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Vapor Permeability of Thin-Film Composite Materials Based |on Polyethylene

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The study of the vapor permeability and surface structure of polyethylene films modified with organic filler (casein) and mixed organic-mineral fillers stored under closed storage conditions have been shown. Changes in diffusion characteristics are shown depending on the type and amount of filler in long-term (up to 7 years) studies. It was established that the injection into the polyethylene matrix of fillers and additives significantly changes the structure formation with long-term aging. Water vapor permeability of polyethylene film modified by fillers increases along the subsequent aging. However, the deviation of characteristics at 7 years of storage does not exceed the value of WVTR = 0.6 mg·m^{-2}·s^{-1}, even taking into account the small thickness of the samples, which in most cases the long-term use of such a product is permissible.

Electron microscopic studies of modified films have been carried out.

Key words: polymers, polyethylene films, water vapor permeability, structure, aging.

Introduction

Polymer films based on thermoplasts, modified with organic and inorganic fillers are used mainly as an additional technical material. Application of the modifying material in the film is associated with a decrease in the cost, and with the improvement of consumer properties. At the same time, there is a change in the physico-mechanical and chemical characteristics of the material, which causes the need for additional research.

The general questions of changes of the diffusion characteristics in polymer thin films were described in the works of Massey L.K., Bridson J.A., Aksimentyeva O.I., Siracusa V. [1-4]. Separate questions of the influence of physical aging on the transfer processes through polymer membranes are presented in the works McCage M. S. and Paul D. R. and Laot C. M. [5, 6].

However, the coverage of the problem of the influence of aging processes on the water vapor penetration through polymer film materials has not been reflected in the current scientific literature, which makes the presented work relevant.

The purpose of the research was to determine the possibility of using films with fillers for long-term protection against water vapor and moisture penetration, as well as comparing the results with known literary data and establishing their conformity.

I. Experimental part

The object of research was the low density polyethylene (70 - 80 wt. %), for which granulate (LDPE 15803-020) was used. As additives, organic (up to 9 wt. % - Casein) and mixed (up to 30 wt. %) fillers were brought into a polymer matrix. Mixed fillers were highly filled polyethylene compositions of the LDPE (~20 wt. %) and calcium carbonate CaCO$_3$, known under the commercial names Credolen of the brand KPG-012 and Vatpol 210. The size of the individual particles of the filler added into the polymer did not exceed 8 μm (average size - 1.5 μm). The charge composition was injected up to 4 wt. % of various technological additives (the slip impurities based on oleamide, antioxidants, light stabilizers, etc.) for ensures the technical parameters of production.

Samples of the films were fabricated on a laboratory extruder.

The thickness of the polymer films was in the range from 45 μm to 50 μm.

The polymer films were saved in non-heating warehouses at temperatures from 278 to 293 K and

relative humidity from 55 to 75 %.

Investigation of water vapor permeability of films was carried out using a weight method (dry cup method) by means of metal cups, in accordance with the international normative documents ISO 7783, ISO 2528 and ASTM D 1653.

Elektron-microskopy investigations were done on microscope EVO 40XVP.

II. Research results

The initial water vapor transition rate (WVTR) of preliminary (immediately after fabricating) polyethylene films without modifiers were WVTR $\approx$ 0.45 mg·m^{-2}·s^{-1} (permeability coefficient P_{wv} = 1.95 $\frac{g \cdot mm}{m^2 \cdot day}$). The water vapor permeability of unmodified films decreased and stabilized within 30 days at the level of WVTR $\approx$ 0.325
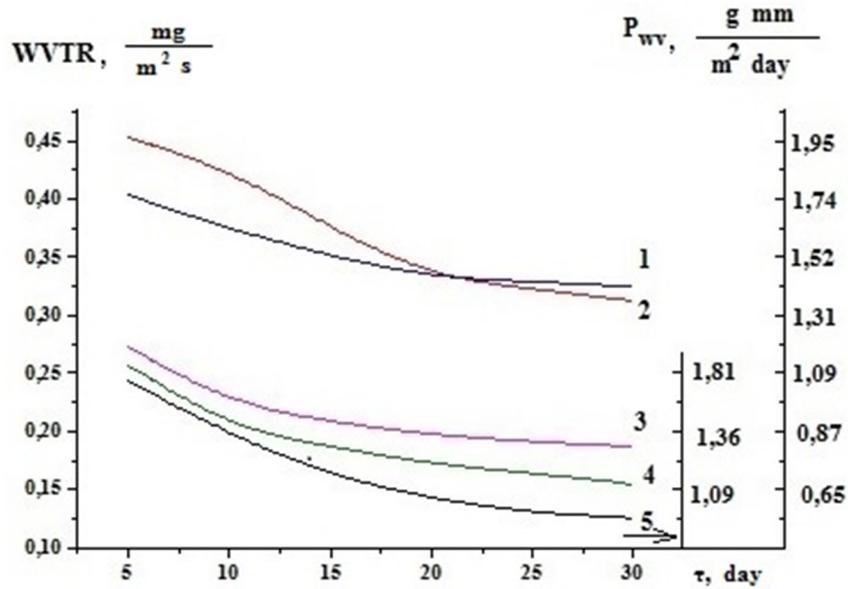

