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RESEARCH ARTICLE

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Design and multilevel structuring of shape memory polymers for pleochroism control

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Abstract

Brands and products counterfeiting, and falsification are global problems for the development and distribution of high-tech industrial and food products, which affect world economies. One way to solve these problems is to develop original packaging with protection elements and labeling against counterfeiting, which excludes the possibility of replication and forgery by printing or other methods. The most reliable way to protect packaging from counterfeiting is the use of new materials with unique optical properties and constantly updated technologies for packaging manufacturing and labeling. This paper proposes a new multi-level technology for the design, manufacture and hidden labeling of polymer packaging made from several layers of transparent polymer films. The design and marking of the multilayer films are combined with perforation, thermal treatment and heat sealing of the package. The reliability of the proposed markings is based on the characterization of optical pleochroism effects in transparent multilayer polymer materials with shape memory. The thermomechanical and optical properties of films made of bulk thermoplastics (polypropylene, polystyrene, polyvinyl chloride and polyethylene) were characterized in polarized light. The modification and combination of these films provide a high color difference and sufficient contrast of hidden markings, allowing to identify genuine products by bar codes formed from shape memory films in sealing seams of flexible polymer packaging.

KEYWORDS

color difference, dichroism, differential scanning calorimetry, film lamination, hidden barcode on the package, pleochroism, polarized light, shape memory film, spectrophotometry, thermoplastic polymers

1 | INTRODUCTION

Pleochroism is the color dependence on the light direction and polarization or the viewing angle and occurs in transparent solids of mineral and organic origin. Color effects are quite diverse and sensitive to external factors in multiphase compositions of macromolecular compounds containing polymorphic crystalline fractions or transparent mineral ingredients.[1] There is no single reason or a single physical mechanism for the manifestation of multicolor effects when natural or polarized light passes through transparent polymeric and composite materials.[2] Many original and review articles are devoted to the study of the multicolor effects when

natural and/or polarized light passes through crystalline natural and artificial objects.[3] Pleochroism effects can be the result of spontaneous and forced structural transformations in crystallized homopolymers, random and block copolymers, polymer-polymer composites with interpenetrating networks of macromolecules. Multicolor and quantitative parameters of pleochroism depend on the relative position of the transparent object and the instrument that registers the light flux, temperature, optical and physical–chemical properties of the environment. Block copolymers can self-assemble into periodic photonic structures that have different intense colors in the transmitted light due to spontaneous phase separation of chemically different polymer blocks in macromolecules.[3,4] Spontaneous structuring processes of filled polymer compositions are intensified by introducing large polystyrene and small silica spheres into a high molecular weight binder.[5] Liquid or solvent vapors sorption from the environment affects pleochroism. It has been proven that the penetration of liquid into polymer films made from block copolymers causes the appearance of a reversible structural color.[6] An even more interesting mechanical-optical behavior was found in films containing cholesteric liquid crystals dispersed in a polymer.[7] Multicolor films with useful optical properties that respond to various external actions can be commercially produced for optical sensor applications.[8] The optical properties of these sensors are very sensitive to changes in temperature, light polarization, electric field, mechanical stress, or sorption of vapors and liquids.[9,10] However, technologies for producing protective and sensitive materials use expensive.[11] Transparent shape memory polymeric materials made of large-capacity thermoplastics[1] and modified natural polymers[12] are more economical, commercially available and can exhibit pleochroism.

Polymeric materials with shape memory effects are used in medicine,[1–6] orthopedics,[7–13] and pharmacology[14–18] for manufacturing endoprostheses[19–21] and implants.[22] Fibers and films with shape memory are used as biodegradable sutures and patches pulling together living tissues of the body.[23,24] Tubular products with shape memory effects are used as stents in cardiovascular surgery,[25-38] allowing access to hard-to-reach areas of the circulatory system for minimally invasive surgery.[39] These materials serve as flexible bandages in orthopedics,[40] which also have an antibacterial function, capable of releasing antiseptics during deformation.

Shape memory is most often manifested as thermally stimulated spontaneous compressive deformation or changes in one or two dimensions of the product with the ambient temperature. However, if the deformation of such products is constrained during heating due to mechanical fixation of dimensions, the shape memory effect is realized at the macromolecular and supramolecular levels in polymers by displacement of macromolecule segments and internal stress reduction. The internal stress changes in the films during heating can be measured at the macroscopic level by strain sensors connected in series with the films[41] or optically by spectrophotometers in a polarized light.[42] The conditions of such geometrical constraint of materials during heat treatment are called isometric and are used to stabilize or modify the supramolecular structure of oriented thermoplastic films. During repeated isometric heat treatment, the supramolecular structure of a stressed deformed polymer material changes from a non-equilibrium state to a state approaching equilibrium under changed conditions. In this case, the color optical effect of pleochroism appears or disappears in polarized light,[43,44] which is greatly enhanced in multilayer films[45] and can be used to record coded information, for example, by security marking of film packaging in the Microsoft Tag binary color code system.[46-48] Patents describe high-cost and material-consuming methods of producing artistic works with pleochroic effect and protective packaging elements with the use of rare expensive pigment ingredients or toxic dyes.[49]

The present study aims to demonstrate the concept of decorative multicolor films made from common bulk polymers that change color in polarized light when viewed at different angles without using toxic dyes.

2 | MATERIALS AND METHODS

2.1 | Materials preparation

Different shrinkable polymer films and multilayers with shape memory were used in this study. Vinyl chloride/vinyl acetate copolymer and polyvinyl chloride PVCLF-T147/07 T25 manufactured by Klockner Pentaplast were used as components of laminated multicolor decorative films. Other starting materials included 50 μm thick PVC films made by Dongil Chemical (South Korea), 60 μm thick PVC films made by Don-Polymer (Russia), and 45 μm polyethylene terephthalate and polystyrene shrinkable films produced by Pentalabel (Germany), and 25 μm isotactic polypropylene shrinkable biaxially oriented films, along with 45 μm low-density polyethylene films produced by Biaxplen (Russia).

