Determination of the contribution from light-transforming polymer films to red portion of transmitted solar radiation due to UV-excited luminescence

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The contribution of the red luminescent component to the solar radiation transmitted through the light-transforming polyethylene films with 0.05–5% m/m additives of photoluminophore based on organic and inorganic europium compounds has been determined. The investigations into this field are connected with the study of factors determining a marked increase in the economical productivity of plants when cultivated under such films (polysvetan effect). The data obtained based on the spectra of solar radiation transmission and reflection by light-transforming films and the initial disperse photoluminophore have shown that the contribution of luminescent radiation in the region near 600 nm is 0.01–0.1% or 0.004–0.39 W/m^2. In this case, the variations of transmission for the radiation in the same spectral region by light-transforming films due to uncontrolled reflection and scattering are two to three orders of magnitude greater than the contribution of the luminescent component. The data obtained do not confirm the hypotheses existing on the polysvetan effect by the action of the phytochromic mechanism of plants due to the enhanced portion of the red component in the transmitted solar radiation. The polysvetan effect may be an example of the low-energy photoluminescent biostimulation analogous to the known low-energy photoinduced biostimulation under the exposure to the red laser and LED radiation.

Studying the changes in the spectral composition of the solar radiation transmitted through a polymer film with photoluminophore additives is of interest in connection with investigation of the factors determining an effect of this radiation on the growth and development of plants. This effect accompanying the accelerated growth and ripening of plants, referred to as a polysvetan effect,[1] is now widely used in practice. Polymer films with additives of narrowband red photoluminophores (light-transforming films) are now in mass production by the Russian industry[2] and thus are widely used in greenhouses in the agriculture.[1–4]

Despite the high efficiency of the practical application of light transforming polymer films is known for a rather long time, no scientifically justified explanation to the nature of the polysvetan effect has been given so far. This is connected, in the first place, with few results of investigation into the effect exerted by the light-transforming films on the spectral composition of solar radiation passed through such films. The paucity of data can be explained by a multifactor dependence of the changes in spectral composition on the numerous and continuously varying natural conditions. This multifactor dependence is also an obstacle in studying the factors confirming the existence of the polysvetan effect. The most important part in determination of such factors is determination of the contribution of the UV-excited luminescence component to the solar radiation transmitted through light-transforming films. Besides, if this contribution will be determined for typical light-transforming films, it will become possible to obtain the polysvetan effect under strictly controllable laboratory conditions, rather than under the natural conditions that vary widely.

Experimental techniques

These investigations have been carried out with the most typical greenhouse light-transforming films – high-pressure polyethylene (HPPE) films modified by organic photoluminophores based on europium compounds. Narrowband red-light photoluminophores – complexes of 1,10-phenanthroline with europium nitrate (PE)[5] and with the mixture of europium and lanthanum nitrates (PLE)[6] – were used as modifiers.

Films of 120 μm thickness were fabricated through mechanical mixing of 0.05–5.0% m/m powdered photoluminophore additives with HPPE granules by the technology described in Ref. 7 and the following extrusion of the obtained melt on a flat-die extruder at the temperature of 170–200°C or the blown extrusion on a URP-1500 film line under the conditions that accord with the Russian State Standard No. 16337.

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The features in the photophysical properties of the films due to addition of photoluminophores were studied using series of (120 ± 1) μm thick samples from different film sets.

The transmission spectra of the films were recorded with a Uvicon 933 spectrometer. The spectra of transmission and reflection of the solar radiation by the films were recorded with a Kvarts-3102V photoacoustic spectrometer under sunshine following the technique described in Ref. 8.

The relative intensity of the luminescence of the light-transforming films was determined using a fluorimeter with crossed filters following the technique described in Ref. 9 (a DDS-30 lamp with an UFS-2 filter as a source of the exciting UV radiation, and an OS-12 filter for isolating the reemitted radiation).

Results and discussion

The easiest way to determine the contribution of the luminescent radiation to the solar radiation transmitted through the films is to use the transmission spectra of the films with the 0.03–0.2% m/m luminophore content[8] typical for the light-transforming films used in practice (Fig. 1).

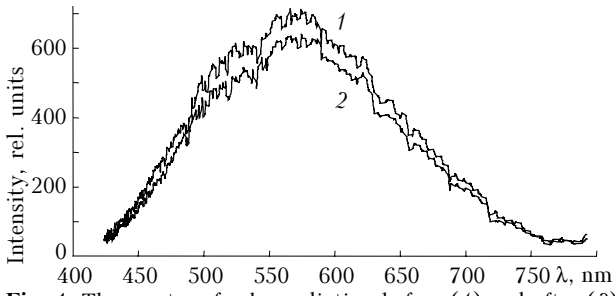

Fig. 1. The spectra of solar radiation before (*1*) and after (*2*) transmission through the film with the 0.1% m/m PE luminophore content. The spectra are not corrected for the spectral sensitivity of the photodetector used.

