 Research Article

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Recording digital color information on transparent polyethylene films by thermal treatment

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This study characterizes the use of transparent low-density polyethylene laminate films for the purpose of recording digital information in the form of linear and color two-dimensional matrix codes that are distinguishable in polarized light. Color characteristics of multilayer laminated materials made from polyethylene and heat treatment methods for changing their coloring are examined. The contribution of the number of multilayer film interfaces to the lightness and color of the laminate is shown. Melt-extruded industrial polyethylene film heat treatment methods by convection, conduction, and radiation, to control their optical characteristics and color in polarized light, are studied.

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1. INTRODUCTION

Recording optical information by means of printing is of great importance for the development of new print technologies (high-performance planar technologies). New materials and methods for obtaining, storing, and recording optical information ensure the confidentiality of information transmission and its authenticity (protection against forgery). Color two-dimensional codes [1–5], such as the high-capacity color barcode of the Microsoft TAG [5], have a higher information capacity than black and white codes due to the greater number of colors a single element of the two-dimensional code matrix can be painted with. Also, using colors instead of gradations of gray provides higher reliability of matrix decoding in different illumination conditions [1,4]. Furthermore, the use of color for recording information is ideal for creating the foundations of the optical logic array processor for optical computers [6], which in the future will use laser radiation of several different wavelengths. This illustrates the need for light-emitting [7] and photo-switching optical logic elements, as well as printing methods utilizing flexible polymers [8]. The optical methods of information processing make it possible to use the phenomenon of light polarization [9,10] and new pleochroic materials [11–13] for selective radiation and polarization, which, through horizontal and vertical polarizations of light, increase the potential information capacity by 2× compared with thin-film elements using unpolarized radiation. However, the effect of pleochroism in polymer films depends on their thickness and thermal history [12]. The highest intensity of color change and dependence on the scale factor were established for multilayer low-density polyethylene (LDPE) films [13] obtained by extrusion blow molding. Local heat treatment of films makes it possible to change the polarized light transparency and color of small sections of film having the shape and dimensions of single elements of two-dimensional codes [5]. The accuracy of the shape, size, and coordinates of the single color element of the two-dimensional codes depends on the method of transfer of thermal energy during local heating and the effectiveness of protection against heating (screening) of the sections of the film adjacent to the local heat treatment site.

The purpose of this article is to experimentally evaluate the effectiveness and compare the technical possibilities for color management of polyethylene films in polarized light using three different types of heat treatment. The optical characteristics of polyethylene films were measured after heat treatment by convection, conduction, and radiation. Three methods of heat treatment by IR radiation, heating in an air stream, and direct contact with a metal surface at a temperature below the melting point of the polyethylene crystals were used.

2. MATERIALS AND METHODS

The LDPE films, with thicknesses of 40 μm, 70 μm, and 100 μm, were manufactured by the ZAO Kotovsky Plant of Nonwoven Materials in the Russian Federation. The film was made with a single extruder using an extrusion blow molding method in compliance with the Russian Federation GOST standard 10354-82. As an insert for the optical measurement tool operating in the reflection mode, a laboratory grade, unbleached, clean cellulose filter paper conforming to specification "F" of the

Russian Federation GOST standard 12026-76 was used. To obtain and instrumentally analyze the polarized light, Nitto polarizing film (G1220DUN, Nitto Denko Corporation, Osaka, Japan) with 99.97% polarization efficiency of polarizer films in the parallel (open) position was used.

A. Instruments

Precision measurement of the overall dimensions and thicknesses of the films before and after heat treatment was carried out using the Constanta KC6 thickness gauge. Colorimetric measurements in reflected light were carried out using the X-Rite SpectroEye spectrophotometer with the Gretag Macbeth KeyWizard V2.50 software. Measurements of the optical density and color coordinates in the transmitted polarized light were carried out using the SF-2000 spectrophotometer operating in daylight transmission mode (source D65). The color difference ΔE^*_{ab} between layered materials in polarized light is estimated by using the following formula:

$$\Delta E^*_{ab} = \sqrt{(L^*_2 - L^*_1)^2 + (a^*_2 - a^*_1)^2 + (b^*_2 - b^*_1)^2}. \quad (1)$$

Here, L^* is the lightness, i.e., the value of tone, while a^* and b^* are coordinates in the CIE $L^*a^*b^*$ color space of the International Commission on Illumination (Commission Internationale de l'Eclairage, CIE).

