Scaling Effects on Color and Transparency of Multilayer Polyethylene Films in Polarized Light

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ABSTRACT: Transparency and color of polyethylene film layered packages change with the number of layers. When polyethylene layer thickness is between 50 μm and 200 μm, each additional subsequent layer in the package leads to an abrupt change in color and transparency. Polarized light optical effects can be used to manufacture packaging films and labels with forgery protection. A significant influence of the scaling factor on the latent effect and optical properties of the film package is demonstrated for one to six layers with the total thickness of 200 ± 50 μm. Prior thermal treatment of individual layers before they are assembled into a package or assembled package heat treatment change the laminate color. This allows hidden marking and recording text or graphics on the multi-layer films, not visible under normal lighting conditions, but appearing when viewed in polarized light, or through the polarizer. The paper demonstrates obtaining bright colored decorative or packaging materials, along with light filters for advertising and information displays, which change color with the viewing angle. New materials can be prepared using standard industrial equipment and widely used polymers. By changing the location of the film polarizers, the number of layers and the film thickness, laminates vary in brightness and color from blue to red. © 2016 Wiley Periodicals, Inc. Adv Polym Technol 2018, 37, 21708; View this article online at wileyonlinelibrary.com. DOI 10.1002/adv.21708

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Introduction

Multilayer polymeric materials are used for packing banknotes and anti-forging protection elements of securities, credit cards, documents, checks, check cards, passports, tickets, certificates and passes, etc.[1] These complex security elements allow verifying product authenticity using visual and/or automated methods. Quite often, several security elements are combined, where some of them can be detected only by using special techniques and equipment (light filters, polarizers, UV or IR illumination, etc.), while others can be simply touched or seen by a naked eye. Various security printing materials have been patented with diffractive layered structure exhibiting color shift, or the latent effect, where color changes with the observation angle.[2,3] Multilayer structures with bright colors are typically produced by metal physical vapor deposition.

A more complex technique allows obtaining multilayer films with security markings, where micro-relief structures are formed in the inner layers of the security elements. Thin layers of transparent polymer are deposited over the micro-relief between the films to create interference and angle-dependent color shift (latent effect).[4] The authors noted a significant role of the aspect ratio between the size of the micro-relief elements and the thickness of the polymer layers to obtain multicolor optical effects.

Scaling effects in terms of the thickness and the number of polymer film layers on optical properties of multilayer materials have been systematically studied.[5,6] It has been demonstrated that the absorbance and reflectance of fluorescent light from the transparent laminate vary monotonically with the thickness and the number of layers. This variation was estimated using layered film copolymers (5 or 15 layers) of propylene and ethylene (7–5 mol%. ethylene), 25–60-μm thick. Laminate processing in terms of co-extrusion or subsequent thermo-compression of layered films had little effect on the overall package optical characteristics. The authors found that these relations changed qualitatively when evaluating optical properties of laminates in polarized light. Polarized light optical effects have been proposed for manufacturing packaging films and labels protected against forgery.[7] The aim of this paper was to determine the scaling factor effects on transparency, reflectivity, and color of the laminates in polarized light.

Materials and Methods

Industrial high-pressure polyethylene (PE) films with 22 ± 2-μm, 55 ± 3-μm, and 100 ± 4-μm thickness were obtained by extrusion of the 15803-020 PE with 2×10^5 molecular weight, 0.92 g/cm^3 density, 2–2.2/10 min melt flow index and 33% crystallinity. Polymeric Polaroid films (Nitto Polarizing Film, G1220DUN, Nitto Denko Corporation, Osaka Japan) with high polarizing efficiency of 99.97% and integral light transmittance through the two films in parallel of 0.9 were studied in this paper.

Some of the unconstrained extruded industrial high-pressure polyethylene films were subjected to heat treatment at 90 ± 2°C for 10 min in order to reduce internal stresses. No significant changes in the samples' planar dimensions and the film thickness were found. Isothermally treated samples were tested under the same conditions as the samples made from industrial high-pressure PE films for their optical properties comparison. The goal was to identify possible dependencies between the internal stress and the interference color effects in films in polarized light when packaged into multi-layers.