However, this method fails to provide for a reliable estimate of the contribution of the luminescent radiation because of a very low intensity of the luminescent radiation excited by the solar UV radiation against the background of the intense spectrum of solar radiation. Such spectra allow calculation of only total transmission coefficients of the light-transforming films for the sunlight.

In general, a detailed determination of the spectral composition of solar radiation passed through the light-transforming films under natural conditions, in particular, the intensity of the luminescence, from these transmission spectra is a very complicated problem because of the large number of variable factors determining the integral properties.

These factors can conditionally be divided into two groups.

The first group incorporates the factors connected with the time variations in the spectral composition and the intensity of the solar radiation incident on the light-transforming films. These sunlight parameters vary widely depending on the season and time during a day, as well as on the particular weather conditions, ecological situation, and many other factors.[10] These factors produce crucial changes in the spectral composition and the intensity of the shortwave and, first of all, UV component[11]: even during one daylight hour the intensity of the UV radiation may vary by more than 300 times. At the same time, the UV component of the solar radiation excites luminescence of photoluminophores in the light-transforming films and determines their general luminescent properties. In this connection, the results obtained under different experimental conditions may be not comparable.

The second group includes the factors connected with the film properties determined by the properties of the initial material – high-pressure polyethylene, which is a crystal polymer. The degree of crystallinity of the material, 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 the technology of production of the initial basic polymer and its processing in the film. These differences in the optical properties of the unmodified HPPE films result in practically unpredictable variations of the transmission coefficients for the UV and visible radiation in a wide range (from 0.6 to 0.95) [Refs. 12 and 13], as well as variation of the fraction of the direct and diffuse radiation. In addition, these factors introduce a significant error in determination of the regular changes in the spectral composition of the sunlight transmitted through the light-transforming films due to addition of photoluminophores.

The simplest way to avoid the effect of the most of the above factors is to obtain the spectral characteristics for a series of light-transforming films made of single-set HPPE by the same technology at the same equipment under strictly identical conditions with the only difference that is the amount of additives. The sunlight transmission spectra for one set of the films should be recorded on the same day near noon characterized by the highest intensity of the UV radiation for the as short as possible time (no longer than 1 hour for the whole series).

So, using these approaches, we have revealed that, for reliable determination of the intensity of luminescent radiation of the light-transforming films, it is necessary to increase the content of luminophores in them by 10–50 times as compared to that typical of the practical films up to 5.0% m/m. The bands of luminescent radiation nearby 617 nm are clearly seen in the sunlight transmission spectra of these films (Fig. 2).

This allows us to calculate reliably the intensity of the luminescent radiation of the photoluminophores in the films at excitation by the UV solar radiation by relating the signal area to the total area of the transmission spectrum corresponding to the region of the photosynthetically active radiation (PAR), namely, 380–710 nm.

However, the use of the spectra not corrected for the spectral sensitivity of the spectrometer gives the understated result, because Kvarts-3102V

spectrometers have low spectral sensitivity in the shortwave (nearby 400 nm) and longwave (nearby 700 nm) regions and their maximum sensitivity is in the region of the luminescent radiation (Fig. 3). So we have calculated the correction coefficient, which accounts for different areas of the sunlight spectrum recorded with a Kvarts-3102V and the net sunlight spectrum in the PAR region.[10]

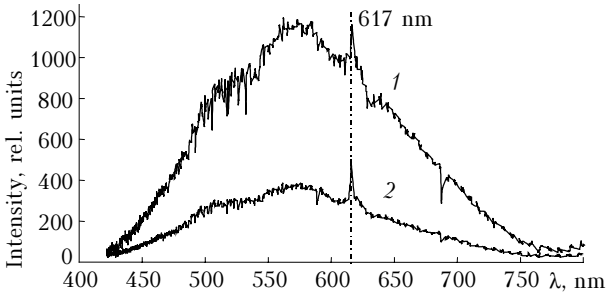

Fig. 2. The spectra of solar radiation transmitted through the HPPE film with 5% m/m addition of PLE luminophore (*1*) and transmitted by the HPPE film with 3% m/m addition of PLE luminophore (*2*). The spectra are not corrected for the spectral sensitivity of the photodetector used.

