Investigation of peculiarities in conversion of the UV and visible sunlight by light transforming films with europium luminophores

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We have studied how the sunlight energy is converted in polymer films doped with europium photoluminophores that are widely used as greenhouse polymer films. From the transmission spectra of various light films, the contribution of luminescence is quantitatively determined, in the regions of natural luminescent emission and absorption of plant phytochromes. The enhancement of electromagnetic radiation in the red spectral region due to luminescence at propagation through the films is found to be less than 1% of the sunlight intensity in the same spectral region, or 0.001–0.01 W/m^2. Uncontrolled change in the transmission of electromagnetic radiation by high-pressure polyethylene films in the same spectral region due to reflection by the polymer matrix is two to three orders of magnitude greater than that due to photoluminescence. The determined indices of change in the spectral composition of the electromagnetic radiation transmitted through the films do not confirm the hypotheses explaining faster growth and development of plants under such films (polysvetan effect) by currently known mechanisms of photoregulation of the plant growth. The explanation of the polysvetan effect as an example of the low-energy photoluminescent biostimulation similar to the low-energy light-induced biostimulation under the exposure to LED luminescent radiation and low-energy laser radiation is discussed.

Introduction

The study of spectral composition of the sunlight transmitted by polymer films doped with europium photoluminophore is of interest in connection with their efficient practical application.[1] Such films, called light transforming films, are used as greenhouse material for farm, ornamental, and young plants.[1,2] The usage of light transforming films significantly increases the crop and shortens the growth and ripening period.[1–4] This effect, called the polysvetan effect, has not been so far explained scientifically.

The factors determining the presence of the polysvetan effect remain unstudied, and no unified theory exists. The existing hypotheses of this effect are based on the statement that light transforming films absorb significant fraction of the UV sunlight and transform it into the red spectral region.[3,4] The change of the spectral composition of the red radiation under films, in its turn, affects the photoregulation system of plants, which functions through red (Φ_r) and far-red (Φ_{fr}) phytochromes with the absorption peaks at 660 nm and 720 nm, respectively. The system functions according to the principle of competing photochemical reactions and further development of

the corresponding chains of biochemical reactions leading to regulation of plant growth and development.

However, recent experiments on determination of the absorption of the UV radiation transmitted by light transforming films do not confirm these hypotheses.[5,6] The most typical light transforming films doped with europium photoluminophores absorb only insignificant amount (about 1%) of the incident UV sunlight. The contribution of the red luminescent component to the photosynthetically active solar radiation in this case was estimated as only 0.01–0.001% [Refs. 7, 8]. Such a low contribution of the luminescence radiation makes it unlikely that the polysvetan effect be explained by the plant phytochromic regulation system. This contradiction can be resolved based on experimental determination of the changes in the spectral composition of the solar radiation transmitted through typical light transforming films in the regions of absorption of Φ_r and Φ_{fr} plant phytochromes and natural luminescence emission of photoluminophores in light transforming films.

Experiment

For the experiment, we took high-pressure polyethylene (HPPE) films modified by organic

europium photoluminophores that are most typical of light transforming films.

Modifying agents were narrow-band red photoluminophores: organic one is based on the complex of europium nitrate with 1,10-phenanthroline (FE grade)[9] and inorganic photoluminophores is based on oxysulfide of yttrium activated by europium (KS-626, PUL-1, KTC-626 grades).[6]

Films of 120-μm thickness were made by mixing 0.1–3.0% (m/m) powder photoluminophores with HPPE granules by the technology described in Ref. 10 and by the following extrusion of the melt on an extruder with a flat die at the temperature of 170–200°C or blown extrusion under the conditions corresponding to the Russian State Standard No. 16337.

Photophysical properties of the films in connection with the photoluminophore doping were studied using samples with the thickness (120 ± 1) μm taken from film series without previous conditioning.

The transmission spectra of the films for artificial radiation were recorded with an Uvicon-933 spectrometer, and the transmission and reflection spectra for the sunlight were recorded with a Kvartz-3102V photoacoustic spectrometer on a fine sunny day by the method described in Ref. 7.