The thermophysical properties were determined by differential scanning calorimetry (DSC) using the DSC 204 F1 (NETZSCH) instrument in an argon atmosphere, with a heating and cooling rate of 10°C/min.

B. Preparation of Samples for Optical Measurements

Samples of film material in the form of 10 mm wide tapes were cut along the extrusion direction and stacked into 10 layers in a stepped fashion. The films stack was fastened with a bracket or pulse welded to fix the arrangement of the layers. Above and below the fixed layers, film polarizers were stacked so that the polarization axes of the light stream passing through the polarizer and the analyzer were located at an angle of 0° (open position) or 90° (closed position). A schematic diagram of the assembled multilayered polyethylene film package is shown in Fig. 1.

To investigate the effects of heat treatment conditions and temperature on the optical properties of multilayer films, a series of film packets subjected to heating and cooling was prepared. Heating of the samples of polyethylene films of each thickness was carried out before assembling the packets

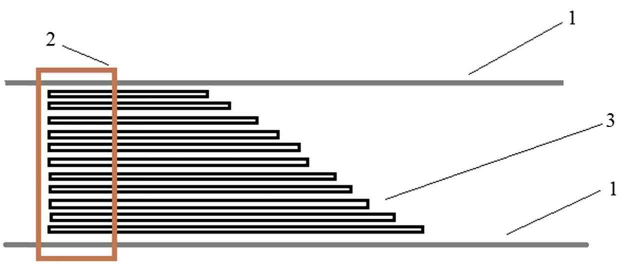

Fig. 1. Assembled multilayered polyethylene film package for colorimetry studies in polarized light: 1, polarizers; 2, bracket securing the polyethylene film; 3, multilayer stack (packet) of 10 layers of polyethylene film.

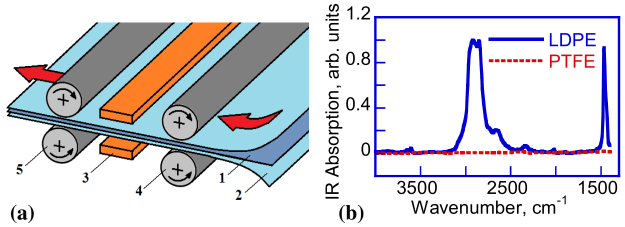

Fig. 2. (a) Diagram of the setup for heat treatment by IR radiation using a laminator: 1, a stack or several layers of polyethylene films; 2, guide envelope made from the PTFE film; 3, thermoelectric heater; 4, feed rollers; 5, heat-resistant receiving rollers. (b) IR absorption spectra of the PTFE and the LDPE films.

using three different heat treatment methods: IR radiation, convection from heated gas, and contact heat transfer. Convective heat treatment was carried out by maintaining a set temperature of the heat transfer medium to within ±0.1°C in the CVET-800 chromatograph. Direct surface contact heat treatment was carried out using an embossing press with a set of aluminum dies with a prism shape and a rectangular base of different widths. The temperature of the press was varied in the 100°C to 150°C range. IR heat treatment was carried out with the Profi Office Prolamic HR 330 D laminator. An envelope made from clear polytetrafluoroethylene (PTFE) was used to hold and guide the polyethylene film while still allowing exposure to IR radiation. A diagram of the setup is shown in Fig. 2(a), and the IR absorption spectra of LDPE and PTFE films are shown in Fig. 2(b).

The Profi Office Prolamic HR 330 D was also used for laminating several polyethylene films of different thicknesses together to create single monolithic multilayer sheets.

3. DISCUSSION

To confirm the chemical composition and validate the process used for forming the investigated LDPE films of different thicknesses, Fourier IR spectroscopy and DSC measurements were conducted. The IR absorption spectra of the films with various thicknesses are identical and completely coincide with the IR spectrum of LDPE from the information database of the X-Rite SpectroEye spectrophotometer. Thermograms of the first and subsequent melting of the LDPE samples of different thicknesses, heated to melting and cooled in DSC 204 F1 (NETZSCH) in an argon atmosphere at a rate of 10°C/min, are shown in Fig. 3.