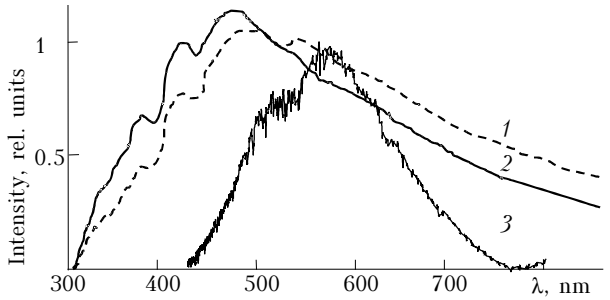

Fig. 3. Energy distribution in the solar spectrum: net (*1*) and diffuse (*2*) radiation (clear sky); the spectrum recorded with the Kvarts-3102V spectrometer (*3*).

The contribution of the luminescent radiation as determined from the sunlight transmission spectra of the light-transforming films with PLE luminophore additives with the allowance made for the correction coefficient of 1.75 (Table 1) is not very significant even at the maximum intensity of the UV radiation. For the films with the PLE luminophore content up to 1% m/m under sunshine conditions at noon for the net solar radiation in the PAR region equal to 214 W/m^2 and the intensity of the UV component equal to 18 W/m^2, it is equal to hundredths of W/m^2. The increase of the luminophore content up to 5% m/m leads to an obvious increase of the contribution up to tenths of W/m^2.

Determination of the total intensity of the luminescent radiation excited by the sunlight allows calculating the specific contribution of the luminescent radiation from the luminophore of the light-transforming film – the contribution at the unit relative luminescence intensity (Table 1). The specific contribution is roughly the same for all films, except for film 2 in Table 1, with the luminophore content of 0.5% m/m. This may be due to insufficient accuracy of determination connected with a rather low intensity of the film luminescence and the impossibility of accurately calculating the area of the luminescence band commensurable with the level of background noise in the spectrum. The increase of the luminophore content in the films and, thus, the luminescence intensity allows reliable determination of the index.

The obtained values of the specific contribution allow us to calculate the total luminescence intensity of the films with almost any, even very low, luminophore content from their relative luminescence intensity measured under identical conditions by the technique described above. For the most typical film with the PLE luminophore content of 0.1% m/m and the particular weather conditions of the experiment, this contribution is about 0.01 W/m^2 (film 1 in Table 1). It should be noted that the luminescence intensity is given in the Table 1 up to the third and fourth decimal point to illustrate the order of magnitude of variations in response to the changes in the composition of the light-transforming films. These results can be obtained only if the above conditions, namely, recording of the spectra under sunshine, are met. The sky radiance varying due to clouds and close in the intensity to the net radiation (Fig. 3) results in the fast and significant changes of the spectral composition of the recorded radiation.

Table 1. Contribution of the luminescent component to the sunlight transmitted through the light-transforming films with PLE luminophore additives

Film #	PLE content, % m/m	Luminescence intensity, rel. units	Contribution determined from the transmission spectra		Contribution determined from the reflection spectra	
			W/m^2	Specific, W/m^2 per unit intensity of luminescent radiation	W/m^2	Specific, W/m^2 per unit intensity of luminescent radiation
1	0.1	6.1	0.007*	–	0.01*	–
2	0.5	38.5	0.03	0.0008	0.06	0.0016
3	1.0	66.7	0.08	0.0012	0.10	0.0015
4	2.0	89.7	0.12	0.0013	0.15	0.0017
5	3.0	115.4	0.14	0.0012	0.18	0.0016
6	5.0	141.0	0.19	0.0013	0.22	0.0016

* Calculated from the luminescence intensity and the specific contribution of the luminescent radiation.

The attempts to determine the luminescence intensity in the immediate proximity to a plant community give the same result. Insignificant air motions move leaves reflecting about 20% of the incident radiation, which results in chaotic and continuous variation of the spectral composition of the incident radiation and the increase of the background noise in the spectrum up to the level higher than the magnitude of the factors to be determined. For the real conditions of the use of typical light-transforming films as a greenhouse material, the film luminescence intensity is much lower than the level of noise, namely, continuous and chaotic changes in the spectral composition of the solar radiation due to numerous factors, especially, at the low intensity of the UV radiation in the morning and evening hours and at dense cloudiness.

The accuracy of the experimental determination of the luminescence intensity of the light-transforming films can be increased by using the spectra of solar radiation reflected from these films. If luminophore particles in the films are considered as point sources of radiation emitting uniformly into the entire sphere, the luminescence intensity above and under the illuminated films must be practically the same. In this case, the specific contribution of the radiation to the radiation reflected by the films (about 10%) must be much higher than that to the transmitted radiation (about 90%). Actually, the relative intensity of the bands corresponding to the luminescent radiation in the sunlight reflection spectra is much higher than in the transmission spectra, all other conditions being the same as shown in Fig. 2.

