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Study of New Composite Materials Based on Epoxy Resin with Photoluminescence Effect

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Abstract. Strontium aluminate doped with europium with various particle sizes was added to epoxy resins ED-20 and Crystal 85-5 in a mass concentration from 0% to 17%. Mechanical tests for three-point bending and instrumental indentation were carried out. The relationship between modulus of elasticity and hardness and concentration of the filler were obtained. The photoluminescent properties of the resulting composites have been studied. The relationship between luminescence intensity and decay time and the content of composite components were established.

Keywords: epoxy resin, photoluminescent powder, elastic modulus, hardness, glow intensity, decay time.

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Introduction

Photoluminescent powder is used in materials and products to give them the ability to glow in the dark after removing light sources such as room lights, sunlight, ultraviolet lamps [1]. In general, luminescent materials are used in manufacturing safety instructions, signs to mark escape routes in the case of a power outage and decorative elements. As a result of excitation from an external light source photoluminescent materials are able to accumulate light energy and release it in the dark for a long time. Over the past few decades, the focus of researchers has redirected from studying the photoluminescent characteristics of phosphor powders to studying the properties of materials and devices based on them [2]. There are a large number of inorganic phosphors capable of emitting light of various wavelengths such as in the red, green or blue regions of the spectrum [3–5]. Phosphors are characterized by excellent chemical and thermal stability, non-toxicity, high brightness and long service life.

Polymeric materials are widely used in technology. By choosing a polymer matrix and a filler, as well as methods to combine them, composite materials are developed with the required physical, mechanical and other operational properties. Such materials can replace metals and alloys in a number of applications. Composite materials based on epoxy resin have a set of advantages such as good electrical, optical and magnetic properties, fire resistance, gas impermeability,

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resistance to mechanical damage and wear [6]. Fillers are introduced into epoxy resins in order to improve physical and mechanical characteristics, increase hardness, thermal conductivity, dielectric characteristics [7–8]. The introduction of a photoluminescent powder into an epoxy resin provides the composite with new characteristics that are not characteristic of an unfilled polymer. Mechanical properties of the material, its density and its suitability for processing are not changed since the additive is used in very small quantities. The effect of photoluminescent powder on the physical and mechanical characteristics of the resulting composite has not been studied in sufficient depth. When developing such materials, priority is given to the photoluminescent properties of the composite which are studied in detail [9, 10]. Mechanical characteristics of such composites were not practically considered. The present work is intended to eliminate this gap in the study of such materials and to propose a composition that is optimal in terms of mechanical and luminescent characteristics.

1. Materials and study methods

In this work, two types of two-component epoxy resins were used as a polymer matrix: Crystal 85-5 (China) and ED-20 (Russia). These two types of resins differ significantly from each other in the values of dynamic viscosity in the uncured state. The viscosity of Crystal 85-5 is about 10 P while the viscosity of ED-20 is about 150 P. In addition, Crystal 85-5 is transparent and colourless, and ED-20 has a light yellow-brown hue.

Two brands of phosphor in the form of micro-powder were used as a filler: MHG-4E (China) and FB-530D (Russia). The characteristic particle size for the MHG-4E powder was 5–15 μm and 25 μm for the FB-530D powder. Energy-dispersive analysis of the phosphors used was carried out using Zeiss EVO MA 15 scanning electron microscope (SEM). The results of the analysis of the elemental composition of two types of powders showed that main substance for both brands of phosphors is strontium aluminate ($SrAl_2O_4$). Europium (Eu) atoms act as the main dopant.

The fabrication of material samples was carried out according to the following procedure. Epoxy resin and hardener in the established mass ratio (1:3 for Crystal 85-5 resin and 1:10 for ED-20 resin) were poured into separate containers. Then, the mass of the added phosphor powder was calculated in accordance with the value of the required mass concentration. The portion of the powder was added to the hardener. Mixture was treated with the Bandelin Sonopuls HD 3200 ultrasonic homogeniser, and powder was evenly distributed in the volume of the hardener. The action of ultrasonic waves prevent formation of large powder particles agglomerates. The resulting mixture of hardener and phosphor was poured into the prepared portion of resin. The resulting final mixture was stirred for 3–5 minutes. Then it was treated again with ultrasonic homogeniser in order to remove large air bubbles from the mixture.

