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Transparent layered materials based on variable color polyolefins

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Abstract

Color bright visual effects in polyolefin layered film materials for the production of consumer goods packaging are described. A multi-color light reflection by a package of films varies in case of a light angle change, depends on a thickness and number of layers. The relation between anisotropy, crystallinity and nanostructure of polyethylene and polypropylene films and their color in polarized light is identified. The fact of recrystallization of a part of fibrils in heat treatment in the course of films duplicating which reduces the effect of pleochroism is established by differential scanning calorimetry and electron microscopy techniques. The films duplicating processes with a simultaneous marking protecting the packed production against counterfeit are suggested.

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Keywords: polyolefins; pleochroism; multilayer films; fibrillar structure; recrystallization, DSC; SEM

1. Introduction

Among products of petrochemical industry used by people polyolefin products are most widespread. It is packaging of bread, milk, drinks, personal care items and other consumer goods. The possibility of polyolefin films direct contact with a person and consumed products is caused by a biological inactivity, hydrophobic properties and high transparency enabling to store products for a long time and estimate their quality through a package. Optical properties of the polyolefin films combined with their high strength, the possibility of heat sealing and duplicating with many other materials make them indispensable in printing and packaging production. The application of colored modified polyolefin films has significantly enhanced in recent years due to their use in construction, in interior design, in advertising, in electronic and lighting engineering [1].

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Additional opportunities of polyolefins employment in different areas of industry, design and lighting engineering disclose the effect of anisotropic films pleochroism. Bright saturated colors of transparent layered materials shown in polarized light enable to avoid the use of toxic organic dyes and colorants for giving desirable colors to flexible packaging of goods, stained-glass windows and luminous panels [2]. The color of these products depends on and can change in varying of illumination direction, luminous flux polarization and/or if a material is deformed. New opal-like materials [3-4] consisting of microcapsules arranged in regular layer structures have similar properties. Big advantages of the polyolefin layered films compared to opal-like materials are high durability and elasticity, low cost of raw materials – petrochemistry products, and the possibility of their manufacturing using efficient equipment to produce polymer films from thermoplastics.

The purpose of the work is to show and quantify a color palette of the transparent layered materials based on polyolefins in transmitted and reflected polarized light flux, to establish the relationship between coloring and number of layers, a surface nanostructure, technological heredity and local heat treatment of polyolefin films, and also to justify prospects of use of pleochroism effect layered materials in manufacturing of packaging protected against counterfeit by a hidden marking.

2. Study subject

Industrial extruded films of 20, 55, 100 and 185 microns thick made of high-density polyethylene (HDPE), Mw=2x105, crystallinity is 60%, after crystallization and a five year storing period in a warehouse; extruded before tests isotactic polypropylene films(PP) of 100 microns thick, with tradenames Capten 020 and "Sibur" according to TU 2211-001-93911504-2012, Mw=3x105, crystallinity is 54%, film polaroids of Zagorsk optical-mechanical plant of "G" category.

3. Methods

The structure of films was studied by means of the polarization microscope POLARM R-312 and field emission scanning electron microscope JSM 7500F (Jeol) in the detection mode of secondary electrons under 1kV acceleration voltage. To reduce charging and prevent decomposition of nonconducting samples under an electron beam a preliminary platinum deposition (about 5-7 nanometers thick) under 10-1 Pa pressure on the samples surface in the magnetron evaporator AutoFineCoater JFC-1600 was performed. The spatial resolution was at least 1.4 nanometers, the pressure in a samples' chamber while shooting was not higher than 9,6×10-5 Pa. Colorimetric measurements of color coordinates in CIE La*b color space *, optical density and daylight and polarized light reflection coefficients in the range of wave lengths from 380 to 730 nanometers was performed using the spectrophotometer X-Rite SpectroEye with GretagMacbeth KeyWizard V2.5 software. Thermophysical properties were determined by the differential scanning calorimetry method (DSC) using the DSK 204 F1 (NETZSCH) device in an argon atmosphere, by heating and cooling with the 10 s/min velocity. The expansion of polymodal peaks was done in the ORIGIN v 6.42 program.