The investigated LDPE films of three different thicknesses have an average melting point of 106–110°C and a uniform degree of crystallinity of 35 ± 1.5% (Fig. 3, curves 1–3). The re-melting thermogram (curve 4) repeats the shape of the first melting curves but differs in the temperature range of 40°C to 80°C. This change in the thermogram is due to different recrystallization conditions of polyethylene during cooling in DSC compared to the blow molding manufacturing process. When the melt of the polyethylene is cooled during molding, the film is in the stress–strain state [14], and its cooling rate is much higher than the cooling rate of a sample of molten polyethylene in the DSC. Part of the enthalpy during

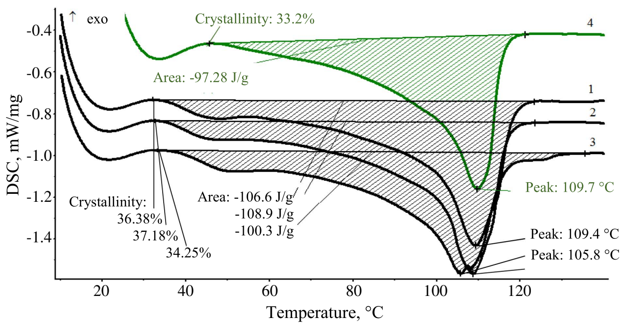

Fig. 3. DSC diagram of polyethylene films heated to melting point: 1, 40 μm; 2, 70 μm; 3, 100 μm; 4, second melting of samples 1, 2, and 3.

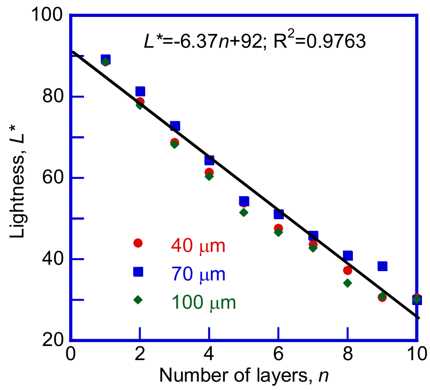

Fig. 4. Lightness of multilayer films made from monofilament polyethylene layers of different thicknesses.

polyethylene melting in the temperature range of 40°C to 80°C is caused by the supramolecular structures formed during manufacture by the material being in a state of tensile stress as well as non-equilibrium conditions caused by forced-air cooling and orientation of crystals during drawing. In heat treatment of the unstressed films, the rate of heating and cooling in the DSC is slower than the rate of forced-air cooling during extrusion. Therefore, non-equilibrium supramolecular structures are not formed, and the optical properties of the films change. These changes can be detected only in polarized light [15].

A. Optical Characteristics of Multilayer LDPE Packets in Daylight

It was previously shown [16] that the optical density and clarity of multilayer polyethylene films increase with the total packet thickness in accordance with the Bouguer–Lambert–Beer law due to light scattering by crystalline formations and microrelief of the polyethylene film surface. To compare and quantify the effects of these two factors on the optical properties of polyethylene films with daylight transmission, the optical density, color coordinates, and transparency of single sheets of polyethylene films of different thicknesses as well as multilayer laminates were evaluated. The combination of film layers provided a total thickness of laminate equal to the thickness of some single films.

It has been established that the optical density and transparency of 40 μm, 70 μm, and 100 μm film sheets of LDPE all have practically identical values of measurement error, which in this experiment is 3%. This allows stating that the attenuation coefficient of the flux of unpolarized daylight is on the order of 1%. The lightness of a packet of two and three 40 μm thick films, with a combined thickness of 80 μm and 120 μm, is 80 and 70, respectively. When two 70 μm films, or films 100 μm and 40 μm thick are combined, the total thickness is 140 μm, and the optical density and lightness are the same for both combinations.

The significance of the number of interfaces in laminated materials and the negligible influence of the thickness of individual layers of polyethylene films is confirmed by the results of the measurements shown in Fig. 4.

The universal dependence of lightness of multilayer LDPE films L^* on the number of layers n is described by an empirical equation:

$$L^* = -kn + b. \tag{2}$$

Here, L^* is lightness; k is the coefficient of attenuation of the light flux by the interfaces of the layers in the film stack; n is the number of layers; and b is a constant.

