Absorption of UV radiation by polyethylene films with addition of luminophores based on europium compounds

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The first attempts at using additions of luminophors to polymeric materials were made as far back as the middle of the twentieth century in the context of a search for effective UV absorbers. As a result, it was concluded that “fluorescing UV absorbers have no practical value as light stabilisers, which is connected with their low resistance to irradiation” [1].

However, in the 1980s, extremely successful research, not from the viewpoint of the stabilisation of polymers but from the viewpoint of the physiology of plants, was carried out on the use of polymer films with additions of luminophors based on complex europium compounds in the growing of a wide range of agricultural crops under greenhouse conditions [2]. Wide-scale tests have now been carried out on such films both in Russia and abroad under greenhouse conditions on a total area of over 100 hectares [3]. It has been shown that the use of polymer films with 0.02–0.05 wt.% additions of such compounds as a complex of europium nitrate with 1,10-phenanthroline, europium o-benzoyl benzoate, etc., to cover greenhouses makes it possible to shorten the maturation times, to accelerate growth, and to increase the yield of agricultural crops to 100% by comparison with films without modifying additives. This property of the given films has been called the “polylight” effect [2].

In spite of the high effectiveness of using such films, their photophysical properties, which determine the “polylight” effect, have hardly been investigated to date.

Publications on this theme point to secondary luminescent radiation of europium compounds in the red region of the spectrum, which arises through the transformation of ultraviolet radiation absorbed by them, as the main factor. At the same time, data on the absorption of ultraviolet radiation by polyethylene films with additions of europium compounds that are now available in the literature are extremely numerous and contradictory. In a number of patents, for example refs. [4] and [5], data are given on the absorption of 90–99% UV radiation by low-density polyethylene (LDPE) films with additions of luminophors based on complex compounds of europium and inorganic crystallophores activated by europium. Such properties are open to doubt in view of the almost complete absence of solubility of most complex europium compounds and, especially, inorganic crystallophores in low-polarity organic solvents. This, in turn, determines the heterophase, dispersed nature of polyethylene–luminophor systems.

We made an attempt to study the values of transmission and absorption of UV radiation by LDPE films with additions of complex europium compounds.

A complex of europium nitrate with 1,10-phenanthroline, which is the most widely used luminophor, was chosen for investigation, produced by the procedure described in ref. [6].

Specimens of hose films (45 Ch2) Ch0, 120 (150Ch2) Ch0, 120 m were manufactured by blow extrusion using technology set out in ref. [7] from LDPE of grade 15803–020 to GOST 16337 with a content of the complex of 0.05 and 0.1 wt.%.

Spectra of the transmission of UV radiation by films were recorded on a Uvikon 943 and Specord M40 spectrophotometer, and also on a KSVU-12 spectral
The transmission spectra obtained by the standard procedure with film specimens arranged in the cuvette holder of a spectrophotometer are presented in Fig. 1.

To eliminate the additional influence on the transmission spectra of thickness variation of films, specimens for taking the spectra were cut out over the width of a roll with a thickness of 120 ± 1 µm.

To compare the UV transmission spectra of films with luminophors, the spectrum of a similar film without additives was recorded (Fig. 1, 1). As follows from Fig. 1, the introduction of luminophors into films leads to a 10–12% reduction in UV radiation transmission by comparison with an unmodified LDPE film over the entire UV region. This can be attributed to the reflection of radiation by luminophor particles or the crystalline structure of the film material, which changes on account of the introduction of dispersed filler into its composition. This is indicated by the type of transmission spectrum that is characteristic of dispersed polymer systems. In the 250–360 nm region, such a trend of the curve is disrupted (the shaded section on spectrum 3 in Fig. 1) and the transmission of the films is 1–3% lower, which is in good agreement with the region of fundamental absorption of the complex of europium nitrate with 1,10-phenanthroline (the spectrum of excitation of luminescence). However, this quantity cannot be considered to be the fundamental absorption of UV radiation of the luminophor in the film, even under the condition of its complete absorption by particles, which is due to the design of modern UV spectrophotometers. In the instruments used by the present authors, the investigated specimen is set in the path of a monochromatic beam passing through a monochromator. After passing through the specimen, the radiation is then recorded by a photodetector without additional separation. With the presence in the investigated specimen of additions of luminophor in the region of excitation of its luminescence, instruments of such design record both the base UV radiation that has passed through the specimen and the secondary luminescent radiation of the luminophor. Thus, the magnitude found will be the difference between the intensity of absorption of UV radiation by the luminophor and the intensity of secondary luminescent radiation (in the present case, the red region of the spectrum). The true value of absorption of the exciting radiation can be determined on instruments with the specimen placed in front of a monochromator or on instruments with two monochromators (before and after the specimen).

Transmission spectra of films positioned in front of a monochromator, obtained using a home-produced KSVU-12 spectral universal computer complex, are presented in Fig. 2.

As can be seen in Fig. 2, the spectra are similar to the corresponding spectra obtained on a UV spectrophotometer and indicate both the additional reflection by films with luminophor additions of about 10% radiation in the entire UV region and fairly marked absorption in the region of excitation of the luminophor (250–360 nm) with a minimum at 260–280 nm. The magnitude of absorption in this region, as expected, is greater than that calculated from data of UV spectrophotometry and amounts to 4–5% for the given region.

The difference in the areas of the shaded sections can serve as a measure of the transformation of UV radiation absorbed by the luminophor in the red region of the spectrum. The maximum value of this difference is observed in the wavelength range 260–280 nm and amounts to 2–3%. It must be pointed out that the given magnitude lies at the level of reproducibility of measurement of the index for specimens of the same type.

The ratio of the difference in the areas of shaded sections to the total area of the spectrum can serve as a measure of absorption of artificial-source UV radiation by a luminophor in polyethylene films. For the films investigated, this quantity amounts to about 1%.

An attempt to estimate from UV spectrophotometry data the proportion of solar UV radiation that can be...
absorbed by such films in real service conditions can be made with allowance for the fact that UV radiation reaches the Earth's surface with a limit in the shortwave region of 290–300 nm. For the films investigated, such an estimate gives a value of about 0.1%. This indicates the fundamental difference of the investigated films from previously described [8] PVC films with additions of complex europium compounds in their capacity to absorb UV radiation. Data on the complete absorption of UV radiation by PVC films similar in composition to those investigated are presented in ref. [8]. The data are presented without description of procedural details, which makes it impossible clearly to judge the nature of such differences. The most probable reason is the production on the basis of PVC of composite materials with a homogeneous distribution of additions of luminophors in the polymer matrix, which is in good agreement with values of the coefficients of molar extinction that are characteristic of true solutions of complex europium compounds in organic solvents. This indicates the fundamental difference in the photophysical properties of polyethylene light-correcting films with a dispersed nature of distribution of luminophors within them from the properties of PVC films, which may determine features of the "polylight" effect exhibited by them.

REFERENCES

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