The resulting final mixture was cast into the prepared sample mould. The resin was cured at room temperature for 3 days. Certain mass concentrations of the filler were chosen for two types of epoxy resins. The mass concentration of the filler varied from 0% to 17%. After curing material samples were additionally polished.

To determine the flexural modulus of composite experiments were carried out on the Zwick Roell Allround Z005 test set-up. According to the test standard ASTM D 790, rectangular material samples with sides 4×10×80 were made. Three-point flexural test is carried out as follows. The sample is installed symmetrically on two supports. The distance between supports was 65 mm. The sample was loaded by a moving punch at the centre point of the straight line segment between supports. The cross-head constant speed is 2 mm/min. The relationship

between applied load and absolute displacement of the traverse was continuously recorded during experiment. The test was carried until 10 mm displacement was reached or until the destruction of the sample was observed.

Instrumental indentation experiments were carried out on the Nanoscan 4D+ test complex. To determine the hardness of samples and their reduced modulus of elasticity kinetic indentation with the Berkovich diamond pyramid was used. When indenting the surface of the samples, a square grid of 5×5 indents was set. The distance between indents along each orthogonal coordinate (X and Y) was 30 μm. The maximum load was 30 mN. Loading and unloading occurred with a linear change in the applied force.

The following technique was used to record the intensity decay curve. Cylindrical material samples were prepared. To achieve a high afterglow intensity samples were placed in the 6073 Byko spectra pro lighting chamber. They were irradiated for 90 minutes by a D65 lamp simulating the spectrum of solar radiation. The light source created illumination of about 1800 lx near the surface of samples. It was assumed that indicated charging time of the photoluminescent material is sufficient to establish an equilibrium between irradiating light flux and samples.

The illumination created by a sample of a photoluminescent material at a fixed distance from its surface was taken as a parameter describing the intensity of the afterglow. This parameter describes the recorded intensity of the light flux at some distance from the extended source. Schematic of the set-up used to record illumination is shown in Fig. 1. A cylindrical sample 1 with a diameter of D =55 mm and thickness of $h = 7$ mm was placed on a flat horizontal surface in dark chamber 4. A lux meter probe 3 was installed on supports 2 adjacent to the edges of the sample at a distance of $L = 20$ mm from the lower base of the sample. Illumination values measured with the lux meter were sent to an external PC 5 and saved at specified intervals. An eLight01 light meter with an eLight03 photo probe was used as a recording device. At the beginning of the glow decay process, when the rate of change in illumination values is high, data were recorded with a frequency of one measurement in a second. When the rate of change in the registered illumination was decreased to 0.01 – 0.02 lx/s the interval between successive data records was increased to 60 seconds.

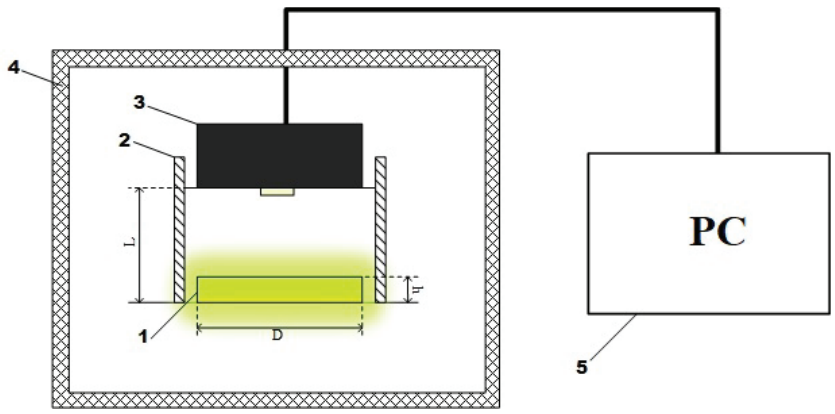


Fig. 1. Schematic of the set-up for recording afterglow intensity: 1 — material sample, 2 — sensor mounting supports, 3 — photo probe of the lux meter, 4 — dark chamber, 5 — external PC