4. Results and discussion

As we know [5], and as we showed in the case of screens for luminous panels with elastic films moving beds [6], the intensive effect of pleochroism appears while passing of polarized light through anisotropic polymeric bodies with a high (more than 40%) crystallinity degree. HDPE and PP films obtained by a melt extrusion with subsequent linear drawing under the temperature below a melting temperature or by blowing of cooled extrudate in the form of a sleeve are referred to such materials. If anisotropy of the films obtained by melt processing is insignificant, their coloring in the polarized light is imperceptible regardless of the arrangement of polarizing light filters (fig. 1).

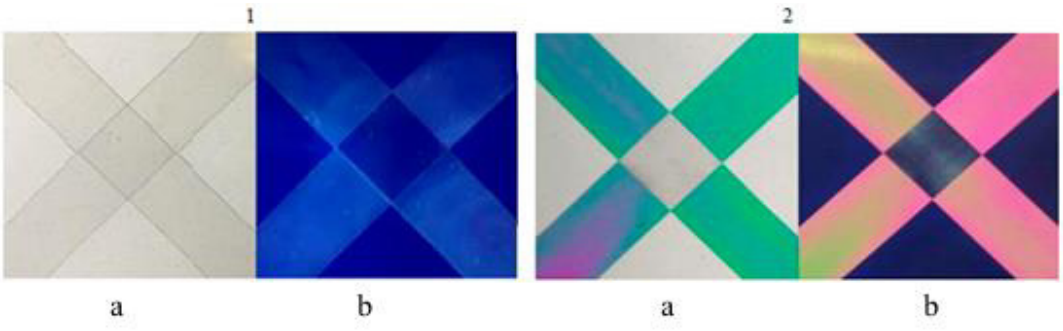

Fig. 1. Two polypropylene filmstrips before (1) and after a cold stretch by 220% (2) at a parallel position (a) and at a crossed right angle position of sunlight polarizers.

The polarized light practically does not change the intensity and coloring while passing through one or two polypropylene films. The color of two film layers is visible in the center of the photo on strips crossing. After stretching of polypropylene films by 200±50% the package consisting of films and external polarizers has a bright color depending on a mutual arrangement of polarizers, thickness and film layers number in a package. At the photo (fig. 1) made in a passing sunlight, strips cut from a polypropylene film are laid at right angle to show the effect of various layered film material on coloring relative to the direction of a light polarization vector (relative positioning of a polarizer and analyzer).

The effect of multiple layers on a polyolefin films package color in the passing polarized light represents a material sample with HDPE films step arrangement of the same thickness (fig. 2). We can see that multilayered film materials with the increase of polyethylene layers obtain various and periodically repeating colors caused by a selective transmission and reflection of the polarized light in the optical wavelength range. There are practically all colors of the rainbow of various saturation and lightness from violet to a red color [2] and their mixed tints in the palette. Materials color lightness in the passing flux and luminous reflectance also periodically increase and decrease with the increase in layers in a package with an amplitude of about 30% at reflectance coefficients maximum up to 40%.