Fig. 1. The water vapor transition rate (WVTR) and permeability coefficient (P_{wv}) of polyethylene film with different content of filler Credolen in the thickness h = 50 μm (1-4) and h = 160 μm (5): 1 - LDPE + 5, 6wt. % Credolen 2 - LDPE; 3 - LDPE + 16.6 wt. % Credolen; 4 - LDPE + 23.2 wt. % Credolen; 5 – LDPE.
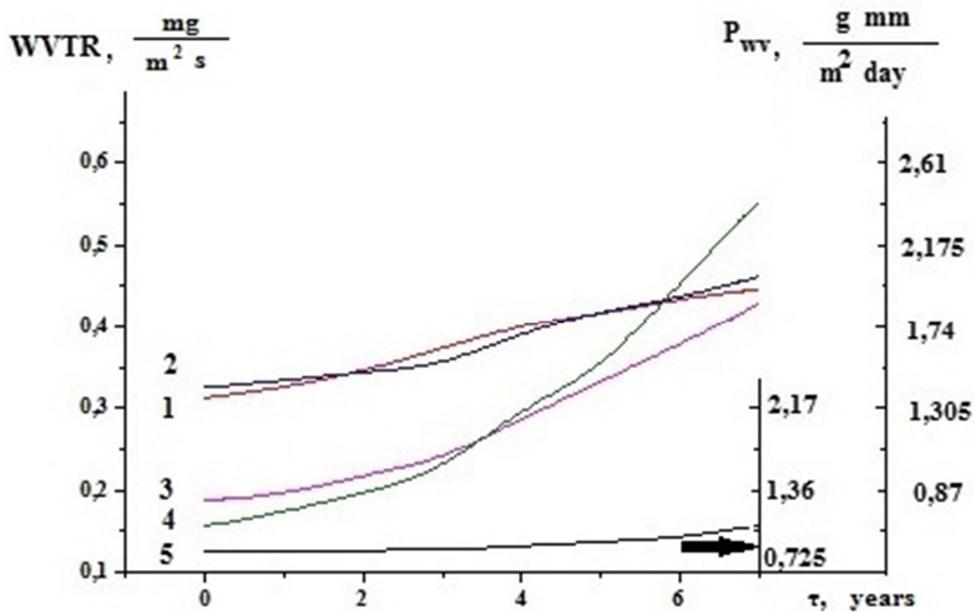

Fig. 2. Change in vapor permeability indexes of polyethylene films with mineral filler, which were aging in warehouse conditions for 7 years. Designation of the samples correspond to the Fig. 1.

$m^{-2} \cdot s^{-1}$ ($P_{wv} = 1.415 \frac{g \cdot mm}{m^2 \cdot day}$) (Fig. 1).

The value of initial parameters of vapor permeability changes after injection fillers to the films. Adding a small amount of mixed polyethylene-mineral filler Credolen (5.6% wt.) slightly reduces the initial value, and after 30 days of exposure for stationary diffusion, the vapor permeability of such films is significantly different from those of non-fill films (Fig. 1). An increase in the amount of filler in the film results in a decrease in the value of the initial vapor permeability due to the hydrophobicity of $CaCO_3$ and owing to the increasing in the total volume of the crystalline phase. The characteristic of unmodified

film with a thickness of h = 160 μm is given on fig. 1 for comparison.