All films were commercially produced by the polymer melt two-stage stretch extrusion. The films were stored in an airconditioned room at $20 \pm 2^{\circ}C$ in rolls. Polymer films are anisotropic in terms of mechanical and optical properties and have preferential orientation direction of macromolecules, which does not coincide with the direction of melt extrusion and roll unwinding. Laboratory

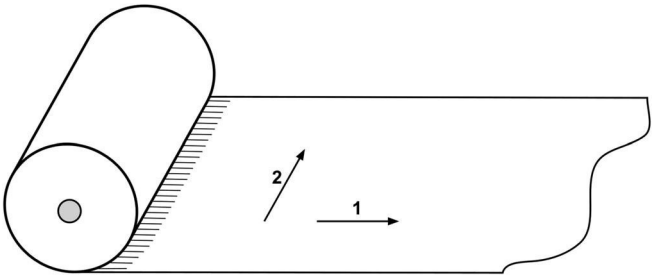


FIGURE 1 Cutting of a linearly oriented film. Here, 1 – macromolecules preferred orientation direction =, 2 – perpendicular direction ⊥.

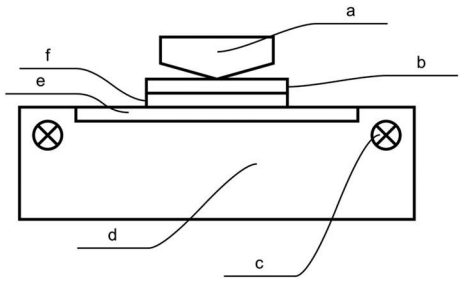


FIGURE 2 Schematics of the lightbox for obtaining spectral characteristics of film packet samples. Here, a is a spectrophotometer, b is the rotating polarizer, c is the LED strip, d is the chamber, f is the film sample, and e is the fixed polarizer.

samples for structuring and assembling multilayer materials were cut in two perpendicular directions as shown in Figure 1.

2.2 | Films characterization

Nitto general-purpose polarizer with 44.5% single transmittance and 95.8% polarization was used to polarize the light. The chemical composition of commercial polymer films with a shape memory effect was controlled by the multiple frustrated total internal reflection method using FSM 2201/2202 IR Fourier spectrometer and spectra libraries (HR Spectra Polymers and Plasticizers by ATR, HR Hummel Polymer and Additives, Hummel Polymer Sample Library, Synthetic Fibers by Microscope, HR Nicolet Sampler Library). Differential scanning calorimeter (DSC, PC–DSC 204 Phoenix, NETZSCH, Germany) was used to obtain thermograms for optimal structure modification temperature at 10°C/min heating rate. The DSC thermograms were used to determine the melting temperature of crystallizing polymers and the glass transition temperature of amorphous polymers. Short-term contact of shape memory polymer films with a heated metal surface was carried out under isometric conditions at the glass transition temperature of amorphous polymers and at the melting temperature of amorphous-crystalline polymers for 5 s.

2.3 | Films treatment and measurements

To modify the supramolecular structure of polymers by local isometric heat treatment of films and multilayer film packages, a custom-built laboratory setup was used designed to simulate the process of thermal welding of thermoplastic materials of conveyor and press type (Figure 2) with high-precision control of temperature, time, and pressure in the contact area of the films. Varying heat treatment parameters of the films forming multilayer packages makes it possible to modify the anisotropic structure of multilayer-forming polymers during duplication and ensures color optical effects. Heat treatment of film packages to modify the supramolecular structure was carried out in two ways. The first included a special temperature–time regime in which no adhesive monolithization of adjacent layers takes place. In the second, the contacting layers are thermally welded (monolithized) and liners are combined with the surrounding layers. Images and bar codes were cut out from transparent polymer films for stacking between monolithic layers using rod knives, considering the direction of preferential orientation of macromolecules in the polymer film (Figure 1).

Thermal treatment of mono-films packages of 8–12 films in the form of Stoletov pile, and layouts of multilayer packaging with a bar code in the sealing area were performed on a laboratory thermo-welding stand HSE-3 by RDM Test Equipment Co Ltd (United Kingdom) under 0.2 MPa (30 psi) pressure and an automatic roller welding machine Hualian FRB-770I by Hualian Machinery (China, Figure 3) in mutually perpendicular directions along and across the preferred orientation of macromolecules in the samples (Figure 1).

The internal stress in shape memory materials is estimated by measuring the film shrinkage force using a strain gauge and a water thermostat. The tensiometer makes it possible to measure the internal stress in a shape memory polymer in real time according to the tension force of the film when heated in a liquid.[41] Drops (or a thin layer) of a plasticizing liquid are applied to a package of films in the form of a Stoletov stack[38] with a brush or an inkjet printer. A colorless printing varnish or ink jet printers containing a "thermodynamically good" solvent of the film-forming polymer can be used as a plasticizing liquid. In this case, a "thermodynamically good" solvent should have high volatility (low boiling

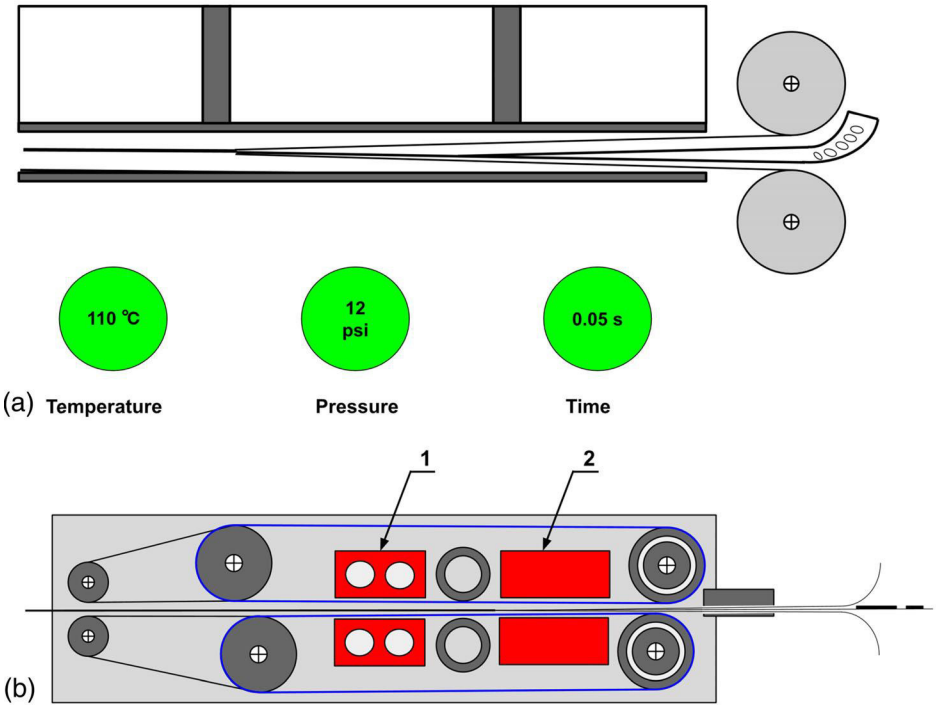


FIGURE 3 Schematics of devices for local heat treatment: (a) Precision thermal press for modeling polymer welding and heat treatment processes; (b) Automatic roller welder for high-speed heat treatment and film welding. Here, 1 is the heater and 2 is the Peltier cooler. [Color figure can be viewed at wileyonlinelibrary.com]

point) and a minimum value of the criterion of thermodynamic compatibility with the Flory-Huggins polymer (less than 0.5).[50] The solvent quickly penetrates into the polymer film after application, and, as a result, the local internal stresses decrease where the liquid is absorbed by the polymer.[51–53] A tetrahydrofuran solution was used to control color effects in polyvinyl chloride films.