The afterglow intensity decay curve was approximated by the three-parameter relationship

used to describe the decay of the luminescence of crystal phosphors with time [11]:

$$I(t) = \beta (1 + \alpha t)^{-\gamma}, \tag{1}$$

where I is the integral intensity of the afterglow, t is time, and α, β, γ are constants determined from experiment.

Let us introduce threshold value of intensity I_0 and divide (1) by it. Then, one cane obtain the following expression

$$\frac{I}{I_0} \equiv \tilde{I} = (1 + a(t - \tau))^{-\gamma}, \tag{2}$$

where $a = \alpha \left(\frac{\beta}{I_0}\right)^{-\frac{1}{\gamma}}$, $\tau = \alpha^{-1} \left(\frac{\beta}{I_0} - 1\right)^{\frac{1}{\gamma}}$.

It can be seen that constantτ which has the dimension of time corresponds to the decay time of the glow intensity from the value of β to the value of I_0.

The curve of the decay of illumination in time obtained from the experiment was approximated by relation (1). The least squares method was used to select parameters. The problem of finding the minimum error was solved numerically using the Levenberg–Marquardt method. To minimize the error associated with the registration of illumination in the initial section set of points and approximation curve in logarithmic scale was used to select parameters. After selecting parameters α, β, γ, parameters a, τ, γ were determined according to (2). Parameter I_0 was taken equal to 0.014 lx or 0.015 lx. It approximately corresponds to the transition of the lux meter readings during registration of a smoothly fading glow from 0.02 lx to 0.01 lx at a division value of 0.01 lx and relative error of 8% for eLight03.

The glow decay time of the sample was determined as the time from the start of data recording to the moment when the value of the recorded illumination was decreased to 0.01 lux which is the sensitivity limit of the lux meter used. As an integral value that reflects the energy intensity of samples exposure J was used. It is defined as

$$J = \int I(t)\, dt, \tag{3}$$

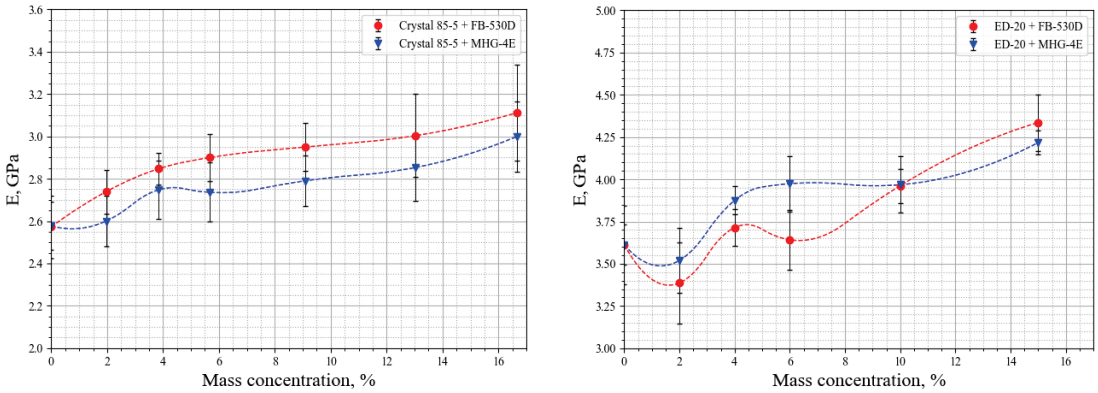
where $I(t)$ is the time-dependence of illumination. To determine the exposure from experimental data conditional numerical integration by the method of left rectangles was used.