Preparation of identical layered film samples with polarizers as outer layers was performed as described in reference.[7] Spectrophotometric measurements were carried out using a spectrophotometer X-Rite Spectro Eye and Gretag Macbeth Key Wizard software, version 2.5. The package consisting of several (1–10) polyethylene films was placed between the polarizer films stacked on the white filter paper and placed under a fluorescent light source spectrophotometer X-Rite SpectroEye (type D65).[8] Spectrophotometer indicates lightness and color coordinates in the CIELAB space of the laminate film package in a light beam reflected from white filter paper and passed through two polarizers. Macro photography was employed for visual inspection of the samples using day and polarized light to record transmitted color with Adobe Photoshop version 6.

Films microstructure was studied using field emission scanning electron microscope (SEM, Jeol, JSM 7500F) operated in secondary electron mode at 1 kV accelerating voltage. To reduce sample surface charging and damage by the electron beam, polyethylene films were coated with a thin 7.5 nm platinum layer using magnetron sputtering (AutoFineCoater JFC-1600).

Results and Discussion

Transparency of the tested polyethylene films package and reflectance of the day unpolarized light decreased monotonically with the total thickness of the layers. This dependence obeys the Beer–Bouguer–Lambert law:

$$I(l) = I_0 e^{-k_\lambda l}, \tag{1}$$

where I and I_0 are the intensity of incident and passed through the film light, l is the polymer thickness and k_λ is the polymer light absorption rate. This was confirmed by the experimental data obtained from films made of thermoplastic polyolefin polymers: polypropylene and its copolymers,[5] low density polyethylene[9] and super high molecular weight polyethylene.[10] The influence of the film surface nanosized crystal structure and bulk structure on its transparency is clear and depends on the cooling rate of the polymer melt during molding.[9]

In order to determine the film structure effect on the laminate color change, polymer surface morphology was studied using scanning electron microscopy. Pronounced fibrillar structure is clearly seen in Fig. 1. Fibrillar structure elements have transverse dimensions on the order of 10 ± 3 nm and longitudinal sizes up to 500 nm. Fibrils location on the film surface is chaotic and does not allow drawing a conclusion about micro or macro coincidence of the fibrils orientation with the melt extrusion direction. Fibrillar film structure causes diffuse scattering of transmitted or reflected daylight on LDPE films of different thickness or laminates. Intensity of unpolarized daylight passing through polyethylene film or packets can be adequately described by the Beer-Bouguer–Lambert law in Eq. (1). Unpolarized daylight intensity is reduced by a factor of two after passing through a package of four 55-μm-thick films.

A different picture is observed when studying transparency of a single layer or laminated package of polyethylene films in polarized light. High enough transparency is combined with intense color of a single layer low density polyethylene film with special nanosized crystalline structure.[7] This layer is able to change color of passing polarized light, similar to selective light scattering surface of insect wings.[11] The color and transparency of the polymer multilayer stack film observed at a certain angle primarily depend on the relative position of the polarizer and analyzer outer layers.[7]

Figure 2 shows the color and lightness of the PE package films with different number of layers placed between polarizer and analyzer in two extreme positions: parallel and perpendicular to provide maximum transmission, or almost complete absorption of light. The color and transparency (lightness) of the polyethylene film packets in polarized light changed discontinuously and periodically over a wide range of intensity