Results and discussion

The quantitative characteristics of the changes in the spectral composition of electromagnetic radiation can be determined from the transmission spectra of the light transforming films for the sunlight at the peaks of natural luminescence and the peaks of absorption by plant phytochromes and in the spectral intervals determined by FWHM (full width at half maximum) of the bands. The absorption intervals for phytochromes determined in this way by the data from Ref. 11 are: 620–680 nm (peak at 660 nm) for Φ_r and 675–750 nm (peak at 720 nm) for Φ_{fr}. The ranges of natural luminescence of photoluminophores in light transforming films were taken equal to the base width of the fundamental bands in their fluorescence spectra obtained using artificial sources of inducing UV radiation.[6,7] For the organic photoluminophores such interval is 610–630 nm (peak at 617 nm), and for the inorganic ones it is 620–650 nm (peak at 626 nm).

The transmission spectra of the light transforming films doped with organic and inorganic photoluminophores for the sunlight in the visible spectral region show the increase in reflection of radiation all over the spectral region at photoluminophore doping (Figs. 1 and 2).

In contrast to the line transmission spectrum of the films, the luminescence bands can be correctly determined not for all samples of light transforming films. The very low intensity allows determination of the luminescence parameters only for films with rather high content of luminophores: about 0.05% (m/m) for the organic ones and about 0.5% (m/m) for the inorganic ones, which is 2 to 5 times higher than their

typical content used in practice. At the lower contents of these photoluminophores in the light transforming films, their natural luminescence band has low intensity and cannot be used for reliable quantitative calculations.
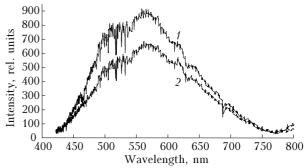

Fig. 1. Spectra of the solar radiation (curve *1*) and the solar radiation transmitted through the film with 1% (m/m) FE (*2*) without correction for spectral sensitivity of the photodetector.
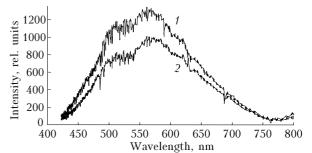

Fig. 2. Spectra of the solar radiation (curve *1*) and the solar radiation transmitted through the film with 5% (m/m) KTC-626 (*2*) without correction for spectral sensitivity of the photodetector.

Tables 1 and 2 summarize the results on the intensity of solar radiation transmitted through the films at the peaks of luminescence (617 and 626 nm) and phytochrome absorption (660 and 720 nm).

These results show that photoluminophore doping leads to a decrease in the transmittance of the sunlight as compared with unmodified films at the wavelength corresponding to the peaks of phytochrome absorption and the peaks in the luminescence spectra of photoluminophores. The value of this decrease is determined by the nature of photoluminophores and their content. Thus, as 0.05–2.0% (m/m) of the FE luminophore is doped to the HPPE film, the transmittance for the sunlight decreases by 1.7 to 24.1% as compared to the unmodified HPPE films at all the wavelengths chosen. Similar changes are also observed for the films doped with inorganic luminophores (see Table 2).

This decrease in the transmittance is expected and connected with additional reflection and scattering of radiation by disperse photoluminophore particles in the films as compared to unmodified films made of the same material. However, these changes can be detected only when comparing films made of the same batch of basic HPPE at the same equipment under rigorously

identical conditions. The use of HPPE of different basic grades, different batches of the same grade, or variation of extrusion conditions during fabrication of films leads to significantly different transmission characteristics for even unmodified HPPE films (samples 1, 5, and 7 in Table 1 and sample 1 in Table 2). Significantly different indices of reflection and scattering are also characteristic for HPPE films, since HPPE is a crystalline polymer material.[12]

The degree of crystallinity, shape and arrangement of crystals, and the state of the film surface significantly affect the optical properties of the films and are determined, in their turn, by features of the polymer and film production technologies. Foreign solids and substances in the polymer can also significantly change the analyzed indices. The content of such foreign solids and substances in HPPE films, as regulated by the Russian State Standard No. 16337, is close to the typical content of photoluminophores in light transforming films (from some hundredths to 0.2% (m/m) of polymer).

