Express diagnostics of polymeric petroleum products for its usage in latent watermarks of the smart packaging

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Abstract

The express-method of diagnostics and selection of polymeric petroleum products is substantiated. Such products are processed by hot melt extrusion into films with technical purposes and then used in packaging. Bright visual effects in layers of polyolefin film materials are used in packaging of consumer goods; they can be seen in polarized light and depend on chemical and phase composition of films. For films application in smart packaging, for example, frozen food products, input control and diagnostics is required not only of mechanical and optical properties, but also of sensitivity of their optical properties to heat treatment. The two-stage method is suggested for checking the suitability of polyolefin films for the latent marking in polarized light for their usage in the production of intelligent packaging for frozen foods or other products with a strictly regulated mode of storage.

Keywords: method of polymeric petroleum products diagnostics; polyolefins; heat treatment; multilayer films; optical properties; latent marking

1. Introduction

The most common large-capacity secondary products of oil refining are polyolefins. They are used practically in all spheres of human activity: medicine, construction, engineering, production and processing of food products, military and space equipment.
In every industry new innovative products are created with a high initial cost, the developers promote them to the world market at a significant cost. The intelligent packaging and a variety of protective marking methods are used to protect such products from the counterfeit [1].

We proposed [2] and economically substantiated [3] new methods of protective labeling for product packages with films made of large-tonnage polymers such as polyethylene, polypropylene, polyvinyl chloride. The possibility of effective application of protective marking packaging, manufactured from these refined polymeric petroleum products, is determined by the peculiarities of polymers chemical structure, the fractional composition of macromolecules and the films supramolecular structure.

Manufacturers of polymer films characterize their products by a large set of quality indicators, including: density and MFR of the polymer, thickness and overall size, gloss, transparency, mechanical properties, etc. With such set of indicators it is impossible to determine the industrial suitability of polymer films for the optical marking, which is visible in polarized light [4].

The purpose of the research is to develop a method of industrial polyolefin films express diagnostic for material purposeful selection for smart packaging and for the assessment of its protective marking possibility.

2. Study subject

- 50±2 μm industrial high-pressure polyethylene films (PE-1), M_w=2x10^5, crystallinity 33-36% by MICROTHENE CR 89002 NEAT U.S.INDUSTRIAL CHEMICAL COMPANY, Melt Index= 150 G/10 min;
- 50±2μm industrial high-pressure polyethylene films (PE-2), M_w=2x10^5, crystallinity 35-37 % by PETROTHENE NA 596 NEAT. U.S.INDUSTRIAL CHEMICAL COMPANY;
- 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.

3. Methods

The measurements of the films optical characteristics were carried out in three ways: the first one – visually, on a polarizing microscope POLAM R-312; the second one – using a portable spectrophotometer X-Rite SpectroEye in ‘reflectance D65 daylight mode’ and ‘polarized light mode’; and the third one – by using spectrophotometer SF-2000 in the mode ‘on a gleam’ in daylight D65.

The FTIR spectrometry was carried out using a device brand FSM 1201.

The heat treatment of the films was carried out in three ways. The first way – by heating in a free state between the films of the polytetrafluoroethylene in the dry-air thermostat of the chromatograph Color–800 with an accuracy 0.1 ° C. The second way – by hot relief pressing. And the third way – by processing in the laminator using the special membranous envelope, limiting the warping of the film during the passing through the zone of heat radiation.

4. Results and discussion

Color and transparency of the two polyethylene film samples of different brands placed above and between the layers of the polarizer under the natural light (Fig. 1) and in the polarized light (Fig. 1) were compared. The polarizers were set in the position of maximum transmissive capacity, so that their own color had no significant effect on the color of three-layer package films in both set versions of the film [5].

Fig. 1 shows the lack of the film color in daylight and a different color of the original and heat-treated samples in polarized light. The difference between diagnosed samples of the polyethylene film of equal thickness and crystallinity degree, which were produced in identical conditions of the polymer hot melt extrusion, is explained by the technology of petroleum products secondary processing into polyethylene and thermal prehistory of the film particular brand.
Partial recrystallization of polyethylene films, occurring, as it is known [6], during short-term heat treatment below 100°C, is not visible in natural light. However, the color and the transmission of polarized light through the package of polarizers with one sample of heat-treated film change (Fig. 1). The change of color and lightness of the films significantly increases when placing them between the layers of the polarizer with more layers from 2 to 4 [5].