The contributions of the luminescent radiation calculated from these spectra are 22% higher than those estimated from the transmission spectra. The result is overstated due to complicated determination of the scattering coefficients of the films for the reflected radiation and the corresponding calculation of the intensity of the solar radiation reflected by the films using the model of mirror reflection. The use of the reflection spectra improves the accuracy of the experimental determination, as indicated by the close agreement between the specific contribution for the film with 0.5% m/m of luminophore to that of the other films (see Table 1).

The value of the specific contribution again allows us to calculate the total intensity of the luminescent radiation of the films with any luminophore content. With the allowance made for the scattering by the films of the reflected radiation (the reflection coefficient of 0.78), the values are in a good agreement with those determined from the transmission spectra (Table 2).

The above results on the contribution of the luminescent radiation from the films with PLE luminophore additives demonstrate the possibility of the rather accurately extrapolating the values determined experimentally for the films with the high luminophore content to the films with the known relative luminescence intensity. This allows us to calculate the contributions for the films with the photoluminophore content most typical for practical application.

This calculation of the contribution of the luminescent radiation to transmitted sunlight was made for the films with the PE luminophore. The experimentally determined contribution of the luminescent radiation to the transmitted solar radiation for the film with the 0.5% m/m PE luminophore content was used to perform calculations for the films with the luminophore content of 0.05–0.3% m/m (see results in Table 2).

The specific contribution of the luminescent radiation, related to the relative intensity of film luminescence in 1 rel. unit, calculated for sample 5 in Table 2 is equal to 0.00018 and 0.00023 W/m^2 for the transmission and reflection spectra. The excess of the results obtained from the reflection spectra over those obtained from the transmission spectra is 22% as for the films with the PLE luminophore. The introduction of the reflection coefficient, which was equal to 0.78 in the technique used, results in a good agreement between the results obtained from the transmission and reflection spectra (Table 2).

The obtained values of the contribution of the luminescent radiation of the films to the transmitted solar radiation form, in fact, the calibration curve and allow us to find then the maximum contribution for the films with the studied luminophores from their relative luminescence intensity without recording their sunlight transmission or reflection spectra. However, these results are not universal and can be used only for a particular, in the intensity of PAR and UV radiation, weather conditions during the experiment. To obtain more universal data, it is needed to match the results obtained under different conditions.

Table 2. Contribution of the luminescent component to the sunlight transmitted by light-transforming films with PE luminophore additives

Film #	Luminophore content, % m/m	Luminescence intensity, rel. units	Luminescence intensity, in W/m^2, estimated		
			From transmission spectra	From reflection spectra	
				not corrected	corrected by the reflection coefficient
1	0.03	41.0	0.007*	0.009*	0.007
2	0.05	74.5	0.012*	0.016*	0.012
3	0.1	104.8	0.017*	0.023*	0.018
4	0.3	140.0	0.023*	0.031*	0.024
5	0.5	210.0	0.037	0.047	0.037

* Calculated from luminescence intensity.

One of the simplest ways to match the results obtained from spectra of films from different sets recorded under different conditions may be the use of a film with known fluorescent properties in every measurement series and determination of characteristics of other films in relation to the corresponding characteristics of the reference film, that is, to obtain relative results using a reference. The obstacles on this way are the difficulty in accurate reconstruction of the photophysical properties of the films even having the same composition in different sets[14] and significant variation of their fluorescent properties during storage under laboratory conditions. Thus, the relative intensity of a fresh film containing 2% m/m of the PE luminophore was 240 rel. units. The contribution of the luminescent radiation to the transmitted sunlight in the PAR region amounted to 0.18 W/m^2 as determined on August 4 of 2002 (spectrum *2* in Fig. 4). The storage of the film under the laboratory conditions resulted in a decrease of its luminescence intensity down to 91 rel. units, and the contribution of the luminescent radiation determined on May 23, 2003 was 0.19 W/m^2.

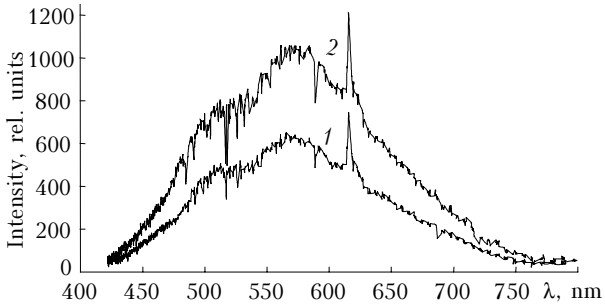

Fig. 4. The transmission spectra, for sunlight, of the film with 2% m/m FE luminophore additive: a fresh film [August 4 of 2002] (*2*), identical film after one-year storage [May 4 of 2003] (*1*). The spectra are not corrected for the spectral sensitivity of the photodetector used.