Aging of polyethylene films in warehouse conditions during 3 years led to slight changes in the water vapor transition rate and permeability coefficient (Fig. 2). However, after this period, the water vapor transition rate of samples with great content of the filler Credolen increases, reaching 0.25 mg/m²·s per 5 years of storage, and in the range of 6-7 years - exceeds the parameters of vapor permeability of the unmodified samples.

Adding to the polymeric matrix of organic or mixed filler type "Vatpol" also reduces initial vapor permeability compared to films without modifiers.
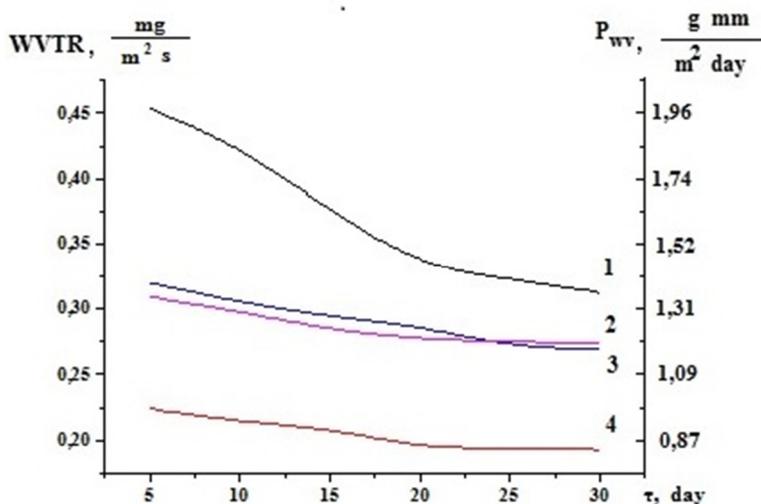

Fig. 3. The water vapor transition rate (WVTR) and permeability coefficient (P_{wv}) of polyethylene film with different content of organic (Casein) and Vatpol fillers by thickness ((h = 50 μm): 1 - LDPE; 2 - LDPE + 27.2 wt. % Vatpol; 3 - LDPE + 21 wt. % Vatpol; 4 - LDPE + 8.6 wt. % Casein.
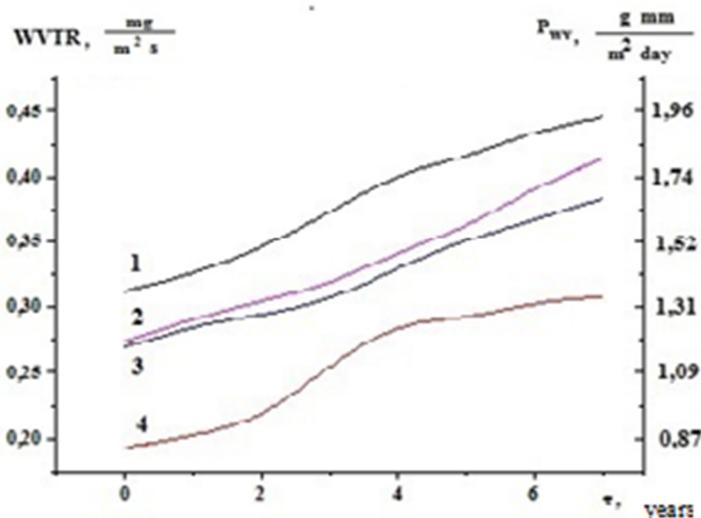

Fig. 4. Change in vapor permeability indexes of polyethylene films with organic and mineral fillers, which were aging in warehouse conditions for 7 years. Designation of the samples correspond to the Fig. 3.

Moreover, the organic filler (Casein), in spite of the smaller amount of the injected material, more effectively changes the diffusion characteristics of the matrix material (Fig. 3). Initial water vapor permeability shows stabilize within 30 - 40 days. However, the difference in the parameters of water vapor permeability in the case of the injection of organic or Vatpol fillers significantly less (11 – 14 %), compared with the use of Credolen (up to 40 %).

The aging of films in the conditions of closed warehouse preservation did not reveal significant deviations in the dynamics of changes in the values of WVTR, in comparison with unmodified coatings (Fig. 4).

The increase in water vapor permeability for 3 - 5 years of storage does not go as fast as in the case of modified by Credolen films. The parameters of vapor permeability of 6 - 7 years of storage are generally lower than in unmodified films.