2. Experimental results and discussion

Relationship between elastic modulus and mass concentration of the filler obtained experimentally using three-point flexural tests for material samples obtained using two different types of matrices and fillers are shown in Fig. 2. The measured flexural modulus was 2.6 ± 0.15 GPa for the unfilled Crystal 85-5 resin. The measured flexural modulus was 3.6 ± 0.1 GPa for unfilled ED-20 resin.

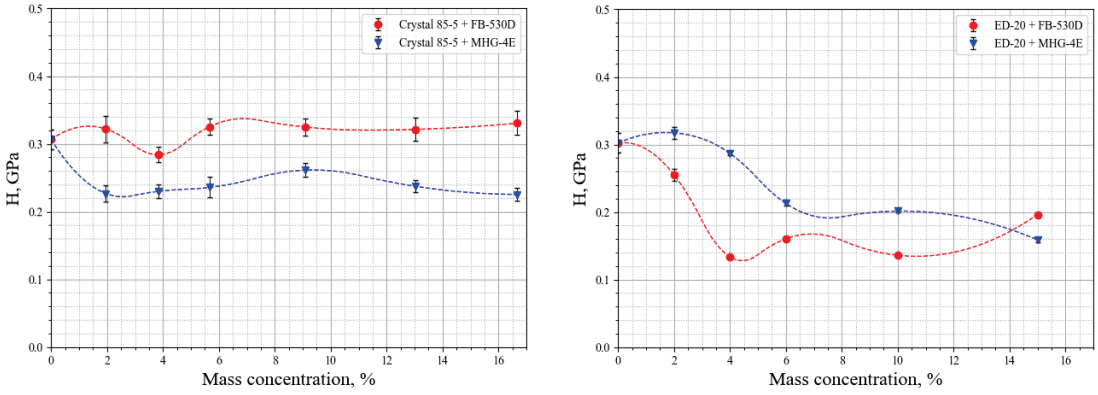
The presented relationship is not monotonic at low mass concentrations of the filler as it can be seen from Fig. 2. It is possible to establish the presence of both local minimum and local maximum in the initial section for most graphs. At higher concentrations, most graphs show a monotonic increase in the modulus of elasticity with increasing mass concentration of the filler.

The measured hardness of material samples versus mass concentration of the filler are shown in Fig. 3. The measured hardness was 0.31 ± 0.015 GPa for unfilled Crystal 85-5 resin. The measured hardness was 0.30 ± 0.015 GPa for unfilled ED-20 resin.



(a) (b)

Fig. 2. Relationship between flexural modulus and mass concentration of the filler for photoluminescent powders MHG-4E and FB-530D and two types of matrices: Crystal 85-5 (a) and ED-20 (b)



(a) (b)

Fig. 3. Relationship between hardness and mass concentration of the filler for photoluminescent powders (MHG-4E and FB-530D) and two types of matrices: Crystal 85-5 (a) and ED-20 (b)

It can be seen that in the case of using Crystal 85-5 resin as a polymer matrix and FB-530D powder as a filler the hardness of the material is almost independent of concentration. It is slightly increased at low concentrations. The maximum 8% increase in hardness was achieved at concentration 16.7%. The hardness decreases sharply already at concentration 2% with the introduction of MHG-4E powder into Crystal 85-5. The hardness changes slightly and it does not exceed unfilled resin hardness with a further increase in mass concentration.

Similar relationship between hardness and concentration is observed in the case of polymer matrix based on resin ED-20 for both types of fillers. A gradual decrease in hardness with increasing mass concentration is observed in the initial section. The hardness of the samples decreases monotonically for mass concentration ranging from 0% to 6%. The hardness of the samples of materials with both types of powders fluctuates around a constant value with a further increase in concentration. At 15% mass concentration, the hardness decreased by 35% in the case of FB-530D powder and by 47% in the case of MHG-4E powder in comparison with the

unfilled resin.