Relation of the specific contribution of the films with the luminescence intensity of 1 rel. unit to the 1 W/m^2 intensity of the exciting solar UV radiation may allow a comparison to be done of the results obtained under different conditions for the films with different values of the relative luminescence intensity. At the solar UV radiation intensity of 3.5 and 18.4 W/m^2 for the experimental conditions of 2002 and 2003, this index for the films with the PLE luminophore is $K_{sp} = 6.8 \cdot 10^{-5}$, and that for the films with the PE luminophore is $K_{sp} = 5.2 \cdot 10^{-5}$. We can see that the values are quite close.

The use of this specific coefficient equal to the contribution (in W/m^2) of the luminescent radiation of a conditional film with the luminescence intensity of 1 rel. unit at excitation by the solar UV radiation with the intensity of 1 W/m^2 permits us to easily estimate the contribution for the films with any value of the relative luminescence intensity for every particular value of the solar UV radiation intensity without recording the corresponding spectra and related calculations.

The values obtained from the transmission and reflection spectra of the films are of the same order of magnitude as those calculated from the intensity of the UV radiation absorbed by similar films.[8] So they can serve the measure of the maximum possible contribution of the luminescent radiation to the solar radiation transmitted through the films.

The results obtained are indicative of the absence of regular integral changes in the spectral composition of the solar radiation transmitted through the typical light-transforming films due to the luminescent component. This, in its turn, gives no grounds for using the ideas of the modern theory of phytochromic photoregulation of plant growth and development to explain the nature of the polysvetan effect. This photoregulation system is in force in the presence of significant changes in the spectral composition of the radiation in the PAR region in excess over the typical continuous and chaotic changes due to numerous factors characteristic of natural illumination conditions, in particular, at the change in the PAR spectral composition due to the use of the HPPE films. These changes in the PAR spectral composition in greenhouses covered with the HPPE films have been studied quite thoroughly for several decades of using the HPPE films,[13] and they are known to cause only a little changes in the plant productivity.

The use of the light-transforming films in greenhouses for plant growing does not result in any significant integral changes in the spectral composition of the transmitted solar radiation as compared to the case of the unmodified HPPE films. The transmission of solar radiation through such films is accompanied by generation of the photoluminescent radiation with the intensity from several hundredths to several tenths parts of W/m^2, even under conditions of maximum intensity. This is 4 to 5 orders of magnitude lower than the intensity of incident solar radiation in the same spectral region and 1 to 2 orders of magnitude lower than the typical noise.

Thus, the effects of considerable acceleration of the plant growth and development and the increase of the plant productivity under the light-transforming films as comparable with that in the case of unmodified HPPE films cannot be explained by the action of the plant photoregulation system in response to the variations in the PAR spectral composition. At the same time, except for the luminescent radiation, there are no other factors distinguishing the properties of the light-transforming films from the unmodified HPPE films with similar technological parameters. This circumstance inevitably shows the necessity of explaining the polysvetan effect by the effect of the super-low-intensity luminescent radiation on plants and to the conclusion that, along with the phytochromic photoregulation system responding to variations in the PAR spectral composition, plants have another one system based on ultraweak interactions with photoluminescent radiation.

By analogy with the widely known effect of low-energy photoinduced bioactivation under the exposure to laser radiation and electroluminescent radiation of

red LEDs,[15] the polysvetan effect can be classified as low-energy photoluminescent bioactivation of plants.

Conclusions

Thus, we have determined the contribution of the luminescent radiation excited by the solar UV radiation to the radiation transmitted by the light-transforming films for the wide range of content of organic photoluminophores based on europium compounds in these films. For the films with the typical luminophore content, this contribution depends on many factors and amounts to about 0.01 W/m^2, which is much lower than the level of chaotic and continuous changes in the spectral composition of the solar radiation due to numerous factors. No regular integral changes have been revealed in the spectral composition of solar radiation passed through typical light-transforming films due to introduction of photoluminophores under typical conditions of their usage. This does not allow us to explain the polysvetan effect by classical theory of photoregulation. This effect can be classified as low-energy photoluminescent bioactivation of plants.

The results obtained allow us to estimate the total doses of luminescent radiation acting on plants under the light-transforming films and to begin modeling of the basic parameters of the polysvetan effect determined for the natural conditions under more stable laboratory conditions.

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