III. Discussion

Parameters of vapor permeability of polymer films are determined by their chemical configuration formula and structure and, to a great extent, depend on the technological conditions of their obtaining and exploitation [1, 2]. In general, the polymer film permeability parameters are always depending on the type of polymer (structure, orientation and compactness of laying fibrils, density of material, crystallinity or amorphous, the presence of bonds between the polymer chains [cross-linking or conjugation], etc.). The permeability is also influenced by the composition and

characteristics of penetrant substances (especially the sorption characteristics relative to the base), their concentration and the pressure difference that arises during the permeability through the polymer barrier-membrane [3, 7].

In addition, measurable parameters for the permeability of polymeric materials are largely corrected by the measurement methods and characteristics of the equipment used for this, as well as the external conditions of conducting experiments (temperature, humidity, deformation efforts, etc.).

The diffusion characteristics of polymer films with fillers to a large extent depend on the type and characteristics of the filler. In the study of vapor permeability, the nature of the filler is particularly strongly showed in two cases - at the initial stage of research, when there are processes of stabilization of the structure (the first 30 days after receiving the films), and after 3 - 5 years (for films stored in a closed warehouse), which are marked by increased restructuring processes.

Coefficients of initial vapor permeability of film materials containing additives of organic filler such as Casein are slightly lower than the corresponding indexes of films containing modified mineral filler. This is mainly due to the decrease in the porosity of the polymer coating caused by the binding effect of organic additives.

The value of the diffusion characteristics of the samples is closely related to the technology of their production, the formation and changes in their structure. Electron microscopic studies of the surface of the initial (freshly extruded) polyethylene films without filler have been found their insignificant defects (Fig. 5). The primary passage of diffusion of penetrant through the surface is established with insignificant crystallinity
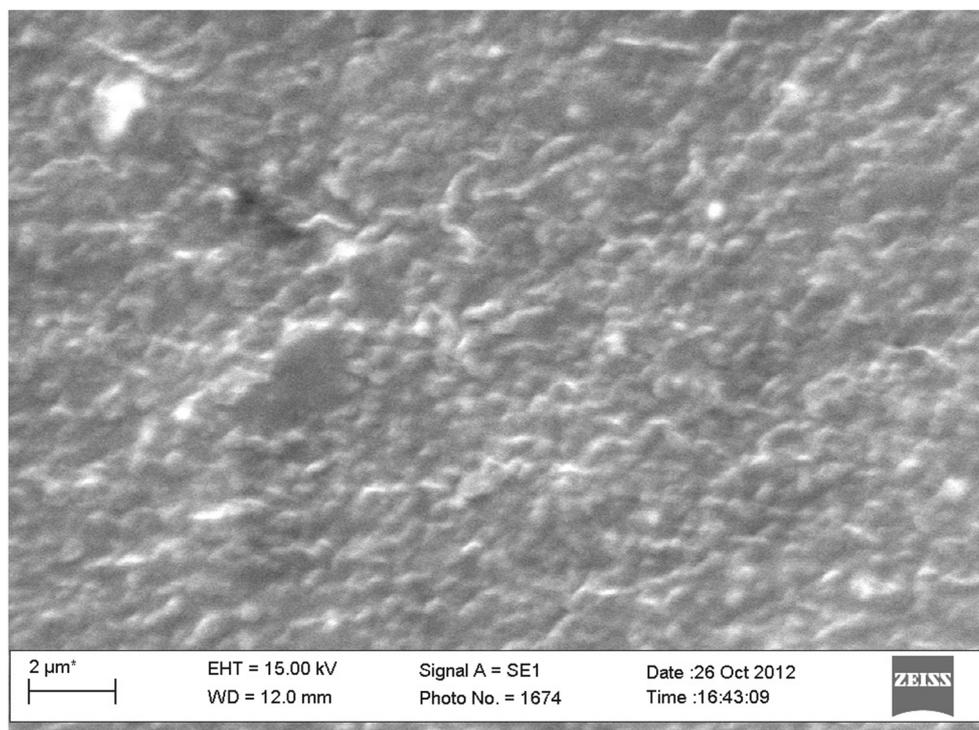

| 2 µm* | EHT = 15.00 kV | Signal A = SE1 | Date :26 Oct 2012 | ZEISS |
| | WD = 12.0 mm | Photo No. = 1674 | Time :16:43:09 | |

Fig. 5. Structure of the surface of the initial unmodified polyethylene film (X 5000).