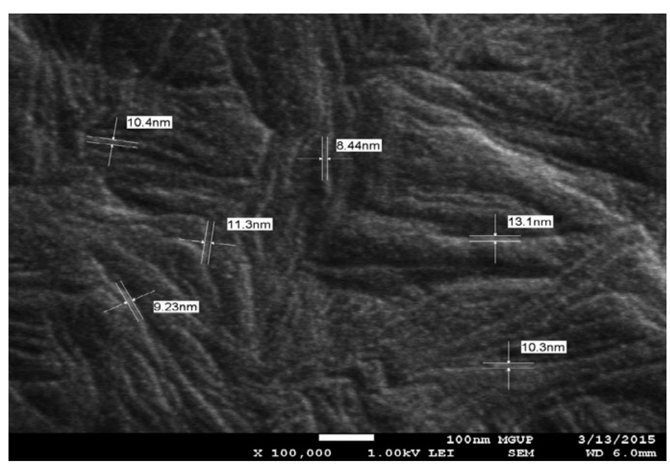
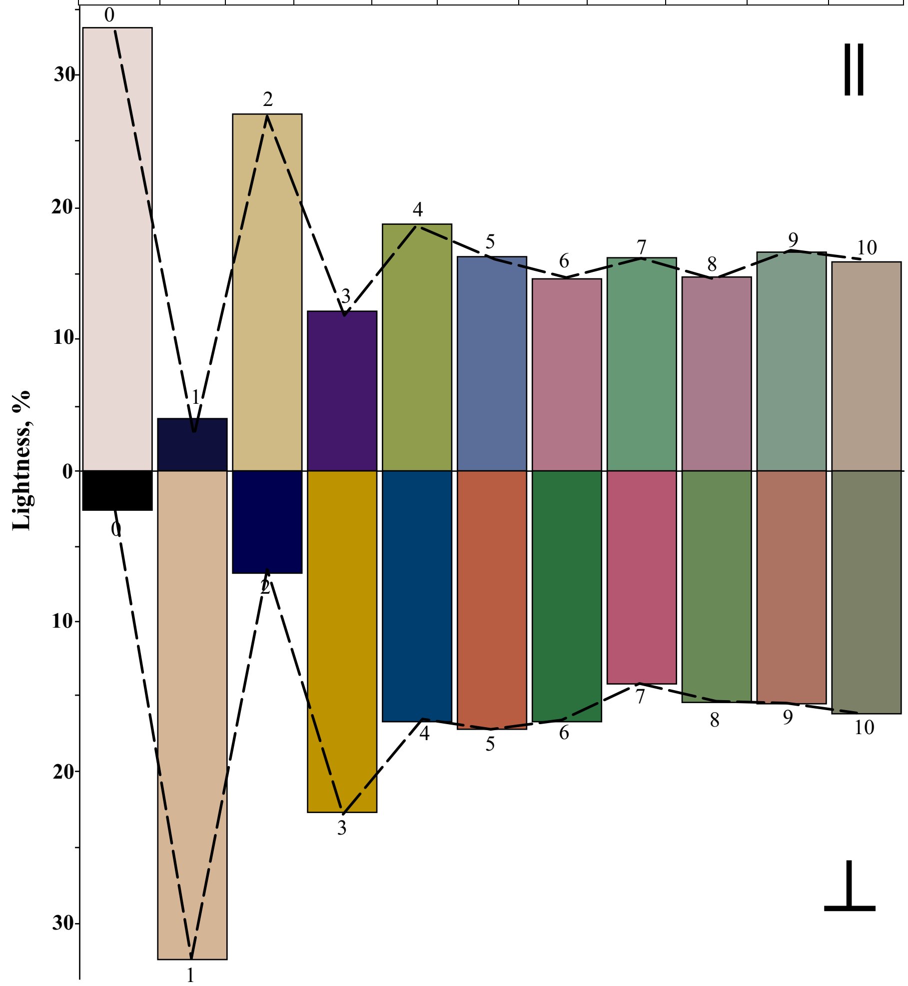


FIGURE 1. SEM image of the 55-μm-thick LDPE film surface showing the size of the fibrillar elements.