To obtain spectral characteristics and transmission coefficients of colored films, a lightbox with an LED strip and a window covered with a polarized film was used. The sample was placed on the lightbox as shown schematically in Figure 2. Measurements were obtained using an X-Rite i1Pro spectrophotometer and the ArgyllCMS version 2.3.0. The instrument operated in the high-resolution spectrum mode (3.33 nm measurement step) and emission measurement mode. As a result, spectral radiance of the light source and samples with polarized film at two angles of rotation on the lightbox surface were obtained.

The spectral transmittance coefficients of the samples were obtained by dividing the spectral radiance of the films with a different number of layers by the spectral radiance of the LEDs when the polarized film was superimposed. From the spectral transmittance coefficients of the films, the CIE 1931 color coordinates for a standard 2-degree observer were calculated assuming a D65 light source, and the color differences between the different numbers of film layers were calculated using the ΔE_{2000} formula. The Color library of the Python programming language was used in the calculations.[54] Optical effects after heat treatment and measurement of film color parameters in transmitted light were described from photographs using an iPhone 8 smartphone camera and the built-in DisplayP3 color profile.

The spectral transmittance coefficients S(λ) of the samples were obtained by dividing the spectral radiance ($L_{e,\Omega,\lambda}$) of the films with a different number of layers by the spectral radiance of the LEDs with the polarized film. From the spectral transmittance coefficients S(λ) of the films, the L*a*b* color coordinates (1–2) for a standard 2-degree observer with reference standard illuminant D65 were calculated, and the color differences (3) between the colors produced by different numbers of film layers.[55] The Color library for the Python programming language was used in the calculations.[54] The color effects were evaluated using the color coordinates of the CIA L*a*b* equal-contrast color rating system and the color difference ΔE_{76}:[56]

$$\Delta E_{76} = \sqrt{(L^*_2 - L^*_1)^2 + (a^*_2 - a^*_1)^2 + (b^*_2 - b^*_1)^2} \quad (1)$$

$$L^* = 116 f\left(\frac{Y}{Y_n}\right) - 16, a^* = 500\left[f\left(\frac{X}{X_n}\right) - f\left(\frac{Y}{Y_n}\right)\right], b^* = 200\left[f\left(\frac{Y}{Y_n}\right) - f\left(\frac{Z}{Z_n}\right)\right] \quad (2)$$

$$\Delta E_{76} = \sqrt{(L^*_2 - L^*_1)^2 + (a^*_2 - a^*_1)^2 + (b^*_2 - b^*_1)^2} \quad (3)$$

Here, L* is lightness, a* is the position between red and green, and b* is the position between yellow and

blue. X, Y, Z describe the color stimulus considered and X_n, Y_n, Z_n describe a specified white achromatic stimulus.[57] For standard illuminant D65: $X_n = 95.04, Y_n = 100.00, Z_n = 108.88$,[46] and $\bar{x}, \bar{y}, \bar{z}$ are color matching functions describing the CIE standard 2-degree observer.[58]

Quantitative results that determine the possibility of identification or visual reading (detection of recording in transmitted polarized light) are the color differences between the background and the symbol or color difference between adjacent areas ΔE_{76}. The threshold of human eye perception is $\Delta E_{ab} \geq 2–3$.[59] Color effects after heat treatment and measurement of film color parameters in transmitted light were described from photographs using an iPhone 8 smartphone camera and the built-in DisplayP3 color profile via L*a*b* coordinates and color differences ΔE_{76}.

Thermal treatment of mono-films with shape memory, packages of 8–12 films in the form of Stoletov pile, and layouts of multilayer packaging with a bar code in the sealing area were performed on a laboratory thermowelding stand HSE-3 by RDM Test Equipment Co., Ltd. (United Kingdom) under 0.2 MPa (30 psi) pressure and an automatic roller welding machine Hualian FRB-770I by Hualian Machinery (China, Figure 3) in mutually perpendicular directions along and across the preferred orientation of macromolecules in the samples (Figure 1).

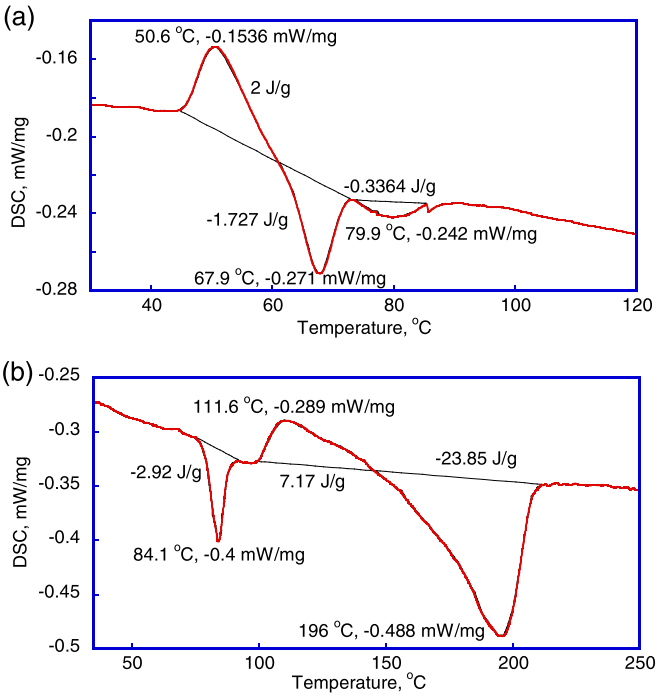


FIGURE 4 Differential scanning calorimeter (DSC) thermograms of shrink-wrap films: (a) polyethylene terephthalate and (b) polyvinyl chloride. [Color figure can be viewed at wileyonlinelibrary.com]