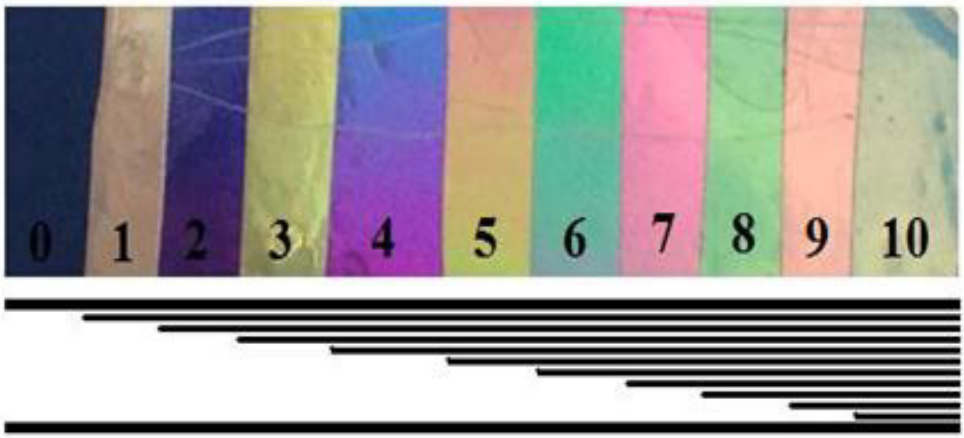

Fig. 2. The color of a multilayered material, consisting of two polymeric polaroids (outside) and 10 samples of HDPE film with their length increasing stepwise. The layers arrangement scheme (from below). Numerals: 0, 1, 2 … 10 – the layers number in each part of a layered package.

To define the films structure influence on the effect of layered material color change, HDPE extruded films surface morphology by means of the scanning electronic microscope was studied. A well pronounced fibrillar

structure of the films stored in a roll under five years' warehousing conditions was discovered. Fibrillar elements of the structure have transverse sizes of about 10±3 nanometers and longitudinal sizes have up to 500 nanometers. The arrangement of fibrils on the film surface is chaotic and does not let to draw a conclusion of a coincidence of fibrils orientation on a micro and macro level with the melt extrusion direction. Nevertheless, the extrusion process and subsequent films stretching at the moment of molten polyethylene crystallization defines the film structure permolecular type, photoelasticity and its ability to selectively reflect the polarized light of a certain wavelength. After a heat treatment of a film or a package of films under the temperature above the melting temperature the relief surface smoothes out (fig. 3) and the ability of a film to obtain coloring significantly decreases. This restricts the thermal application to layered packing materials for their duplication, but enables to create the technology of their hidden marking similar to "watermarks" on paper. Marking can be carried out by a local heat treatment of layers with a heated die having a firm trademark or logo [8].

To clarify the reason of a catastrophic change of a layered material color after the heat treatment by the differential scanning calorimetry method thermophysical characteristics of HDPE films before and after heat treatment were defined. It is established that HDPE films of the same brand with 55, 100 and 185 microns thickness have a similar crystal structure characterized by the maximum melting enthalpy in 106-110ºC melting temperature range. DSC curve shape of the examined polyethylene films during the first heating cycle from 40 to 300 ºC has no significant difference. After the film heat treatment resulting in a package being monolithic and the loss of its ability to change a material color of in the polarized light, quality changes appear on a curve of the first heating in the colorimeter. Endopeak corresponding to polyethylene crystallites melting is split into two parts. An extremum at 113-114ºC is added to an extreme value of melting enthalpy at 106-110ºC.