The attenuation coefficient of the light beam from a daylight source (D65) of the material containing several film interfaces is 6.37 or 637%. Since the change in the value of lightness of the different thickness polyethylene single films is less than two decimal orders, the contribution of the film interfaces (the number of surface layers of monoplanes with a special crystal structure [17]) to the optical properties of multilayer films is decisive [18,12].

Previously, rigid-elastic polypropylene [19] and films of some vitreous thermoplastics such as polyvinyl chloride, polymethylmethacrylate, or polystyrene [20], which were deformed in the adsorption-active liquid medium by the craze mechanism, showed a possibility of recording information with a local thermal effect when under pressure. The pressure in combination with heat treatment at a temperature above the glass transition temperature compacts the microporous structure of crazes in the films and reduces the scattering of light from micropores by several orders. Thus, the local heat treatment areas become transparent and stand out against an opaque background. The symbols for information storage obtained by these known methods can be only monochrome and read visually in a reflected beam of unpolarized light [19,20].

B. Optical Characteristics of LDPE in Polarized Light

The scattering and absorption of polarized light passing or reflected from multilayered LDPE films are selective and depend on the light wavelength. Therefore, the light passing through the material is accompanied by bright color effects [11,12]. The dependency of the optical density and lightness of colored transparent multilayer materials in polarized light on the number of layers of LDPE films differs qualitatively from that of unpolarized daylight (Fig. 4). The dependence of the lightness of a multilayer material on the total thickness and the number of layers of 40 μm, 70 μm, and 100 μm polyethylene single films is described by a complex periodic function and depends on the polarizer position (Fig. 5).

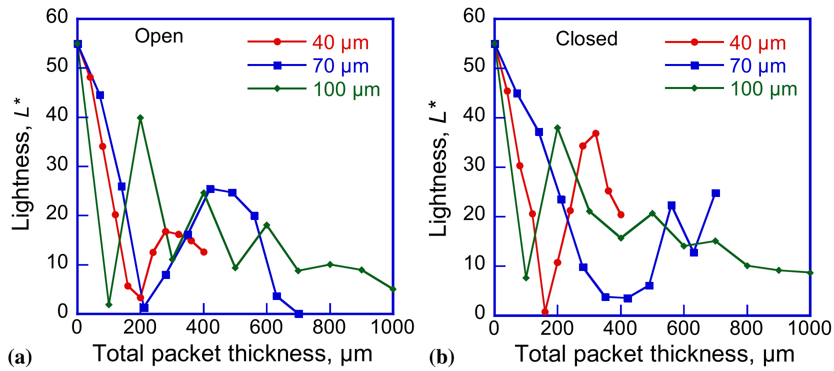

Fig. 5. Lightness dependence on the thickness of the multilayer polyethylene packet with polarizers in: (a) open and (b) closed positions.

For color coding [5,6], when recording digital information, the difference in shades of laminated materials collected from polyethylene films of different thicknesses is important, and coordinates in the CIE $L^*a^*b^*$ color space can be used to estimate the difference in shades instrumentally. The optical density and color coordinates vary from layer to layer, most significantly in a stack of films 100 μm thick. For example, with the polarizers in the open position, a packet containing one layer of a 100 μm polyethylene film produces a blue color, a packet with two layers produces a yellow color, and a packet with three layers produces a violet color [12]. Because color and lightness of a packet of films change due to light wave periodicity, these changes, by analogy with other physical oscillatory processes, can be quantified by an amplitude and a period (half-cycle) of the variations of color.

Wavelength periods were measured by observing the dependence of lightness on the number of polyethylene layers and the total thickness of the polyethylene packets with the polarizers in either the open or closed position. For the lightness of the transmitted light, an absolute scale was obtained by comparing the difference between an empty polyethylene packet with two perpendicular and then two parallel polarizers. After this, the maximum amount of light transmitted through a filled packet of films placed between the polarizers was measured (Fig. 5). The lightness of the light passing through film can be calculated with two methods: using the total film thickness in micrometers or using the number of stacks of known-thickness polyethylene layers.

Lightness period and amplitude with different light are clearly different in the multilayer materials made from films with varying thicknesses and varying thermal history. In addition, the lightness period and amplitude show a dependence on the position of the polarizers in Table 1.