3 | RESULTS AND DISCUSSION

It is well known that the pleochroism of polymer films in polarized light and the shape memory effects are caused by internal stresses in films of amorphous glassy and amorphous-crystalline polymers obtained by orientation stretching in the highly elastic state. Internal stresses arise as the films are deformed by cooling in contact with the massive metal cylinder surface, which provides a high heat transfer rate by conducting the heat energy from the polymer in contact with the high heat capacity body. The distribution of internal stresses over the film thickness is heterogeneous, with a significant gradient perpendicular to the directions of melt extrusion and orientation drawing. Localization of internal stresses in thin layers of the outer film surface in contact with the cooling metal cylinder was detected and quantified by differential scanning calorimetry.[50] The high level of internal stresses in films of isomorphic-crystalline polymers is maintained in the glassy state for a long time and can be quantitatively measured by the exothermic effect of film shrinkage during heating at a constant rate. The exothermic effect can be seen in differential scanning calorimetry thermograms when studying the thermally stimulated shrinkage of crystallizing polymer films with a glass transition temperature over 20°C below the melting point of the crystallites. The maximum exothermic shrinkage effect when heating shrink-wrap polyethylene terephthalate film is located at 115°C in the temperature range exceeding the polymer glass transition temperature by 30°C and 83°C below the polymer melting point in Figure 4a. The exothermic shrinkage effect is 4 times less than the endothermic melting effect of the crystalline part of the polyethylene terephthalate film. The exothermic shrinkage effect of vinyl chloride copolymer film is commensurate with the endothermic melting effect of the crystalline part of the film in Figure 4b.

A quantitative assessment of the internal stresses and elastic energy in films with a shape memory effect can be made by directly measuring the compression force of the samples when heated at a constant rate under isometric conditions.[50] To measure the internal stresses in the films with the shape memory effect and fix the maximum values of tension force, the film samples in the form of ribbons were connected to a dynamometer and immersed in hot water at 60–95 ± 2°C.

When films with the shape memory effect are briefly heated under isometric conditions, there is a partial relaxation of internal stresses and the elastic energy release to restructure the supramolecular structure. Due to the low thermal conductivity of polymers, the

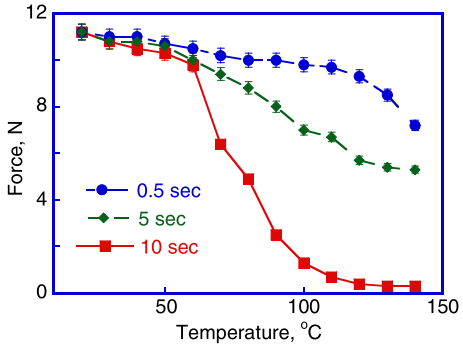


FIGURE 5 Tensile force in polyethylene terephthalate film with shape memory in hot water after preliminary short-term isometric heat treatment for 0.5, 5, and 10 s. [Color figure can be viewed at wileyonlinelibrary.com]

relaxation of internal stresses in films depends more on the heat transfer time than on the heating tool temperature (counter body). For example, the contact of polyethylene terephthalate films with the metal surface of the tool dies heated to the maximum temperature of the exothermic shrinkage effect of 115°C allows for reduction and/or elimination of internal stresses by an order of magnitude in 10 s in Figure 5.

Short-term contact of polymer shape memory films with heated metal tool surfaces under isometric conditions makes it possible to modify the structure of glassy amorphous and amorphous-crystalline polymers and control their color in polarized light. Isometric conditions can be realized without the mechanical constraint of overall dimensions during local short-term heating of polymer films in the glassy state. Isometric conditions are satisfied if the area of local heating of the film is significantly smaller than the size of the entire film surface area. In this case, the stiffness of the surrounding and larger adjacent part of the glassy polymer film prevents shrinkage and warping of the areas subjected to heating. The heat-activated relaxation of internal stresses in the local region causes changes in the supramolecular structure and color in polarized light and manifests itself in changes of the film surface shape.[53] The color and quantitative parameters of polarized light passing through a multilayer package depend on the chemical composition of the film-forming polymer, the structure, and the level of internal stresses in the films. The brightest colors were found in shrink films of polystyrene, polyvinyl chloride, and low-density polyethylene (Table 1).

When visually assessing the color of the PVC film package in the heat-treated areas in Figure 6, the colors of the modified areas with more than 2 layers correspond to the color of the adjacent area with fewer layers, which has not been treated. This effect of "invisibility" of a part

TABLE 1 Thermally-stimulated shrinkage stress in shape memory films.

Polymer film material	Temperature range of isometric heating in hot water, °C	Maximum shrinkage stress, MPa
Polyethylene terephthalate	60–95	13.2 ± 2.5
Vinyl chloride/vinyl acetate copolymer	60–85	11.7 ± 3.3
Polyvinyl chloride	60–75	10.3 ± 2.2
Polystyrene	60–75	8.2 ± 1.4
Polypropylene	50–65	6.2 ± 1.6
Low-density polyethylene	50–65	4.3 ± 1.4

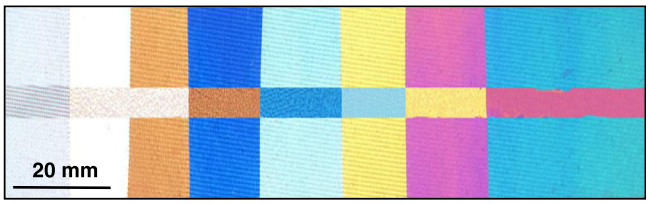


FIGURE 6 Color of eight PVC films package in transmitted polarized light after local heat treatment of the outer layer (band in the center). [Color figure can be viewed at wileyonlinelibrary.com]

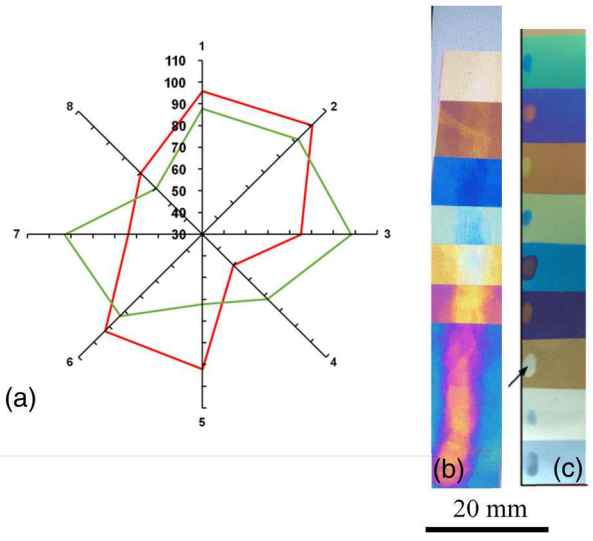


FIGURE 7 (a) Lightness L* of polyvinyl chloride film packages from 1 to 8 layers. Here, 1 is film before modification and 2 is film after treatment with an aqueous solution of tetrahydrofuran. Positions 1 to 8 in the beam diagram correspond to the number of layers in the liquid-treated region of the polyvinyl chloride film package; (b) Photo of a film package after local treatment with a 20% aqueous solution of tetrahydrofuran cut along the roll direction and (c) perpendicular to the roll direction. [Color figure can be viewed at wileyonlinelibrary.com]