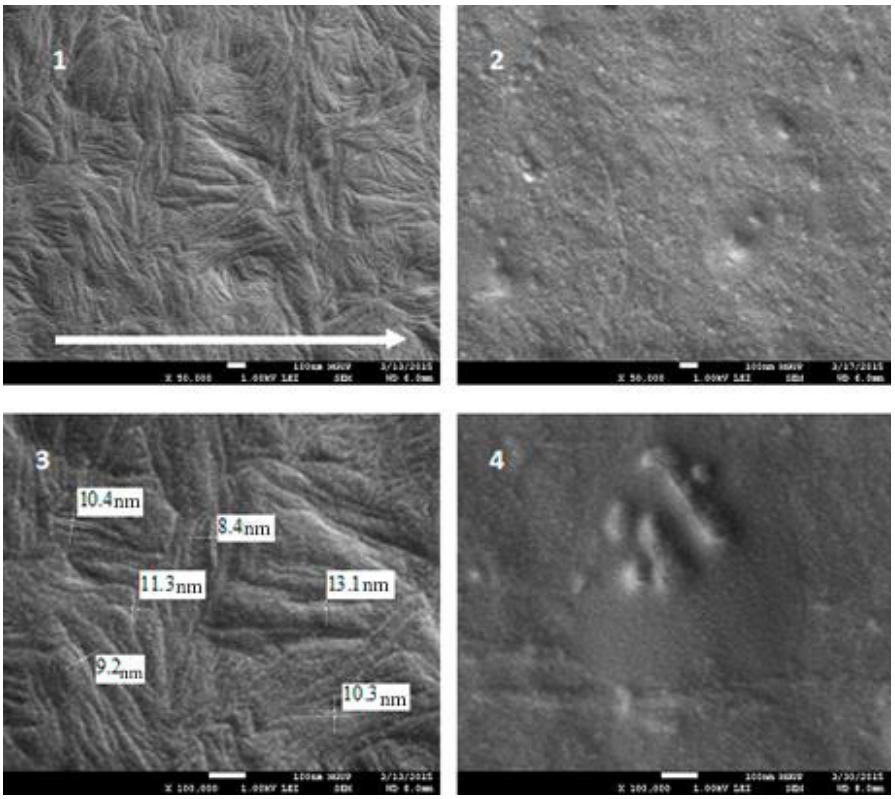

Fig. 3. SEM image of the structure of various parts of HDPE film surface including fibrillar elements transverse sizes before the heat treatment and a films package being monolithic (1,3) and after making the films package being monolithic by the heat treatment in a laminator (2,4) according to [8] technique. The arrow shows the direction of film extrusion.

The total heat of phase transition in 60-120 ºC temperature range slightly decreases from 88÷93 J/g to 71÷85 J/g. These changes are accompanied by a nanorelief change (figure 3) and insignificant shrinkage in the extrusion direction. Decomposing of HDPE melting total diagram in 2 components by means of the program Origin, recrystallization of some part of fibrils and formation of new crystal structures in a film reducing its photoelasticity and "extinguishing" the effect of pleochroism can be reveal.

Table 1. The difference of optical parameters of a layered package of films (background) and parts of a film package heat-treated by a die.

Number of HDPE layers in a package	Daylight D65*		Polarized light			
	Contrast, ΔD	Color distinction, ΔE	Contrast, Δ D	Color distinction, ΔE	Package films color (background)	Logo color
1	0.01	0.5	0.25	14.7	Violet	Beige
2	0.01	0.8	0.30	13.7	Blue	Dark blue
3	0.02	2.9	0.58	25.8	Purple	Blue

* the light source built in the X-Rite SpectroEye spectrophotometer

The negative effect of pleochroism "extinguishing" is suggested to use for obtaining in layered materials hidden color images – logos or transparent color "watermarks" visible only in the polarized light. The hidden marks and images are an effective element of protection and marking of packaging materials [10] and can be made by a local heat treatment of one or several polyethylene layers. The intensity of coloristic changes in places of local heat treatment, in the form of a symbol or a logo of the producer, is shown in the table. The color of HDPE films package in the parts, which are not subjected to the heat treatment, is accepted as a background. The film parts processed by a rectangular flat die heated to 110 ºC are the logo model.

Obviously, within human eye limits (ΔE not less than 3) in the daylight marking or a watermark can not be found (table 1), but in the polarized light they are very visible since a color distinction exceeds manifold eyes sensitivity limits to a color difference.

The obtained results significantly expand known [5] and ascertained before [2,6,7] possibilities of handling of the layered materials color by shifting or stretching of elastic internal layers. The purposeful choice and/or the formation of a fibrelike nanostructure of films surface combined with a local recrystallization in the course of their heat-treated duplication enables to gain multi-color visual effects on multilayered polyolefin packaging materials.

5. Conclusion

The nanostructure is demonstrated and the technology factors defining the emergence and "extinguishing" pleochroism effects in the polarized light passing through multilayered polyolefin films are established. The recrystallization of fibrillar formations in the heat treatment of anisotropic films to duplicate them at the polyethylene melting temperature reduces the intensity of coloristic effects. The described effect is suggested for the first time to use for obtaining hidden images (logos), "watermarks" seen in the polarized light and protective marking of layered packaging materials.

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