The positions of the polarizers and analyzer placed on the surface of the packets of the polyethylene film greatly change the lightness period and amplitude of the light passing through the multilayer material. In the closed position, the lightness values were 76%, 37%, and 24% higher than in the open position for 40 μm, 70 μm, and 100 μm thick films, respectively. Lightness decreases with a symmetrically binary relation to the film thickness and the period. The decrease in lightness through an increase in film thickness decreases the period as the number of layers decreases.

After the 90°C heat treatment, the positions of the polarizers and analyzer have a different effect on the color of the light passing through the material compared to before heat treatment, as seen in Table 1. The maximum color difference is observed with open polarizers, and the minimum color difference is seen with closed polarizers. The lightness period is lower after heat treatment but still depends on the polyethylene layer thickness and decreases as the number of layers decreases.

With this information, it is important to note that the method of film heating used (IR radiation, hot gas convection, or direct metal contact), order of heating (before assembly of packets or with heating complete multilayer assemblies), and even temperature (lower or higher than melting temperature), do not change the lightness dependence of the output light on total packet thickness. This is proven by the testing results using 70 μm films in Table 1 that are melted together after

Table 1. Single and Multilayer Films' Lightness Periodic Characteristics

Polarizer State	Single Layer Thickness, μm	Period: Number of Layers	Period: Multilayer Total Thickness, μm	Lightness Amplitude
Film before heat treatment				
Open	40	5	200	28
	70	3	210	38
	100	1	100	42
Closed	40	6	240	50
	70	4	280	52
	100	1	100	52
Film after 90°C heat treatment				
Open	40	4	160	40
	70	4	280	42
	100	1	100	47
Closed	40	5	200	22
	70	5	350	30
	100	1	100	42
Double-layered film after 120°C heat treatment				
	140 (70 + 70)	2	280	43
	140 (100 + 40)	2	280	43

thermal treatment and form a total thickness of 140 μm or 280 μm in the two- or four-layer laminated packets (Fig. 1).

To check the possibility of information storage using local heating and control of background light, it is necessary to color the multilayer polyethylene film using brief thermal treatment in two temperature ranges: a temperature 30°C to 60°C below the melting point, and a temperature higher than the melting point. Recrystallization of fibrils due to 90°C thermal treatment reduces photoelasticity and suppresses the effect of pleochroism [12]. Suppressed pleochroism is advantageous for the manufacture of latent images, watermarks visible in polarized light, and protective marking of multilayer packaging materials. The results of thermal treatment with temperatures lower than the melting point are shown in Fig. 5. After heating to 90°C, all three periodic functions of the lightness of the film packet with varying film thicknesses behave differently compared to before heating. The lightness amplitude is reduced, while its period is increased. These changes in color and transparency of the packet of films of various thicknesses show that a laminate of material from six films of 70 μm thickness changes from being very transparent to dark after thermal treatment. In this case, the color difference of the materials in polarized light ΔE^*_{ab} reaches 60 units, which is 10 times higher than the sensitivity of the human eye and is completely usable for information storage and retrieval with barcodes [21]. Similarly, the color of the material can be changed by thermal treatment in a laminator at melting temperature, which allows the packet of films to be melted into a single piece for good mechanical characteristics and resistance against delamination.

4. CONCLUSION

The results of quantitative analysis and comparison of color effects in daylight and polarized light, shined on extruded LDPE film of one brand from thicknesses of 40–100 μm, showed new possibilities for digital color information encoding in a proprietary format. The changes of lightness amplitude and color of multilayer materials, assembled from films of various thicknesses, reach 50% through an increase in the number of layers. In addition, the lightness period and color change from one to six layers depending on layer thickness. The color difference of printed symbols and backgrounds of multilayer materials in polarized light is greater than the sensitivity of the human eye by a factor of 10 and allows for a great increase in the information capacity of color two-dimensional barcodes.