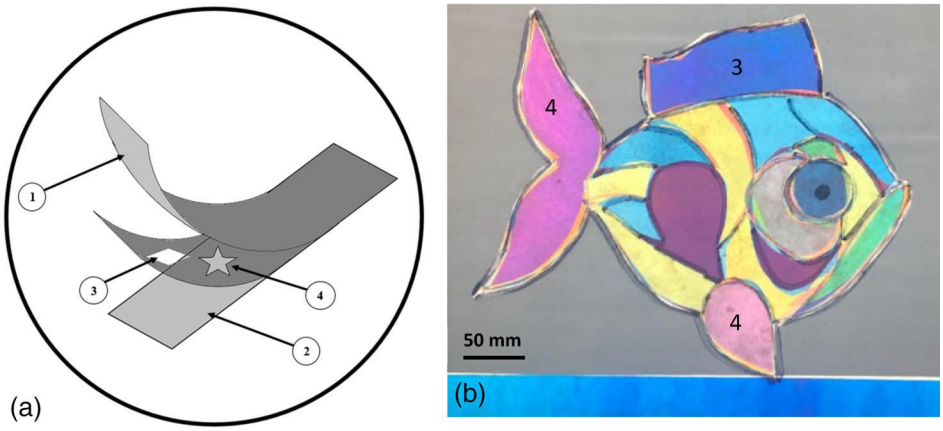


FIGURE 8 (a) Schematics of layer assembly and placement of a flat structure in a layered polymer. Here, 1, 2 are external monolithic layers of a polymer film, 3 is carving of the middle layer, and 4 is the embedding of flat figures; (b) An example of a combination of cutting and placement of flat elements of a figure in a package of polyvinyl chloride films (viewed in a transmitted polarized light). [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Color coordinates of three-layer polyvinyl chloride films. [Color table can be viewed at wileyonlinelibrary.com]

Tilt angle, degrees	15	30	45	60	75	90	105	120	135	150	165
L*	83	73	63	62	63	69	64	63	65	77	86
a*	−4	3	41	32	38	21	29	33	35	−6	−5
b*	−9	−16	−5	−22	28	42	10	−10	0	−17	−7
Color											

TABLE 3 Color coordinates of three-layer polypropylene films. [Color table can be viewed at wileyonlinelibrary.com]

Tilt angle, degrees	15	30	45	60	75	90	105	120	135	150	165
L*	85	81	75	79	71	75	74	82	79	82	89
a*	14	−22	−51	28	48	35	40	35	−46	−30	10
b*	18	30	11	−18	−19	−6	−15	−24	5	48	21
Color											

of the outer layer in the transmitted polarized light that occurs after heat treatment is of practical interest for solving problems in stained-glass design and deserves special research and artistic evaluations. Reducing the level of internal stresses by local heat treatment has been proposed for recording information and covert labeling of film packaging made from these polymers.[50]

An alternative option for the local reduction of internal stresses in films with a shape memory effect is diffusion plasticization with volatile organic solvents.[50] To study the effects of plasticizers and solvents contained in polygraphic varnishes on the color of multilayer polyvinyl chloride films, identical multilayer packages were assembled and a liquid layer was applied using a polygraphic technique with a single movement of the squeegee on a stencil form.

The photos obtained in polarized light show that both organic liquids significantly change the color of the layered polymers in the transmitted polarized light, which seems to be caused by a decrease in the level of internal stresses and rearrangement of the supramolecular structure of shrinkable polyvinyl chloride films. Based on the results of color coordinate measurements, a diagram of the jump change in lightness in the package of L* films in adjacent areas affected by organic liquids was plotted in Figure 7. The diagram shows that the lightness of the packets after exposure to the solvent changes significantly and periodically reaches the level of lightness of the film packet untreated by the liquid, but with a different number of layers. After treatment with tetrahydrofuran (blue dots), the lightness of the package in 3 layers of the film coincides with the lightness of the dry package of 2 films

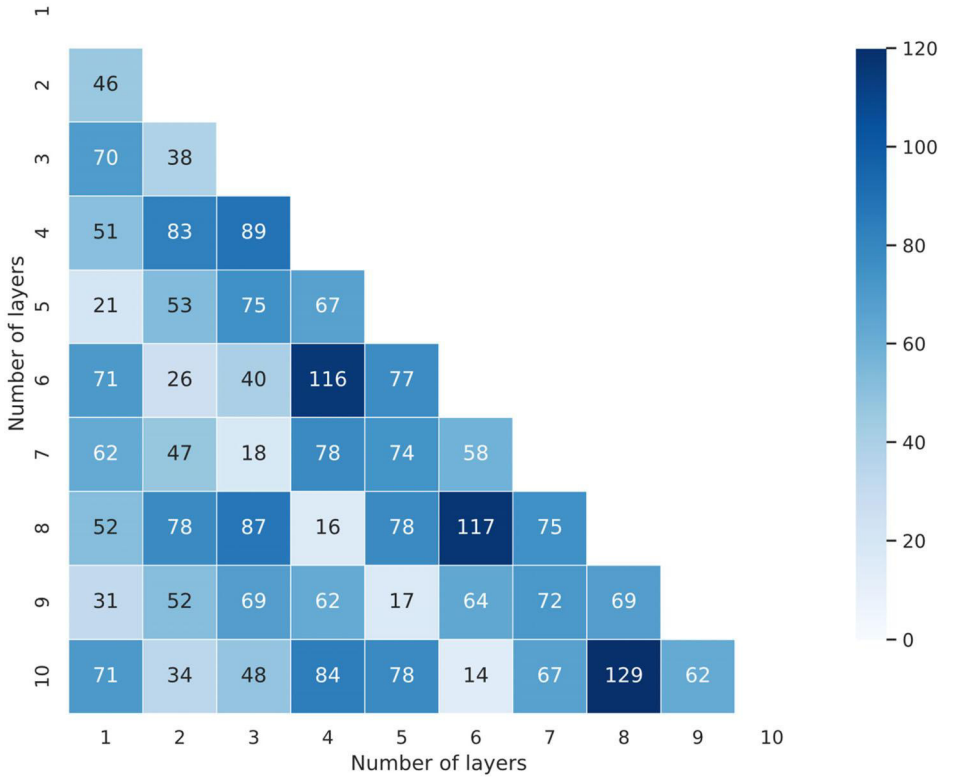


FIGURE 9 Color difference ΔE_{00} of adjacent sections of a transparent 10-layer PVC film with a die-cut of 1 to 9 layers. [Color figure can be viewed at wileyonlinelibrary.com]