For the quantitative assessment of color the measurements of color coordinates and also the measurements of optical density of a multilayer stack with 2, 3 and 4 layers of heat-treated material and original samples of PE-1 with 50 μm thickness were carried out. According to the measured parameters the color difference ΔE was calculated and the signal of the print contrast PCS [7] was found for packets consisted of the original films and the heat-treated films.

As it was shown previously [4], the color of plastic films packs depends on the relative position of the light polarizer and analyzer, which are the outer layers of multilayer material. The position can be "open," i.e., 92% of light passes through two polaroids (without plastic film) and "closed" when 95% of the daylight, which passes through the polarizer, is captured by the analyzer.

The results of optical measurements and calculated characteristics of the color shift due to the heat treatment of packages with multiple layers of polyethylene are presented in Table 1.

The table shows that the color difference ΔE for all the samples exceeds the sensitivity barrier of human vision, which is equal to 2.3. The maximum color differences of the heat-treated films packages, compared to the original films, are observed when the number of layers is 4 for an open position of the polaroids, and only 3 in the case of a closed position. Signal of print contrast is maximum (0.41) with 3 layers of heat-treated films in the package consisted of 4 layers. This important feature must be considered in the practical usage of heat-treated polyethylene films for an effective marking of packaging and it could be used for its diagnostics.
Table 1. The optical properties of layered packages of heat-treated samples

<table>
<thead>
<tr>
<th>Optical characteristics of the marking</th>
<th>The number of layers of LDPE film in the package</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Open position of the polarizers</td>
<td></td>
</tr>
<tr>
<td>ΔΕ</td>
<td>4.63</td>
</tr>
<tr>
<td>PCS</td>
<td>0.30</td>
</tr>
<tr>
<td>Closed position of the polarizers</td>
<td></td>
</tr>
<tr>
<td>ΔΕ</td>
<td>11.64</td>
</tr>
<tr>
<td>PCS</td>
<td>0.19</td>
</tr>
</tbody>
</table>

ΔΕ – the color difference; PCS – the signal of print contrast [7]

The original colors of films (PE-1) and (PE-2) of the equal thickness are significantly different in transmitted polarized light (Fig. 1), therefore, for the diagnostics and prediction of the applicability of the marking films for intelligent packaging, their IR spectra were received and the crystal structure was explored by the method of differential scanning calorimetry.

The difference in the intensity of IR radiation absorption of the films was determined in the wavenumber range 1000÷1150.

Spectrum of the film (PE-1) in the range 1000÷1150 cm⁻¹ has one peak of absorption at 1077.1, its height is 2.45, and the film (PE-2) is characterized by the presence of two peaks with coordinates 1085.6 and 1049.7 which heights are 1.19 and 4.92 respectively. The presence of peaks indicates the presence of NP ingredients in the polyethylene resin and/or on the remains of not polymerized alkenes [8]. These ingredients probably determine the low sensitivity of the color shift of the films PE-2 to the heat treatment and the spectral characteristics of polyethylene can be used in primary diagnostics of the purity of raw materials suitable for the production of smart packaging (Fig.2).

![Fig. 2. FTIR spectrum of two polyethylene films](image)

The DSC thermograms of the films also have significant differences. The melting of the crystals of polyethylene film of high pressure occurs in a narrow temperature range with the extremum at 108° C. The crystal structure of the PE-2 films has about 30% fractions of polyethylene, which melts at 121°C. The total crystallinity of both polyethylene brands is approximately the same (Table 2).
Established significant differences in the optical characteristics of the films, exposed to short-time heat treatment, adding them to the composition of multi-layered materials allows to use the technique of local heat treatment for latent marking and counterfeit protection. The result of local heat treatment of film package is not visible under normal lighting (Fig. 1), but contrast is manifested in the color shift (Table 1), when the film is observed in polarized light.

**Conclusion**

Equal in thickness and the manufacturing method, but different in molecular structure and crystalline structure films of high-pressure polyethylene have different color in polarized light and change color during heat treatment in varying degrees.

Diagnostics of the optical properties of polyethylene films is an important stage of their practical application in smart food packaging with a strictly regulated storage mode. For the best selection of films with the highest thermochromic effect (latent effect) in polarized light and its temperature dependence it was proposed to diagnose the polymeric petroleum products in two stages. The first step is to discover the presence of impurities by IR-spectroscopy and DSC. The second stage is in polarized light to carry out a quantitative assessment of latent effect in magnitude of PCS of the heat-treated film spots in three-layer package.

**References**