-2.08	2.33	0.16	-6.76	12.3	-19.69	13.61	-12.26	6.13	-4.95	0.12
4.32	-9.85	22.98	-16.96	7.67	1.95	-2.14	4.32	-0.01	2.7	-0.76



0.03	-3.01	7.15	6.71	-15.73	13	-16.22	9.39	-8	3.02	-3.13
-0.91	10.95	-22.4	24.16	-5.14	1.12	4.68	-4.4	-2.1	-0.26	2.77

FIGURE 2. Color in the CIELAB color space coordinates and lightness of the 55-μm-thick polyethylene package film in polarized light depending on the number of layers. Numbers in the columns (1–10) represent the number of polyethylene film layers in the a*b color coordinates. D65 light source with built-in X-Rite SpectroEye spectrophotometer was used. || and ⊥ represent parallel and perpendicular arrangement of the outer polarizing layers.

and color. The color difference[7] of packages consisting of one and two polyethylene film layers arranged between the polymer polarizers reaches 30% (points 1 and 2 in Fig. 2 with crossed polarizers (⊥)).

The color difference between packet films with more than four layers is significantly reduced, and their lightness decreases in amplitude with periodic changes in opposite positions of the outer polarizing layers. Adding each of the following layers past fourth changes the reflectivity characteristics of the package by less than 2%, which is comparable to the measurement error. The color change is also small and as shown in reference,[7] is described by a periodic function in the form of the Archimedean spiral in the CIELAB color space coordinates (Fig. 3). The zero point coordinates at the beginning of the Archimedes spiral obtained from the heat treated films are slightly different from the industrial PE samples, but the spiral shape and the number of turns in it are not changed significantly.

For the quantitative study of the scaling factor of color and transparency of layered packages, industrial low density polyethylene films with significantly different physical characteristics were used. The degree of crystallinity and mechanical properties of the samples are listed in Table I. To eliminate possible effects of local internal stress inhomogeneity arising from directional drawing and cooling, some unconstrained industrial PE films were heat treated at 90 ± 2°C. This brief heat treatment did not change the films' crystallinity.

Common feature of all high-pressure polyethylene tested samples was their significant age, as they were stored for more than 3 years prior to testing. Thus, aging fiber-like

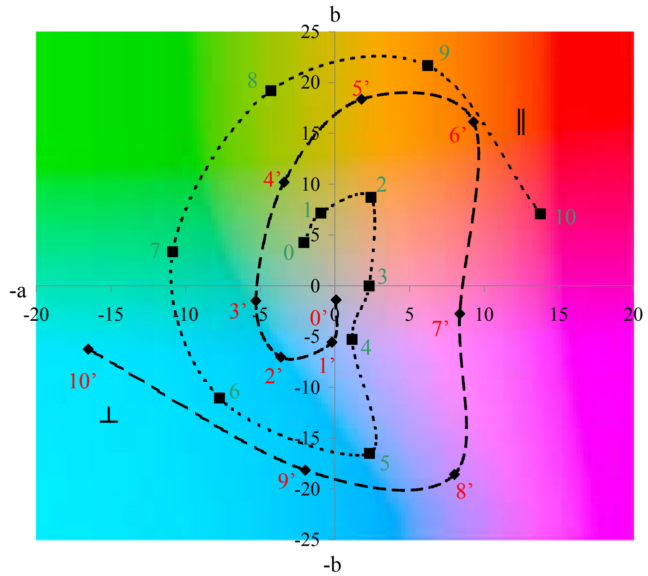


FIGURE 3. The sequence of color change in the CIELAB coordinates of a multilayer stack with the number of layers of 100-μm-thick polyethylene films between two polarizers. Here, 0–10 is the number of film layers between parallel polarizers (∥) and 0′–10′ is the number of film layers between 90° crossed polarizers (⊥).

structure formed on the surface with nanoscale topography (Fig. 1). Similar nanoscale surface topography is shown in reference.[12]

Industrial PE films with 55-μm and 100-μm thickness have a small anisotropy, and similar values of mechanical properties. However, 22-μm-thick PE film is stronger and more anisotropic. To reduce or eliminate anisotropy and internal stress effects on the optical film properties, they were annealed at 90°C for 30 min in air prior to testing. After annealing the color and transparency of the films in the polarized light changed, which is apparently due to a decreased internal stress level. Only annealed samples were used for the subsequent measurements of the films’ optical properties.