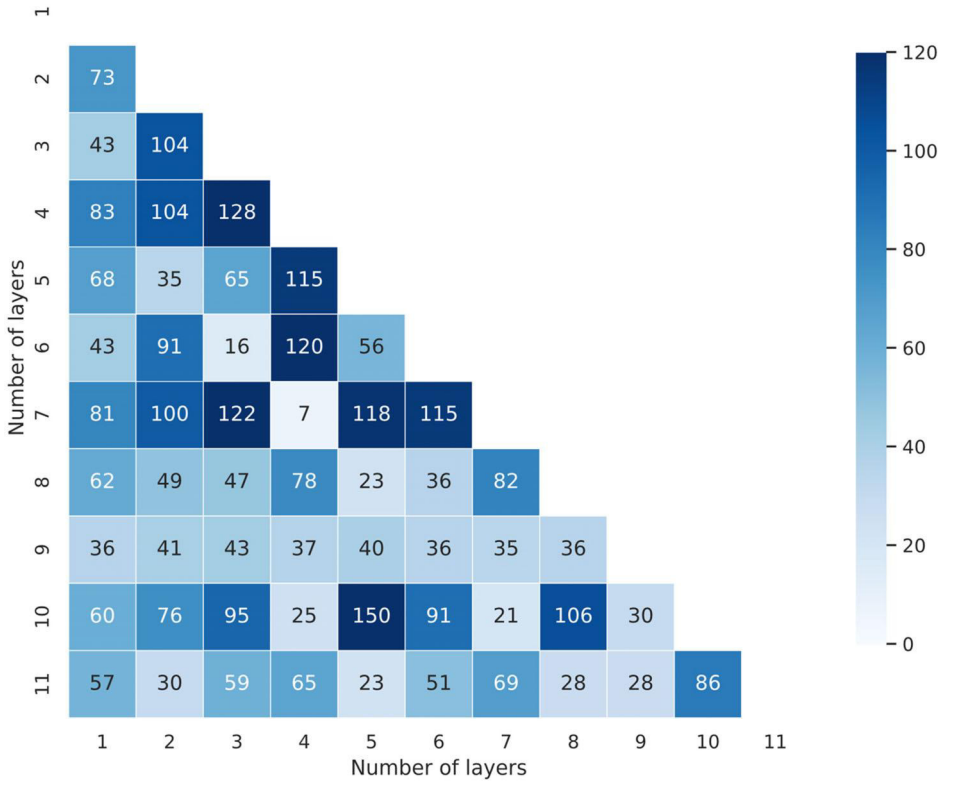


FIGURE 10 Color difference ΔE_{00} of adjacent sections of 10-layer clear polystyrene (PS) film with die-cutting from 1 to 9 layers. [Color figure can be viewed at wileyonlinelibrary.com]

(red dots). After treatment of the film packet with cyclohexanone (green dots) – a violation of the period of alternation of maximum and minimum lightness is observed only in the packets assembled from 7 layers.

The "invisibility" of the outer layer of multilayer film packages due to heat and solvent treatment is the result of the restructuring of polymers at the supramolecular level and appears with maximum contrast and color

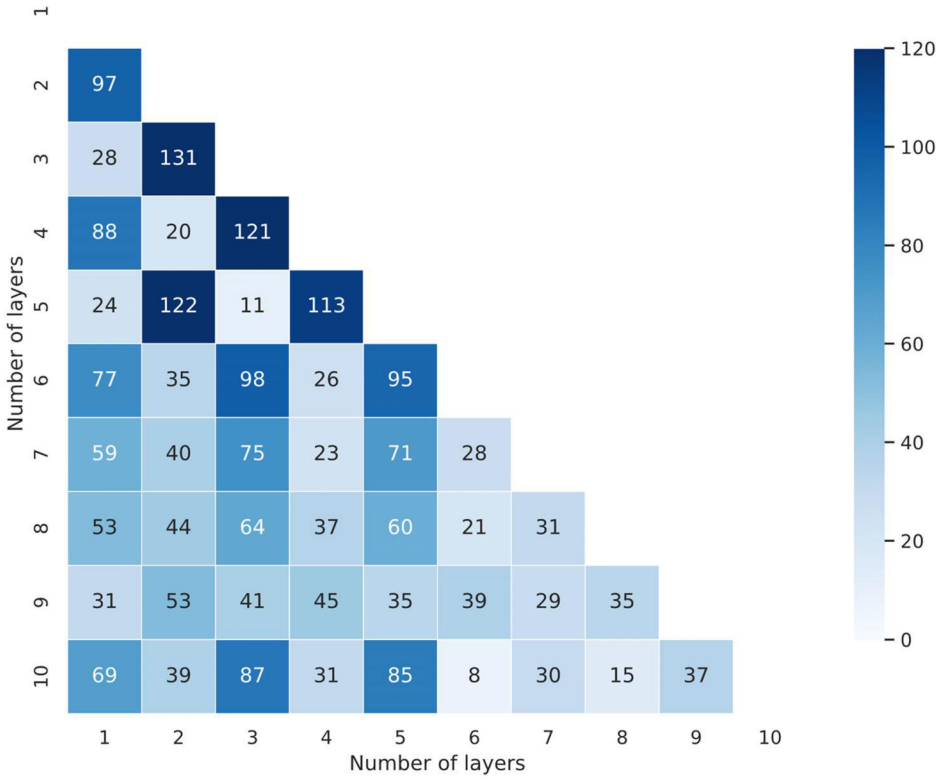


FIGURE 11 Color difference ΔE_{00} of adjacent sections of a transparent 10-layer film of isotactic polypropylene (IPP) with die-cut from 1 to 9 layers. [Color figure can be viewed at wileyonlinelibrary.com]