(about 30%) of the sample.

In common, such substrates should be perceived as forming with a certain amount of crystalline phase, which is distributed in an amorphous matrix. It should not be expected significant penetrant diffusion across this structure, since the percentage ratio between the crystalline and amorphous phase due to some production or operation regimes can reach 60 %, and the crystalline phase itself is not effective material for the diffusion processes [8].

Films containing organic were distinguished on the basis of the dependence of the coefficient of permeability during initial studies. The stabilization of the permeability characteristics of the films in the first 30 days after the extrusion took place on a smoother graph, and the final values for films with mixed filler were slightly higher.

The structure formations of the matrix in which the organic filler was injected are much larger than those in the "pure" sample (Fig. 5, Fig. 6, a). However, the overall visible defects of such a sample are small, as evidenced by the low initial vapor permeability. Exits of diamond-shaped forms to the surface of the sample can testify to the accelerated crystalline formation of the polyethylene matrix under the influence of the filler (Fig. 6, a), where the polyethylene crystallizes precisely in this form [9]. This unusual function of organic filler is quite possible, considering that in addition to the reinforcing function, it can detect a certain chemical interaction with the matrix and is not inert. Of course, the reduction of free volumes of the polymer matrix should be also taken into account at the initial stage of aging. Reducing the vapor permeability indexes of polyethylene films with organic filler can occur precisely by reducing free volumes, as evidenced by electron microscopy [10, 11, 12].

Additives of organic filler in the form of Casein (8.6 wt. %) to the composition lead to a more dense
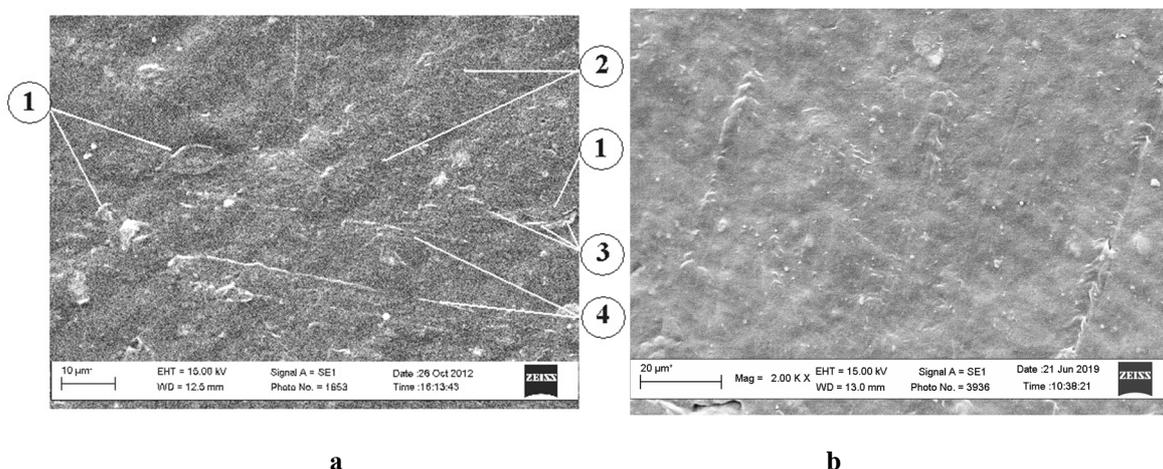