Four types of packets with approximately equal total thickness of about 200 μm were assembled for colorimetric measurements and observations of the latent color shift effect: 8 × 22, 9 × 22, 4 × 55, and 2 × 100 with the opposite location of polarizers, shown schematically in Fig. 4. The transparency and color of layered packages change periodically with the number of layers, as shown in Fig. 2. Relative color frequency and transparency of the multilayer material collected from several identical films of varying thickness are significantly different. When the polyethylene layer thickness is over 50 μm, but less than 200 μm, addition of each subsequent layer to the film package leads to an abrupt change in color and transparency. In a way this layer either “opens” or “closes” polarized light path through the material. Increasing the number of layers in a package discretely changes the difference between the total path of the light rays, contributing to an abrupt color change with a relatively small number of layers. In general, the studied structure is an interference-polarizing filter. Experimentally observed effects indicate the significant influence of the scaling factor in controlling optical

TABLE I
Mechanical and thermal characteristics of the high-pressure polyethylene films

Film thickness, μm	Melting temp., °C	Degree of crystallization, %	Strength, MPa		Strain, %		Anisotropy	
			$\sigma^{\parallel}$	$\sigma^{\perp}$	$\varepsilon^{\parallel}$	$\varepsilon^{\perp}$	$\varepsilon^{\perp}/\varepsilon^{\parallel}$	$\sigma^{\perp}/\sigma^{\parallel}$
22	124.3	36.7	28.1 ± 0.1	12.1 ± 0.5	430 ± 3	900 ± 25	2.1	2.3
55	109.6	33.1	10.2 ± 0.3	9.5 ± 0.2	430 ± 17	570 ± 13	1.3	1.1
100	109	28	8.3 ± 0.5	9.8 ± 0.8	470 ± 38	620 ± 30	1.3	0.8

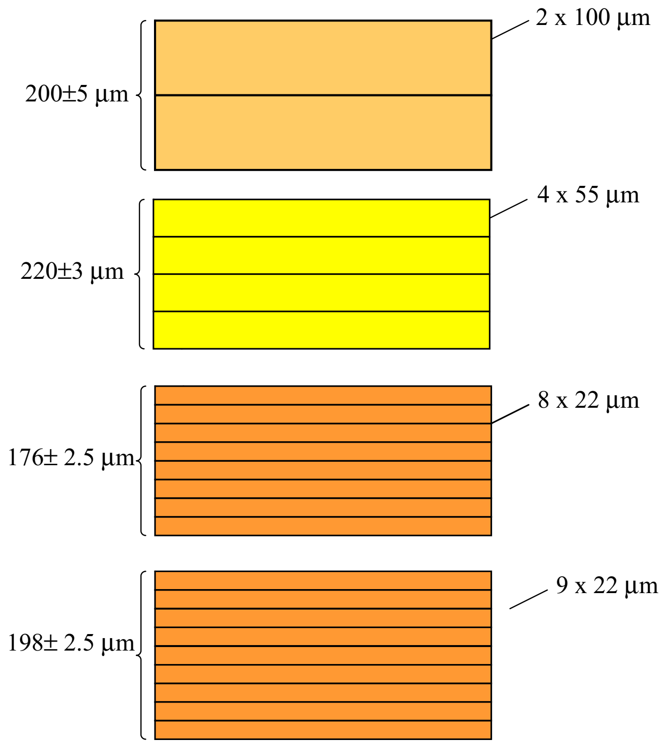


FIGURE 4. Schematics of the layered packages used in experiments.

properties of the film packages, but also restrict its role for the one to six laminate layers with the total thickness of 200 ± 50 μm.

Discrete lightness of the film packages depends on their total thickness in Fig. 4, and in the 200 ± 30-μm thickness range the maximum lightness values vary by 20–25% for all four types of packages, having the same yellow color. Similar optical characteristics of the laminates with a total thickness of 200 ± 30 μm obtained by stacking identical polyethylene films with different thickness in Fig. 5 provide additional control over their color under polarized light and can be utilized for making new packaging materials with various types of protection features.[1–4]

Similar lightness of the packages with the total thickness exceeding 200 μm is due to an insignificant influence of the interlayer spacing on light propagation in thicker materials. Lightness is a periodic function of the total package thickness,[7] corresponding to the reflection coefficient. Its damped characteristics demonstrate weakening of the luminous flux as a result of multiple reflections between the layers and light absorption in bulk polymers. With a large number of package layers (over 50 μm layer thickness in Fig. 2), there is no package lightness change and no significant color change, which is associated with decreased contribution of the lower layers in the overall interference pattern. As a rough approximation, this system with a large number of layers reflects light like a bulk material with an infinite thickness and some effective refractive index. The reflectivity of such material has a constant value (at fixed incident light angle), which is observed in Fig. 2.