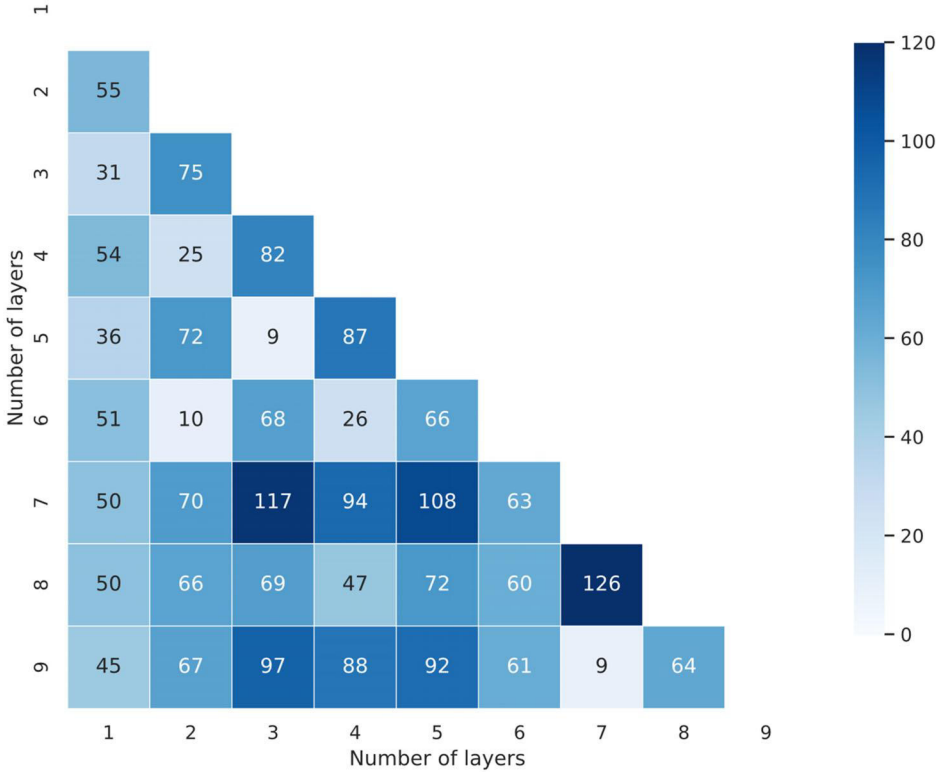


FIGURE 12 Color difference ΔE_{00} of adjacent sections of a transparent 9-layer polyethylene (HDPE) film with die-cut from 1 to 8 layers. [Color figure can be viewed at wileyonlinelibrary.com]

difference when multiple layers of films with the shape memory effect are duplicated. Similar thermal restructuring of polymer mono films with a thermostabilized supramolecular structure without shape memory causes only monochromatic effects and a significantly smaller change in optical properties in polarized light.

There are limited practical applications of the "invisibility" effect in the outer layer of the multilayer film

Number of layers N/n	2	3	4	5	6	7	8	9	10
1	82	31	72	42	65	60	67	58	65
2	—	51	9	40	16	21	15	24	16
3	—	—	41	11	34	29	36	27	34
4	—	—	—	30	7	12	5	14	7
5	—	—	—	—	23	18	25	16	23
6	—	—	—	—	—	5	2	8	0
7	—	—	—	—	—	—	9	2	5
8	—	—	—	—	—	—	—	9	2
9	—	—	—	—	—	—	—	—	8

TABLE 4 Contrast of adjacent sections of multilayer (N layers) isotactic polypropylene film with die-cut part (N–n) layers.

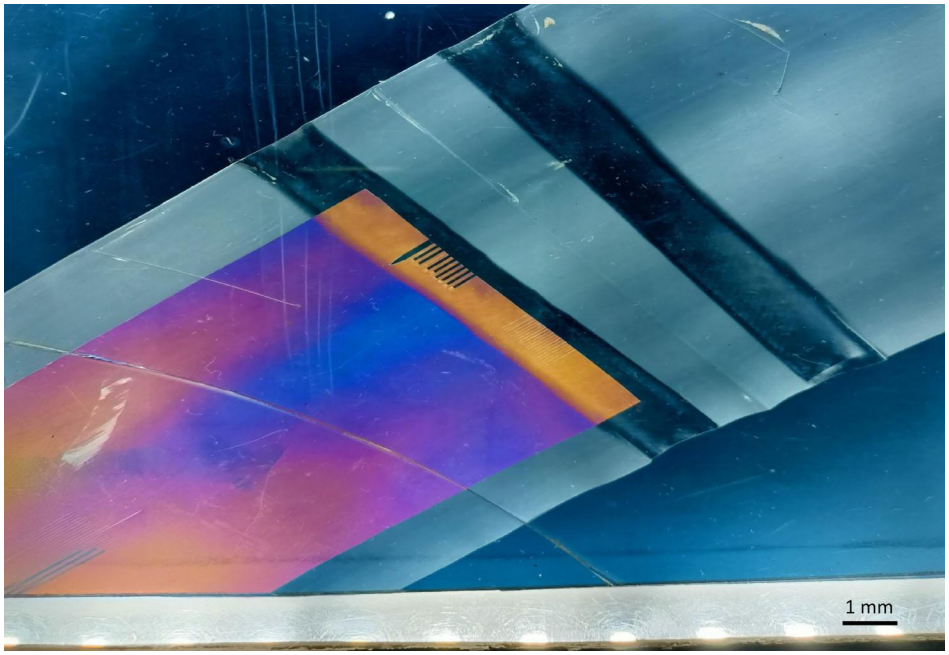
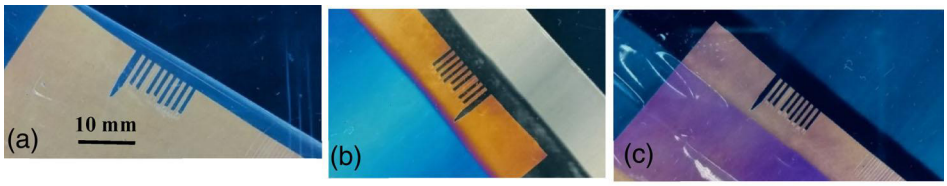
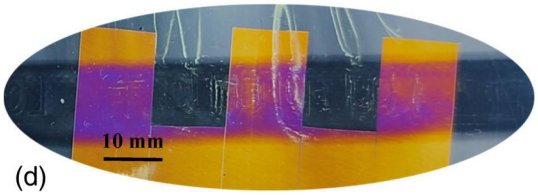


FIGURE 13 Die-cut linear bar code fragment in a biaxially oriented "Biaxplen" polypropylene film. [Color figure can be viewed at wileyonlinelibrary.com]