a   b

Fig. 6. The surface structure of the polyethylene film with Casein (8.6 wt. %) additive: 1 - growth of polyethylene crystals; 2 - area of active structuring; 3 - occurrence of defects on the line of division of the amorphous and crystalline phases; 4 - technological defects: a - after fabricate (X 1000) [3]; b - for 7 years of storage (X 2000).
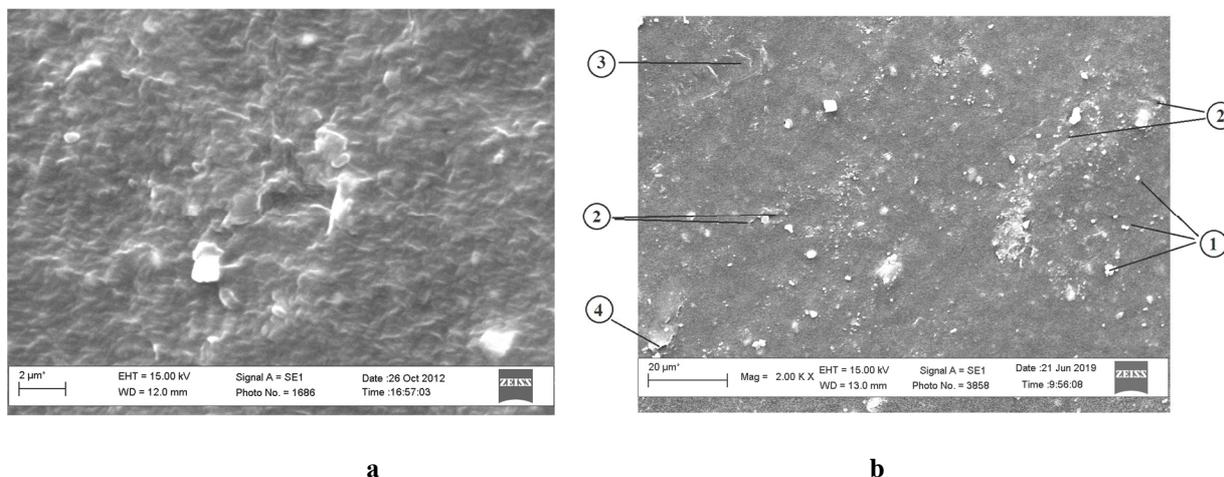

a   b

Fig. 7. Morphology of the surface of the polyethylene film with additives (16.6 wt. %) of the mixed mineral-organic filler Credolen: after fabrication (a) and for 7 years of storage (b): 1 - filler ($CaCO_3$); 2 - pores, caverns; 3 - the origin of polyethylene crystallites; 4 - cracks on the boundary of "amorphous-crystalline phase". a - X 5000; b - X 2000.

structure due to the filling and closing of pores and cracks, although during the joint extrusion of components allows formations of cross-links. All the more that insignificant part of fabrication films is adding of the technical components in the form of slips and antioxidants.

The additives of the mixed mineral-organic filler Credolen in the amount of up to 16.6 wt. % slightly reduce the initial vapor permeability of the polymer material. It should be noted that the vapor permeability index of freshly-formed films with a higher content of inorganic fillers is close to those of polyethylene samples without filler, but of three times greater thickness. The structure of the surface of films with inorganic fillers is characterized by greater relief and defect associated with the injection of crystalline material, which places on the surface in some areas (Fig. 7).

It is clear that adding fillers to the film can significantly reduce the cost of the composition.

However, one must be sure of the insolubility of the applications and the direction of their influence on the structure and properties of the composite in the case of the production of films of any composition [2, 13, 14]. It is recommended that such evaluations be made by separating the following characteristics and application properties [2]:

- Average particle size and size distribution;
- Form of particles and porosity;
- The chemical nature of the surface;
- Presence in additives such impurities as sand, metal ions, etc.

In addition, if the inert filler is compatible with the polymeric base, it can fill the free volume in the polymer matrix and create a winding path for the penetrant molecules create a tortuous path for the permeating molecules. The degree of the tortuosity of the path of molecules is dependent on the volume fraction of the filler and the shape and orientation of the particles
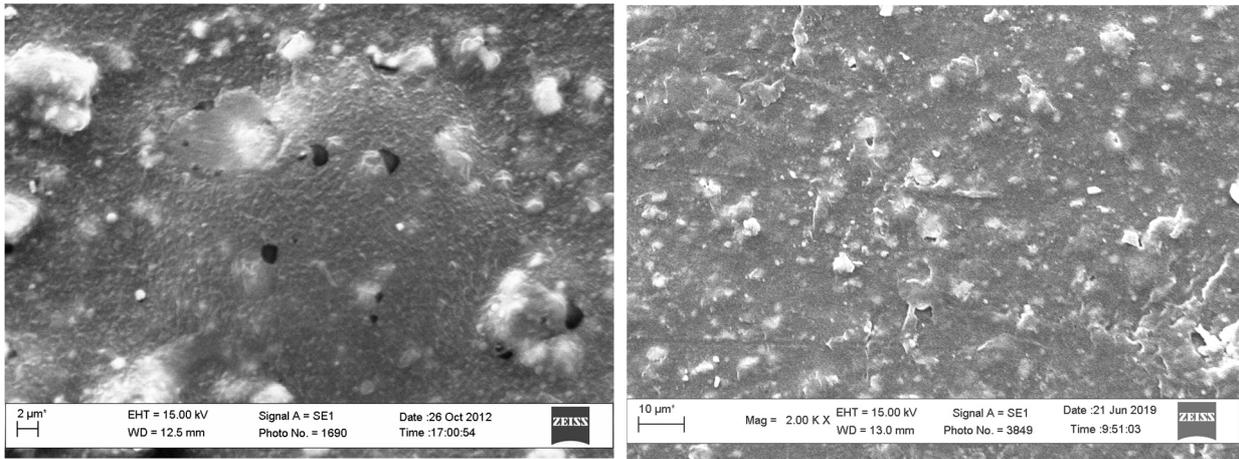
a