The obtained relationships between illumination created by the samples of the material and mass concentration of the filler at various moments of time are shown in Fig. 4. It can be seen that in all cases illumination increases almost linearly with increasing concentration. The closeness of the obtained relationship to linear one is also indicated by correlation coefficient between illumination and concentration that is greater than 0.99 in each case. The slope of these lines changes over time due to gradual fading of the glow.

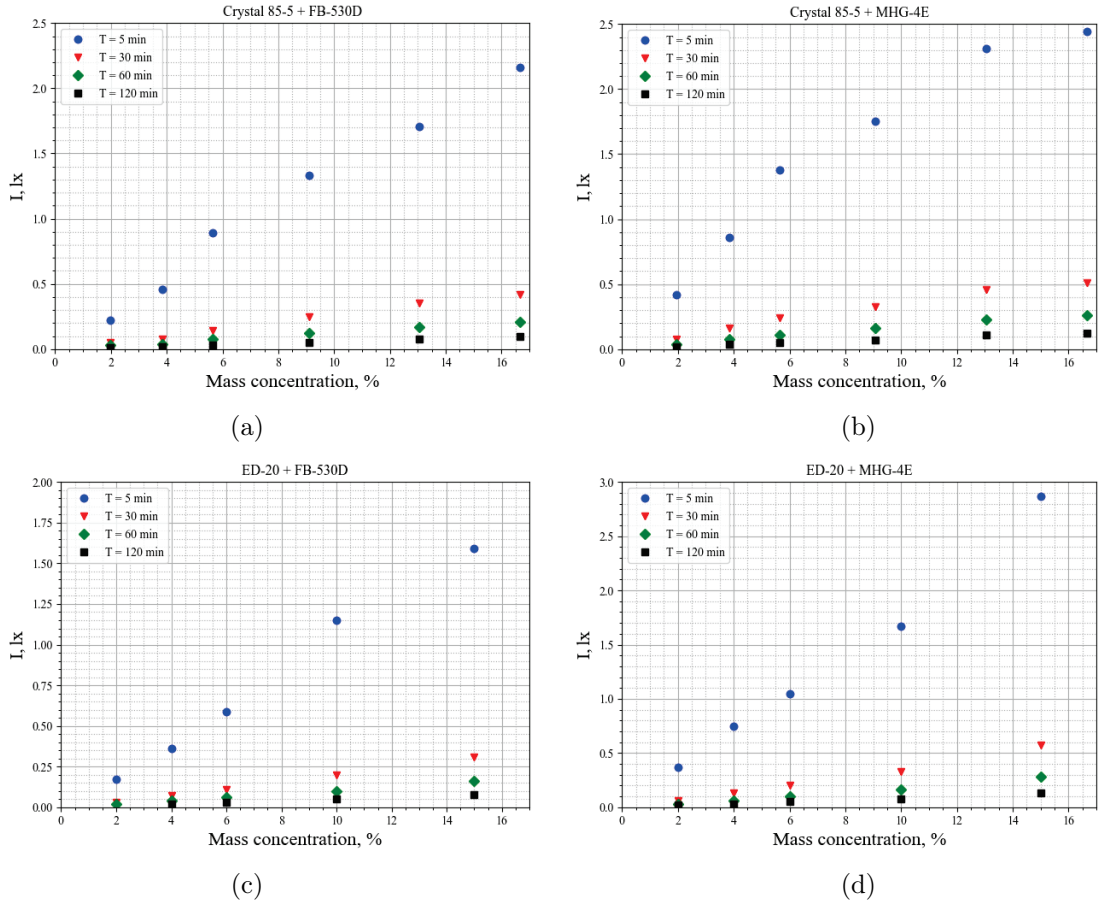


Fig. 4. Relationships between illumination created by the samples and mass concentration of the filler for photoluminescent powders MHG-4E and FB-530D and two matrices Crystal 85-5 and ED-20 at various moments of time