ΔE_{00}=54	ΔE_{00}=64	ΔE_{00}=45.9
Contrast 35.6	Contrast 31.3	Contrast 27.5



ΔE_{00}= 64
Contrast 57

FIGURE 14 Carving a fragment of a linear bar code in a polypropylene film (inside) of the packaging sealing strip. (a) Outer layers: from a polyvinyl chloride film cut along the predominant orientation of macromolecules; (b) perpendicular to the predominant orientation of macromolecules and (c, d) stretch-film of low-density polyethylene. [Color figure can be viewed at wileyonlinelibrary.com]

packages after plasticization and local heat treatment to solve stained glass design problems in architecture and the production of exclusive transparent containers and packaging of goods in plastic films. The reasons for the limitations are the high toxicity of organic solvents and the possibility of changing the optical properties of only one outer layer of the multilayer material. The practical applications of local layer transparency in film packages with a shape memory effect for changing colors and solving design problems can be significantly expanded by die-cutting one or more inner layers in the multilayers or by placing flat pieces cut out from transparent polymers or printed with transparent varnish between the layers (Figure 8).

The local change in transparency and color of layered polymers in a polarized light depends on the chemical composition and the number of adjacent film layers in the die-cut area or the location of the flat piece. Pleochroism of optical effects and individual human perception of color images is determined by the viewing angle and is quantitatively characterized by L*a*b* color coordinates. The technique for measuring pleochroism for gems is described in Ref. 56 using a digital camera and further obtaining L*a*b* color coordinates. A similar approach was used in this paper but with added rotation of the sample to obtain measurements at different viewing angles on polymer films.

Color coordinates and photocopies of three-layer films of polyvinyl chloride and isotactic polypropylene at a view angle varied from 15° to 165° are listed in Tables 2 and 3, respectively. The quantitative results of the color difference of the images in the die-cut area of one or more layers within a shape memory PVC, polystyrene, and polypropylene laminates are presented as tables and/or two-dimensional diagrams in Figures 9, 10, 11 and 12. The cells of the tables contain numerical values of color difference ΔE_{00}[60] of images in relation to the color of the multilayer material in the polarized light in the "open" or "closed" positions of the crossed polarizers.[53]

Additional technological possibilities for enhancing the contrast of color effects in multilayer materials are offered by a combination of die-cutting of inner layers with modification of the supramolecular structure of the outer layer, such as isometric heat treatment or plasticization. Quantitatively, the contrast of multilayer die-cut films is estimated using the spectral transmittance of the films, from which the color coordinates are calculated in the XYZ space, where Y is the brightness parameter (Table 4). For example, the maximum brightness of the light symbol such as an image element or a space of a linear bar code is taken as 100%, and in order to get the contrast value of the symbols, we normalized it by the brightness values of the section of the multilayer film with die-cutting of N-n layers. For optimal code reading by an industrial scanner, the brightness of the light area should exceed the brightness of the dark area by over 25%.

An example of solving such a complex problem is to create a linear barcode inside the welding seam on transparent product packaging made of polypropylene (Figure 13). The contrast of dark and light elements of the barcode, carved in the middle layer of polypropylene film placed between the outer layers, is more than 25%, which is enough to read the information by merchandise scanners of different models.

The color of the barcode elements carved into the middle layer of polypropylene film and placed inside the welding seam of the transparent packaging depends on the chemical structure of the outer layers and their heat treatment mode during welding. Figure 13 shows a layout of the sealing strip (welding seam) of the package in transmitted polarized light made of a three-layer transparent film. The inner layer of polypropylene film has die-cut elements of a linear bar code, and the outer layers are made of PVC film cut along the preferential orientation of macromolecules (a), polyvinyl chloride film cut perpendicular to the preferential orientation of macromolecules (c) and additionally covered with "stretched" film of low-density polyethylene (c).

The combination of several layers of films from different thermoplastics allows solving design problems and protecting the product inside the package. In the example shown in Figure 14a,c, the inner layer of polypropylene ensures compliance with hygienic requirements for food storage conditions, while the outer layers of polyvinyl chloride ensure high-quality printing with different inks and protection against oxygen and vapors of toxic or strong-smelling substances penetrating the package. Figure 14c with outer layers of low-density polyethylene film demonstrates the possibility of preserving the color difference and minimal contrast of barcode elements when using additional layers or group packaging of small goods in the "stretched" film.

4 | CONCLUSIONS

The pleochroism in multilayer polymer films with a shape memory effect has been studied and the possibility of recording images and/or bar codes visible in transmitted polarized light by perforation (cutting) or by adding (application) symbols cut from a film of the same or other chemical composition. Photometry and direct measurement of the color parameters of transparent multilayer films with a shape memory effect made of thermoplastics in a transmitted polarized light at 15°–165° angles to the plane of the

film surface were implemented to determine the contrast of adjacent layers containing hidden information read by barcode scanners. The minimum number of homopolymer layers (polystyrene, polyvinyl chloride, polypropylene, and polyethylene) was established experimentally, at which adjacent sections of different thicknesses (different number of layers) have the maximum contrast and color difference, sufficient to identify hidden images in the transmitted polarized light. Maximum contrast conditions do not coincide with the maximum color difference conditions between adjacent layers of a multilayer film made from one polymer. Maximum contrast of 82 units is between 1 and 2 layers of polypropylene film and 72 units between 1 and 4 layers of polypropylene film. The maximum color difference is between 4 and 3 layers of polypropylene film in the same material, and its contrast is half the maximum. Obtaining sufficient contrast and color difference for bar-coding of adjacent sections of macrostructured perforation multilayer films after local sealing heat treatment (heat sealing of packaging) with additional shielding of the perforation zone with transparent layers of bio-neutral polymers approved for use in food packaging and/or suitable for printing inks (low density polyethylene) is possible.

AUTHOR CONTRIBUTIONS

Alexander P. Kondratov: Conceptualization (lead); data curation (lead); formal analysis (equal); project administration (lead); resources (lead); supervision (lead); writing – original draft (lead). **Alexander Nikolaev:** Conceptualization (supporting); formal analysis (supporting); methodology (equal); validation (supporting); writing – original draft (supporting). **Victor G. Nazarov:** Conceptualization (supporting); formal analysis (supporting); investigation (equal); methodology (equal). **Vladislav Y. Vereshchagin:** Data curation (equal); formal analysis (supporting); methodology (equal); resources (equal); visualization (supporting). **Alex Volinsky:** Formal analysis (equal); investigation (equal); software (equal); validation (equal); writing – review and editing (lead).

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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