b

Fig. 8. Surface structure of the polyethylene film with additives (23.2 wt. %) of the mineral filler Credolen:
a - after fabricating; b - for 7 years of storage (b). (X 2000).
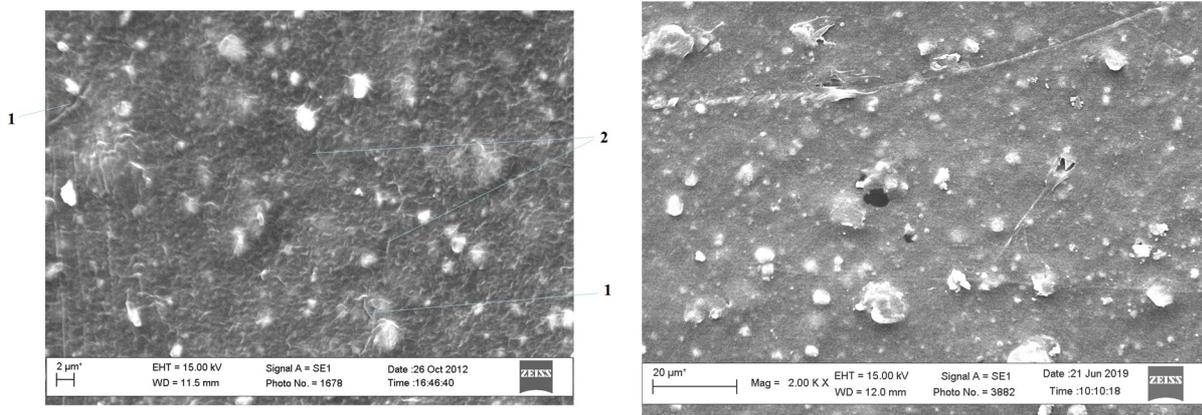
a

b

Fig. 9. Surface structure of polyethylene film with mixed filler Vatpol (21 wt. %): 1 - origin of cracks; 2 – caverns;
a - after fabricating (X 2000); b - for 7 years of storage (X 2000).

[15, 16].

The additives as mineral filler at 23.2 % by weight are so significant that completely change the surface pattern, but no noticeable changes in the diffusion processes are observed (Fig. 8). This may be due to a significant increase in the defect along the section of the mineral filler - polymer and the corresponding increase in permeability, which compensates for the decrease of the WVTR due to an increase in the crystallinity of the sample.

The values of the initial vapor permeability of freshly fabricated films with mixed mineral-organic filler Vatpol are very similar to those of Credolen filler films having the same amount of additives. This is due to approximately the same composition of the filler, in which the mineral component is 4 times greater than the organic supplement. However, due to the latter, the graphic characteristic of the vapor permeability of films with filler Vatpol in the initial 30 days is more stable (Fig. 3). Comparison of the microphotographs of the sample surface of polyethylene films with two mixed fillers of two separate fabricates revealed the similarity of structures by the amount of mineral outlet on the surface (Fig. 8, Fig. 9).

The general defect of the polymer matrix for significant applications of the mixed filler Vatpol is also increasing. The presence of cracks and cavities indicates the complex nature of the influence of the mixed addes, which may vary in different ways, depending on the chemical and physical characteristics of the matrix and the technological conditions of fabricate.

Technological lubricants and "slips" were added to the compositions in order to avoid significant surface destruction, which prevented the appearance of initial damage.