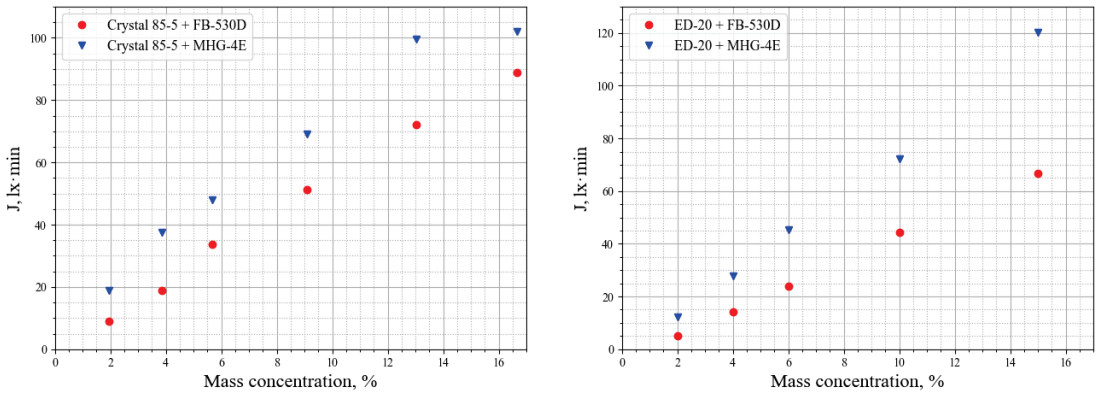
Relationships between exposure determined from the registered light decay curve and mass concentration of the filler is shown in Fig. 5. One can observe that in all considered cases exposure depends almost linearly on concentration in the studied range of concentration values. Only in the case of material consisting of Crystal 85-5 and MHG-4E exposure reaches a constant value, starting from concentration 16.7%.

Let us consider an effect of various types of fillers and matrices on exposure. It can be noted that in the case of using Crystal 85-5 resin as a matrix the line that approximates calculated exposure for samples with FB-530D lies below the line for samples with MHG-4E. The lines are almost parallel. In the case of using ED-20 resin as a matrix, the line that approximates

calculated exposure for samples with FB-530D lies not only below the line corresponding to samples with MHG-4E but it also has a smaller slope. MHG-4E powder particles have a smaller size than FB-530D powder particles. When mass concentration of MHG-4E powder increases the effective radiation capture area increases more intensively. In Crystal 85-5 resin, this effect is possibly suppressed due to particle settling at high concentrations.

Fig. 6 shows the relationship between illumination decay time to the level of 0.01 lx and mass concentration of the fillers for various matrices and fillers. Values of calculated parameter τ are also shown on the graph. This parameter is one of the constants that determine the approximation curve. After finding parameters α, β, γ, parameters τ and a were determined using the value of the threshold illumination I_0 equal to 0.014 lx or 0.015 lx, depending on the set of samples. It can be noted that approximate values of parameter τ determined for given values of I_0 are in good agreement with the experimentally determined values of the decay time.

In general, comparing Figs 5 and 6, one can see that obtained relationships are qualitatively similar. The maximum decay time was recorded for a sample with ED-20 resin as a matrix and MHG-4E powder as a filler and it is equal to 1040 min (17.3 h) at concentration 15%.



(a) (b)

