} (nm)	λ_{em} (nm)	$\Delta\lambda_s$	ϕ_f (%)	T_{em} (%)
10	517.00	578.80	61.80	15.60	94.40
20	523.00	589.60	66.60	22.80	94.97
30	521.90	589.60	67.70	33.80	96.04
40	524.00	593.00	69.00	42.90	97.11
50	521.30	597.20	75.90	90.60	97.65
60	522.10	605.20	83.10	78.40	97.60
70	520.20	609.80	89.60	75.70	97.26
80	520.60	610.80	90.20	39.70	96.22
90	519.50	615.00	95.50	34.60	94.94
100	518.80	623.40	104.60	23.20	93.98

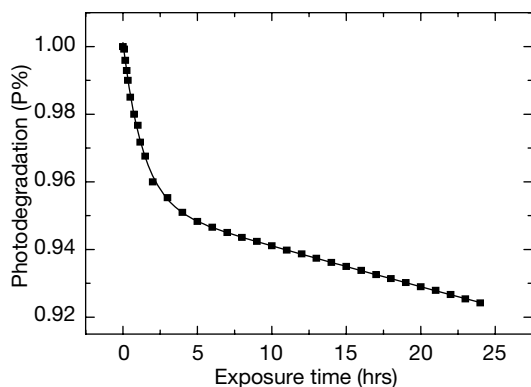


Fig. 6. The photodegradation curve of PMMA/100 ppm MACROLEX Fluorescent Red G film after indoor exposure to artificial sunlight from Xenon arc lamp for 24 h.

density is plotted versus the exposure time as illustrated in Fig. 6 and suggested two degradation rates obeying second order kinetic law

$$P = P_0 + C_1 \exp(-R_1 t) + C_2 \exp(-R_2 t), \quad (3)$$

where $P = P_0$ at $t = 0$ and R_1, R_2 are the photodegradation rates of the dye.

The calculated values of the photodegradation rates are $2.05 \times 10^{-4} \text{ s}^{-1}$ and $8.52 \times 10^{-7} \text{ s}^{-1}$ respectively. This clearly illustrates that the photodegradation rate decreased after two months of direct exposure to sunlight. It is also observed that the dye absorbance is decreased to 92.42% of its initial value after the irradiation for 24 h which is the period corresponding to one year exposure to sunlight. This indicates that PMMA is a good matrix for organic laser dyes since it can protect the dye from thermal and photodegradation.

3.4. Temperature Effect

The absorption spectrum of 100 ppm dye doped film was recorded at different temperatures in the range 273–353 K. It was found that there was no major thermal effect on the dye

molecules at temperatures below the glass transition temperature (T_g) of the PMMA matrix. This result is in good agreement with our published work before [15,16].

On the other hand the obtained fluorescence spectra were found to decrease to 93.35% of its initial value as the temperature increases to 353 K. The normalized fluorescence intensity against temperature is plotted in Fig. 7(a). An increase in the temperature also leads to phonon assisted relaxation processes; the electronic excitation energy can be dissipated by vibrations of the surrounding matrix and the energy levels of the fluorescent species [17]. The energy transfer rate, $K_{ET}(T)$, can be obtained by Arrhenius equation [18]

$$K_{ET}(T) = (K_{ET})_{T\infty} \exp(-E_a/RT), \quad (4)$$

where E_a is the activation energy of the transfer process and R is the universal gas constant and $(K_{ET})_{T\infty}$ equals K_{ET} at $T = \infty$. The value of K_{ET} at a given temperature is proportional to the relative emission intensity of the dye molecule (I_0/I_T) where I_0 and I_T are the emission intensities at zero and T temperatures respectively. Arrhenius plot of $\ln(I_0/I_T)$ vs. $10^3/T$ gives a reasonably good linear fit and the calculated value of E_a found to be 0.794 kJ/mol. After cooling the sample to room temperature the fluorescence intensity retained to its initial value; this indicates that the film exhibits excellent weathering durability in different climates, since our study covered wide range of atmospheric temperatures.

4. Conclusion

The film of concentration 100 ppm showed the closest emission band to the action spectra of photosynthesis in higher plants with a high transmission of red light (97.65%) and a remarkable photoresponse towards UV–VIS solar radiation. More efforts to increase the effective transmission of red light and the stability of the films are in

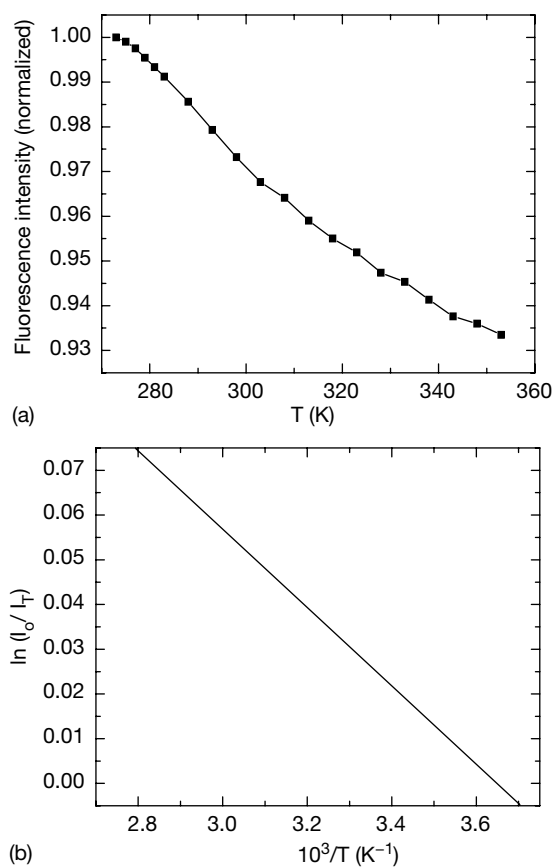


Fig. 7. (a) Fluorescence intensity as a function of temperature and (b) Semilogarithmic plot of emission relative intensities, $\ln I/I_0$ versus $1/T$ for PMMA film embedded with 100 ppm MACROLEX Red G.

progress [19]. These films can act as promising photoselective films which increase the irradiance level for photosynthesis in greenhouses. Also it can be used in growing rooms in which plants are grown for commercial purposes e.g., red algae which are of great economical importance in food, pharmaceutical, cosmetic, and industrial applications [20].

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