Water vapor permeability of polyethylene films for 2 years of aging slightly increases by 4-6 % per year. The lowest indexes were shown for unmodified films with a thickness of 170 μm and films with a small amount (5.6 % wt.) of mineral filler with a thickness of 50 μm (deviation of characteristics by 2 – 3 % per year). Further aging in storage conditions significantly accelerates the growth of vapor permeability. Critical for all films is 3 - 5 years of storage, when the maximum increases of indicators of vapor permeability indexes are fixed - up to 12-25% per year. Of course, such changes are possible only with the active structure changes of the matrix when conditions exist for the formation of a significant number of pores, openings and passages. However, such transformations do not yet correspond to particularly extreme, sharp changes in the physical state of the polymer matrix. After all, the film composition did not contain aggressive components with reference to matrix. In addition, the films were stored in a closed storage (according to research requirements), which lacked the main factors of accelerated change in the structure and properties of composites. For example, the injection of corrosion inhibitors into polyethylene matrix (films intended for corrosion-resistant packaging) contributes to the initial increase in crystallinity of the sample, but accelerates the destructive processes for 2 years of storage. Coefficient of water vapor permeability of samples with significant corrosion inhibitor content (more than 2 wt. %) increases 3 -3.5 times and exceeds the average permeability values for uninhibited films for 3 to 4 years of storage [17, 18].

Water vapor permeability of polyethylene film modified by fillers increases along the subsequent aging. However, the deviation of characteristics at 7 years of storage does not exceed the value of WVTR = 0.6 mg·m^{-2}·s^{-1}, even taking into account the small thickness of the samples, which in most cases the long-term use of such a product is permissible.

A separate question of research is the establishment of the influence of fillers on the change of vapor permeability during long-term storage or exploitation. It was established that the injection of fillers and additives into the polyethylene matrix significantly changes the structure formation with long-term aging. Part of the applications (mineral and mixed fillers, gas corrosion inhibitors, etc.) accelerates the crystallization of an amorphous matrix, which prevents the flow of diffusion processes at the initial stage of storage (mainly for 3 years). This is due to an increase in the overall crystallinity of the matrix (when the amorphous part of the polymer is replaced with mineral filler and / or the growth of the volume of crystalline formations under the influence of applications), the reduction of free volumes in the matrix, and the decrease in the mobility of the polymer chains.

However, the formation of a more crystalline structure negatively affects the total stability of the composite in the long terms storage or exploitation. The emergence of significant amount of defects through the line "amorphous-crystalline phase" at 4-6 years pours into the formation of cavities, rupture of surface material, splits, and cracks. The formation of an elongated structure from overlapping polyethylene crystals emerging from an amorphous matrix is a characteristic feature of accelerated agging under the influence of additives. There is the appearance of deep cracks and pores with further warehouse aging (for 6 - 7 years). Such transformations of the structure cannot proceed without the increase of vapor permeability indexes. The faster aging and, consequently, the change in diffusion properties, can be observed in polyethylene films, modified by gas corrosion inhibitors [17, 18]. Reducing barrier characteristics during long-term aging can be slowed down by applying thicker film materials or by using less active fillers, as well as injection additives that store amorphous matrices (plasticizers, slips, certain organic fillers and impurities, etc.).

Conclusion

For the creation of polyethylene films with fillers for prolonged use, the most appropriate is mixed filler that has in its composition organic and inorganic components. It should not be forgotten that the main obstacle to long-term storage is the processes taking place at the molecular level and leading to the destruction of the film.

In the case of closed storage, this is basically the oxidation processes that, under favorable conditions, may occur immediately during fabrication of film materials. Therefore, the use of anti-aging additives (antioxidants, antiozonants) is quite appropriate provided that they can be used. However, minor additives do not always delay the processes of destruction during long-term use of film samples.

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Vapor Permeability of Thin-Film Composite Materials Based on Polyethylene

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Паропроникність тонкоплівкових композитних матеріалів на основі поліетилену

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Проведено дослідження паропроникності та структури поверхні поліетиленових плівок, що зберігались в умовах закритого складування, при модифікації їх складу органічним наповнювачем та змішаними органічно-мінеральними наповнювачами,. Встановлено залежності змін дифузійних характеристик у залежності від виду та кількості наповнювача при тривалих дослідженнях (до 7 років). Виявлено, що введення в поліетиленову матрицю наповнювачів та добавок значно змінює структуроутворення при тривалому старінні.

Проведено електронно-мікроскопічні дослідження модифікованих плівок.

Ключові слова: полімери, поліетиленові плівки, паропроникність, структура, старіння.