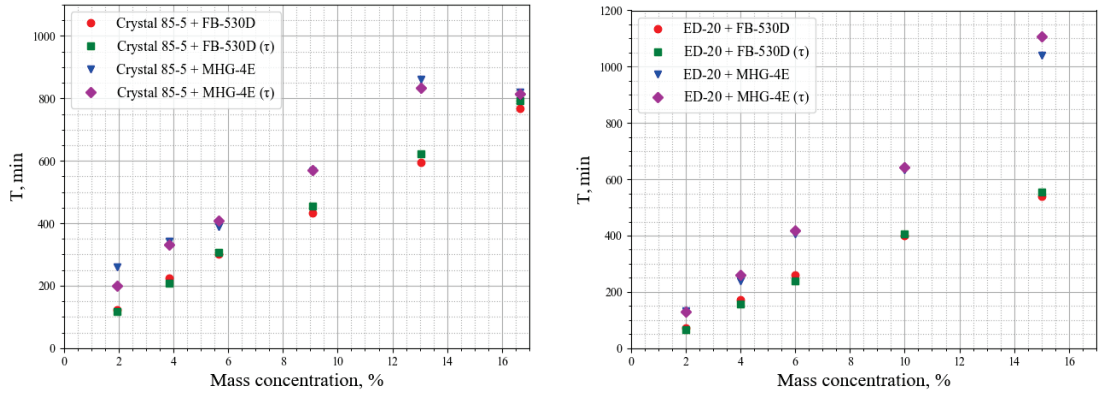
Fig. 5. Relationship between exposure and mass concentration of the filler for photoluminescent powders MHG-4E and FB-530D and two types of matrices: Crystal 85-5 (a) and ED-20 (b)

Fig. 7 *a*, *b* shows the relationship between parameter γ and mass concentration of the filler. One can see that parameter γ changes slightly as concentration increases, and it takes values close to $\gamma = 1.0$. **********

The relationships between parameter a responsible for the time scale in (2) and mass concentration of the filler are shown in Fig. 7 *c*, *d*.

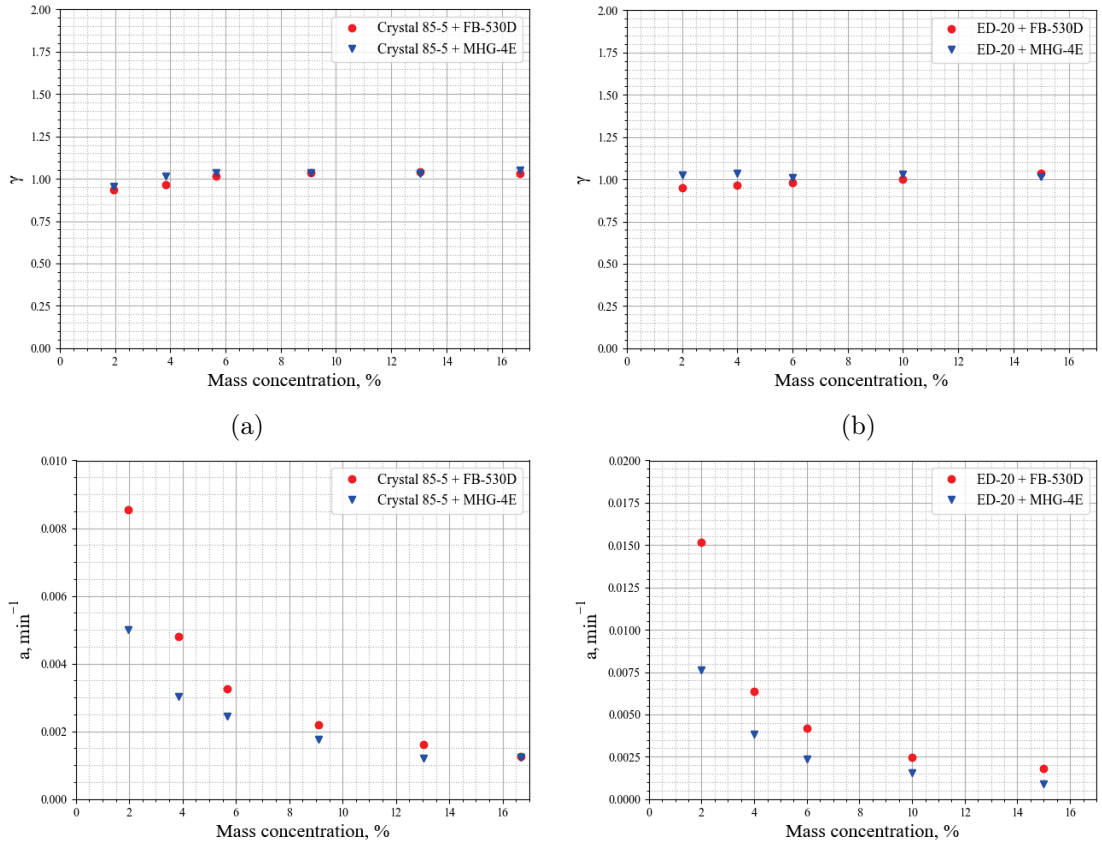
One can see that in all cases parameter a is approximately inversely proportional to mass concentration. It is obvious from general considerations that when concentration is equal to 0% parameter a must take infinitely large value. It corresponds to the absence of glow according to (2). It should be noted that when mass concentrations exceeds the maximum values under consideration parameter a may decrease according to the hyperbolic law. However, starting from some high value of concentration, it is also possible that it reaches a plateau.