In this connection, the systematic study of the effect of photoluminophore doping on the transmittance by measuring the absolute values of various indices of light transforming films is practically impossible even if one uses techniques with strictly standardized conditions, artificial light sources, and constant parameters of spectral energy brightness. A typical approach to solution such problems is to find regular changes in the transmission for a series of films made by the same technology under the same conditions from HPPE of the same grade with only different amount of modifying agents. Comparison of the transmission coefficients determined in such a way will allow us to estimate the value of the regular change due to addition of the modifying agents against the typical intervals of variability of the transmission coefficients for this class of materials.

The typical variability of the transmission coefficients for radiation at the chosen wavelengths due to numerous hard-to-control factors not connected with the photoluminophore doping is $\pm$ 5% of the nominal value for identical HPPE films of different series (samples 1, 5, 7 in Table 1, sample 1 in Table 2). At the same time, the regular changes in the transmission coefficients of the films at the same wavelengths due to photoluminophore doping are much smaller (see Tables 1 and 2). The regular changes of about 10% are observed for the films doped with 1−2% (m/m) FE photoluminophore, but this is 10 times higher than the luminophore content typical of practically used light transforming films. In this case, the changes in the transmittance of the HPPE light transforming films at the wavelengths corresponding to the peaks in the luminescence spectra of photoluminophores due to their natural luminescence are much lower than those due to radiation scattering and reflection (see Tables 1 and 2).

Table 1. Transmittance of light transforming films doped with FE luminophore for the sunlight

Sample	Content of FE luminophore, % (m/m)	Film transmittance, %, at the wavelengths, nm			Decrease in transmittance due to luminophore doping, %, at the wavelengths, nm			Luminescence contribution, %, nm
		617	660	720	617	660	720	617
1	NA	78.8	80.5	81.0	—	—	—	NA
2	0.05	75.0	78.8	78.6	3.8	1.7	2.4	0.9
3	0.3	70.8	70.1	67.8	8.0	10.4	13.2	1.8
4	0.5	60.8	66.2	62.8	18.0	14.3	18.2	3.8
5	NA	85.8	90.1	90.4	—	—	—	NA
6	0.5	73.6	76.1	76.2	12.2	14.0	14.2	6.2
7*	NA	90.9	91.9	90.1	—	—	—	NA
8*	0.5	79.4	78.9	76.9	11.5	13.0	14.8	5.8
9*	1.0	86.2	84.9	81.8	4.7	7.0	8.3	9.5
10*	2.0	66.8	69.1	68.6	24.1	23.8	21.5	9.5

* Film is made by a flat-die extruder.

Table 2. Sunlight transmittance by light transforming HPPE films doped with inorganic luminophore

Sample	Luminophore		Sunlight transmittance, %, at the wavelength, nm			Decrease in transmittance due to luminophore doping, %, at the wavelengths, nm			Luminescence contribution, %, nm
	Grade	Content, % (m/m)	626	660	720	626	660	720	626
1	—	NA	86.9	87.0	87.1	—	—	—	NA
2	KS-626	0.5	76.5	77.2	76.7	10.4	9.8	10.4	2.5
3		2.0	68.1	69.6	70.1	18.8	17.4	17.0	3.1
4	PUL-1	0.5	82.0	80.2	82.1	4.9	6.8	5.0	1.6
5		2.0	70.1	67.1	68.1	16.8	19.9	19.0	3.0

It is worthy to note different directions of the effects. If the luminescence leads to the increase in the intensity of red radiation, then the reflection leads to its decrease. Doping of photoluminophores in the typical amounts of 0.02–0.2% (m/m) results in the total decrease of the radiation intensity due to reflection and scattering, rather than the increase due to the luminescence component even at the wavelengths corresponding to peaks of the luminophore luminescence spectra. As this takes place, the integral variability remains within the interval typical of unmodified HPPE films.