Conclusions

Periodical dependence of transparency (lightness) and color of multilayer polyethylene films in polarized light from the scale factor was determined. The scale factor can be quantified by the two parameters: the number of layers in the package, and the total thickness of the films of the package. When the

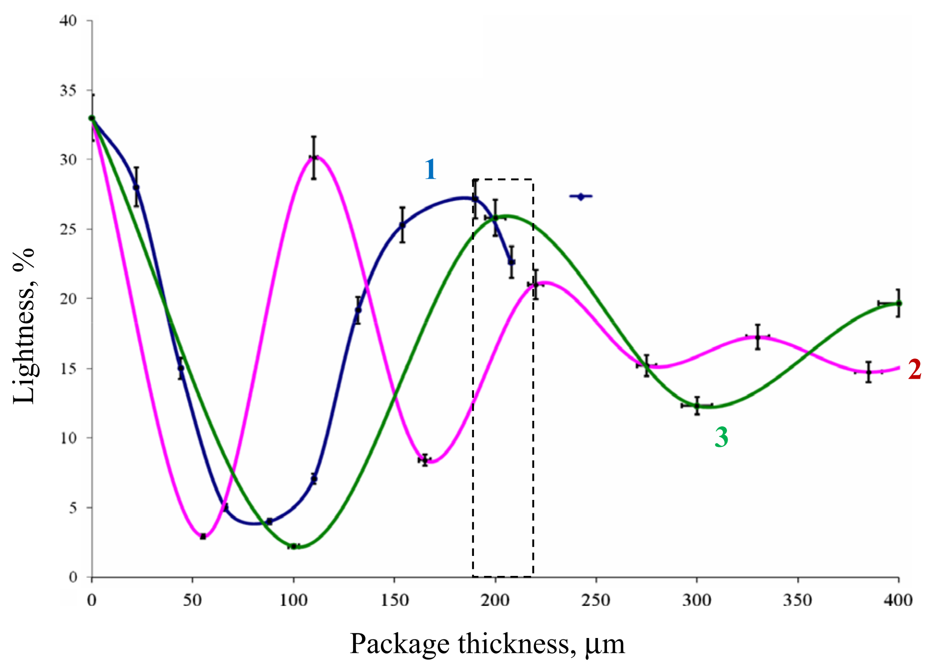


FIGURE 5. Lightness (reflectance of polarized light) in multilayer packages assembled from low density polyethylene films with different thickness: 1 – package with eight 22-μm-thick layers, 2 – package with four 55-μm-thick layers and 3 – package with two 100-μm-thick layers.

total package thickness is 200 ± 20 μm, the laminates made of varying thickness polyethylene films have the same color and transparency. When the total thickness of the laminates is over 200 ± 20 μm, periodic dependence of transparency (lightness) of packets made from polyethylene films of different thickness on the scale factor is no longer present.

The amplitude of lightness and especially color periodic changes in polarized light when varying the total laminate thickness from 22 μm–200 ± 20 μm changes discontinuously (abruptly) by varying the number of layers. For example, 100 ± 10-μm-thick laminate formed by two 55-μm-thick films has yellow color and about 30% transparency, while 100-μm-thick single layer film has dark blue color and about 3% transparency.

Experiments showed that heat treatment of individual films before assembly into a package and heat treatment of individual layers drastically changed the laminate color and equally affected the package color and clarity. This allows using local heat treatment of the layers for labeling and recording text or graphics information on multilayer film materials.

Acknowledgements

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