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REFERENCES

1. L. A. Grillo, M. Querini, and G. P. Italiano, "High capacity colored two dimensional codes," Presented at the International Multiconference on Computer Science and Information Technology, Wisła, Poland, October 18–20, 2010.
2. H. Kato, T. K. Tan, and D. Chai, "Novel colour selection scheme for 2D barcode," Presented at the International Symposium on Intelligent Signal Processing and Communication Systems, Kanazawa, Japan, December 7–9, 2009.
3. T. Shimizu, M. Isami, K. Terada, W. Ohyama, T. Wakabayashi, and F. Kimura, "Color recognition by extended color space method for 64-color 2-D barcode," Presented at the MVA IAPR Conference on Machine Vision Applications, Nara, Japan, June 13–15, 2011.
4. M. Querini, A. Grillo, A. Lentini, and G. F. Italiano, "2D color barcodes for mobile phones," Int. J. Comput. Sci. Appl. **8**, 136–155 (2011).
5. Microsoft Corporation Color Barcode Technology, High Capacity Color Barcodes (HCCB), Microsoft Corporation, 2007, https://www.microsoft.com/en-us/research/project/high-capacity-color-barcodes-hccb.
6. J. Tanida and Y. J. Ichioka, "Optical-logic-array processor using shadowgrams. III. Parallel neighborhood operations and an architecture of an optical digital-computing system," J. Opt. Soc. Am. A **2**, 1245–1253 (1985).
7. J. Jeong, D. Mascaro, and S. Blair, "Precise pixel patterning of small molecule organic light-emitting devices by spin casting," Org. Electron. **12**, 2095–2102 (2011).
8. Y. Yang, S. Omi, R. Goto, M. Yahiro, M. Era, H. Watanabe, and Y. Oki, "Wavelength sensitive photodiodes in the visible based on J-type aggregated films patterned by inkjet method," Org. Electron. **12**, 405–410 (2011).
9. H. Tanaka, H. Yasuda, K. Fujita, and T. Tsutsui, "Transparent image sensors using an organic multilayer photodiode," Adv. Mater. **18**, 2230–2233 (2006).
10. H. Coles and S. Morris, "Liquid-crystal lasers," Nat. Photonics **4**, 676–685 (2010).
11. A. P. Kondratov, "New materials for light strain-optical panels," Lgt. Eng. Svetotekhnika **22**, 74–77 (2014).
12. A. P. Kondratov, L. G. Varepo, I. V. Nagornova, and I. N. Ermakova, "Transparent layered materials based on variable color polyolefins," Procedia Eng. **113**, 423–428 (2015).
13. A. P. Kondratov, A. A. Volinsky, and J. Chen, "Scaling effects on color and transparency of multilayer polyethylene films in polarized light," Adv. Polym. Technol. **37**, 668–673 (2016).
14. R. T. Chen, C. K. Saw, M. G. Jamieson, T. R. Aversa, and R. W. Callahan, "Structural characterization of Celgard microporous membrane precursors: melt-extruded polyethylene films," J. Appl. Polym. Sci **53**, 471–483 (1994).
15. A. P. Kondratov, L. G. Varepo, and I. N. Ermakova, "Express diagnostics of polymeric petroleum products for its usage in latent watermarks of the smart packaging," Procedia Eng. **152**, 469–473 (2016).
16. A. P. Kulkarni, Y. Zhu, and S. A. Jenekhe, "Quinoxaline-containing polyfluorenes: synthesis, photophysics, and stable blue electroluminescence," Macromolecules **38**, 1553–1563 (2005).
17. I. V. Nagornova, L. G. Varepo, E. B. Babluyk, and A. P. Kondratov, "The SEM application for diagnostics of polyethelene films suitability for information recording by thermal printing," Procedia Eng. **152**, 464–468 (2016).
18. C. M. Fratini, "Study of the morphology and optical properties of propylene/ethylene copolymer film," Ph.D. thesis (Virginia Polytechnic Institute and State University, 2006).
19. A. P. Kondratov and M. A. Dryga, "Cryptography and multiple positive-negative reading of information on colorless transparent polymer films," RU patent RU2495753C1, IPC B41M 5/00, G11B 11/00 (10 September, 2013).
20. A. L. Volinsky, A. V. Volkov, M. A. Moskvina, A. A. Tunyan, L. M. Yarysheva, N. F. Bakeev, and A. V. Olenin, "Method for recording information on polymers," RF 2385370, IPC D06P 5/20, C08L 1/00, 25.12.2007 (27 March, 2010).
21. E. B. Bablyuk, Y. M. Berlad, A. G. Letyago, and A. P. Kondratov, "Materials for test objects to configure aviation optoelectronic Earth remote sensing systems," presented at 2016 Workshop on Contemporary Materials and Technologies in the Aviation Industry (CMTAI2016), Moscow, Russia, December 15–16 2016.