A more detailed information about the possible effect of luminescence in the red spectral region on the functioning of the plant phytochrome system can be obtained by determining the changes in the solar radiation transmitted by the light transforming films in the regions of phytochrome absorption and natural luminescence of photoluminophores (Tables 3 and 4). Transmission indices were also determined by comparing the properties of photoluminophore-doped films with those of unmodified HPPE films from some series.

The changes in transmittance in the spectral regions studied generally obey the regularities described above. As 0.05–2.0% (m/m) of organic luminophore is doped into the HPPE films, the sunlight transmittance decreases regularly by 4–29% as compared with the unmodified HPPE films in the luminescence region, by 1.5–24% in the 620–680 nm region, and by 3.8–21% in the 675–750 nm region (see Table 3). The changes due to the luminescence radiation are from 0.056 to 1.03%, which is 2 to 3 orders of magnitude

lower than the changes in the film transmittance due to reflection and scattering. For the films doped with 0.5–2.0% (m/m) concentration of inorganic luminophores, the transmittance in the region of natural luminescence (620–650 nm) decreases by 12–22% (samples 2, 3 in Table 4) for the KS-626 luminophore and by 9–21% for the PUL-1 luminophore (samples 4, 5 in Table 4). The increase of transmittance due to the contribution of the luminescence in the red spectral region is only 0.092–0.18%, which is also 2 to 3 orders of magnitude lower than the decrease of transmittance in the same spectral regions due to reflection and scattering, in particular, at the wavelengths of natural luminescence of the photoluminophores. The integral changes of the transmittance in the analyzed spectral regions for the films with the typical content of additions also fall within the variability domain of the transmittance of unmodified HPPE films.

The obtained values of the changes in the transmittance due to the luminescence in percent of the red radiation transmitted by the film allow us to calculate the changes in the intensity of the red solar radiation transmitted by the films for particular radiative conditions. Tables 5 and 6 exemplify such calculations made for the solar spectral characteristics typical of Tomsk region.

The calculations were made by relating the spectrum areas for some spectral regions to the total area of the spectrum corresponding to the particular solar radiation intensity measured under the conditions of spectrum recording.

Table 3. Sunlight transmittance by light transforming films doped with FE luminophore

Sample	Luminophore, % (m/m)	Radiation transmittance, %, in the regions, nm			Decrease in transmittance at luminophore doping, %, in the regions, nm			Contribution of luminescent radiation, %, in the region, nm
		610–630	620–680	675–750	610–630	620–680	675–750	610–630
1	NA	82.3	84.6	85.3	0.0	0.0	0.0	NA
2	0.05	78.4	83.1	81.1	3.9	1.5	3.8	0.056
3	0.3	72.4	77.3	74.9	9.9	7.3	10.4	0.096
4	0.5	64.2	72.5	69.1	18.1	12.1	16.2	0.62
5	NA	86.7	91.3	92.8	0.0	0.0	0.0	NA
6	0.5	74.5	78.2	78.9	12.2	13.1	13.9	0.52
7	NA	90.3	89.1	88.5	0.0	0.0	0.0	NA
8	0.5*	77.4	77.2	75.0	12.9	11.9	12.5	0.51
9	1.0*	81.6	82.3	81.8	8.7	6.8	6.7	1.03
10	2.0*	61.1	64.4	67.9	29.2	24.7	21.4	0.93

* Film is made by a flat-die extruder.

Table 4. Contribution of luminescent radiation to radiation transmitted by films doped with inorganic luminophores

Sample	Luminophore		Sunlight transmittance, %, in the regions, nm			Decrease in sunlight transmittance due to luminophore doping, %, in the regions, nm			Contribution of luminescent radiation, %, in the region, nm
	grade	content, % m/m	620–650	620–680	675–750	620–650	620–680	675–750	620–650
1	–	NA	90.3	90.1	88.5	NA	NA	NA	NA
2	KS-626	0.5	77.4	76.7	76.7	12.9	12.4	11.8	0.12
3		2.0	67.4	68.6	68.6	22.9	20.5	19.9	0.18
4	PUL-1	0.5	81.1	81.4	83.2	9.2	7.7	5.3	0.092
5		2.0	69.2	68.6	67.4	21.1	20.5	21.1	0.14