According to the results of experiments, one can conclude that at the studied mass concentrations of the phosphor the best afterglow characteristics were observed for samples with MHG-4E powder and transparent colourless Crystal 85-5 resin. This is because particles of MHG-4E powder have smaller characteristic size in comparison with particles of FB-530D powder. The



(a) (b)

Fig. 6. Relationships between illumination decay time to the level of 0.01 lx and parameter τ and mass concentration of the filler for photoluminescent powders MHG-4E and FB-530D and two types of matrices: Crystal 85-5 (a) and ED-20(b)



(a) (b)

(c) (d)

Fig. 7. Relationship between parameters γ (a, b) and a (c, d) and mass concentration of the filler for photoluminescent powders MHG-4E and FB-530D and two types of matrices: Crystal 85-5 (a, c) and ED-20 (b, d)

exception was observed in the cases of high mass concentrations when settling of a large number of powder particles takes place in samples with Crystal 85-5. As a result, the high throughput of the matrix was compensated by high real concentration of the filler in the settling layer. The ED-20 resin is free of such problems due to its high viscosity. Therefore, despite the lower throughput at the maximum studied concentration of the photoluminescent filler it provided a longer decay time than the Crystal 85-5 resin.

Conclusion

A set of experimental studies of the physical and mechanical properties and luminescence characteristics of composite materials based on epoxy resins ED-20 and Crystal 85-5 and photoluminescent micropowder was carried out. The relationships between modulus of elasticity and hardness of photoluminescent composites and mass concentration of the fillers were established. It was shown that for all combinations of matrices and fillers the maximum relative increase in the elastic modulus was about 20% in comparison with the unfilled resin. The maximum increase in hardness was observed for Crystal 85-5 resin and FB-530D powder, and it is equal to 8%. For ED-20 resin and two types of phosphors the hardness is decreased by 40% over the entire range of studied concentrations. It reaches minimum value at the filler concentration of 15%. A monotonic, close to linear, increase in the decay time and calculated exposure which expresses the amount of accumulated energy was observed with an increase in mass concentration of the filler. Samples with MHG-4E powder as a filler and Crystal 85 5 transparent resin have the best afterglow characteristics. For this composition, the maximum illumination produced by the sample at the beginning of the glow decay was 29 lx, and decay time was 860 minutes at mass concentration of the filler equal to 13%.

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Experiments were performed using equipment of the Equipment Sharing Centre "Mechanics" of ITAM SB RAS.

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Исследование новых композиционных материалов на основе эпоксидной смолы, обладающих эффектом фотолюминесценции

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Аннотация. Алюминат стронция, легированный европием с различным размером частиц, был добавлен в эпоксидные смолы ЭД-20 и Crystal 85-5 в массовой концентрации от 0% до 17%. Проведены механические испытания на трехточечный изгиб и инструментальное индентирование. Получены зависимости модуля упругости и твердости от концентрации наполнителя. Исследованы фотолюминесцентные свойства полученных композитов. Установлены зависимости интенсивности люминесценции и времени затухания от содержания компонентов в композите.

Ключевые слова: эпоксидная смола, фотолюминесцентный порошок, модуль упругости, твердость, интенсивность свечения, время затухания.