Table 5. Contribution of luminescence to solar radiation transmitted by films doped with FE luminophore (for different solar radiation intensity in the region of 400−800 nm)

Sample	Luminophore content, % m/m.	Intensity of solar radiation transmitted by films, W/m^2, in the regions, nm			Luminescent radiation intensity, W/m^2
		610−630	620−680	675−750	
			168 W/m^2		
1	NA	9.4	17.3	7.7	−
2	0.05	8.9	17.0	7.4	0.005
3	0.3	8.3	15.8	6.8	0.008
4	0.5	7.3	14.8	6.5	0.05
			215 W/m^2		
5	0.5*	11.0	22.1	9.9	0.057
6	0.5*	11.4	21.8	9.5	0.06
7	2.0*	9.0	18.2	8.6	0.18
			223 W/m^2		
8	0.5*	12.5	23.2	12.0	0.063
9	2.0*	9.9	19.3	10.8	0.092

* Film is made by use of a flat-die extruder.

Table 6. Calculated contribution of luminescent radiation to the solar radiation transmitted by films (for the intensity of 222 W/m^2 in the 400−800 nm region)

Sample	Luminophore		Intensity of solar radiation transmitted by films, W/m^2, in the regions, nm			Luminescent radiation intensity, W/m^2
	Grade	Content, % m/m	620−650	620−680	675−750	
1	KS-626	0.5	13.9	23.0	12.3	0.016
2		2.0	12.1	20.6	11.0	0.021
3	PUL-1	0.5	14.6	24.4	13.3	0.013
4		2.0	12.4	20.6	10.8	0.017

The results obtained (see Tables 5, 6) show that for the HPPE films the typical interval of random, uncontrolled changes in the intensity of the solar radiation transmitted by light transforming films due to reflection and scattering is about 10 W/m^2 in the regions of plant phytochrome absorption. The regular changes of the radiation intensity in the red spectral region due to the contribution of the secondary luminescence of photoluminophores doped in the films even for the maximum intensity of the UV solar radiation during midday are 2 to 4 orders of magnitude lower. The regular changes obtained for the typical light transforming films fall within the variability range of parameters of the unmodified HPPE films. Thus, it can be stated that we did not find regular integral changes in the spectral composition of the red solar radiation transmitted by typical light transforming HPPE films doped with europium photoluminophores.

Conclusion

Doping HPPE films with photoluminophores in the typical amount of tenths percent results in manifestation of photoluminescent properties of the luminophores and the capability of generating secondary luminescent radiation, whose intensity is determined by the luminophore type and content and by the particular conditions of spectrum recording thus being from 0.1 to 0.005 W/m^2, under the exposure to the solar radiation. Such changes in the intensity of the red radiation are 2 to 4 orders of magnitude lower than variations of the radiation intensity in the same spectral region due to reflection and scattering for the

unmodified HPPE films. The integral changes in the spectral composition of the solar radiation fall within the variability range typical of HPPE films.

These changes in the spectral composition of the sunlight give no grounds for explanation of the polysvetan effect by functioning of the plant phytochromic photoregulation system at variation of the red radiation under the light transforming films due to the luminescence. Besides, the results obtained give no grounds for using the modern theory of phytochromic photoregulation of plant growth and development for explanation of the polysvetan effect.

The longer than decade experience of using HPPE films of various basic grades and production methods for cladding greenhouses brings out clearly that the above changes in the spectral composition of the radiation are not accompanied by such a significant physiological effect on plants as the polysvetan effect. The polysvetan effect observed in case of using light transforming HPPE films is determined by the presence of photoluminescent radiation with the intensity from several hundredths to several thousandths of W/m^2. It can be qualified as a version of low-intensity photoluminescent bioactivation similar, in its principle, to the widely known low-intensity photoinduced bioactivation by red LED electroluminescent radiation and low-intensity laser radiation.[13]

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