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Influence of UV Radiation and Atmospheric Factors on Vapor Permeability of Thin-Film Modified Polyethylene Materials

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The vapor permeability of modified polyethylene films after long-term exposure to UV radiation and atmospheric factors was studied. The dependences of changes in diffusion characteristics on the type of modifying additives and the time of action of external factors are established. It is shown, on the basis of polarographic studies, the reduction of the quantitative composition of volatile modifying components of the modified film under the action of UV radiation.

Keywords: polymers, polyethylene, modified films, UV radiation, natural and artificial weathering tests, water vapor permeability, polarography.

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Introduction

The use of polymer film materials for the needs of the computer and electronic product manufacturing, also as of the electrical equipment, appliance and component manufacturing is mainly related to the packaging and storage of production. Accordingly, the characteristics and properties of such packaging materials must provide high corrosion resistance for metal products of any design and configuration, maintain a sufficiently high mechanical strength of packaging and its aesthetic characteristics, and recycling for using products. The main polymer packaging materials are polyethylene, polypropylene and polyethylene terephthalate, the need for which is determined by the characteristics and terms of storage of production, and in special storage conditions – by multilayer films and specific packaging structures [1-3].

The leading factors of action on electronic devices and metal products during storage in polymer packaging are different types of gases in the atomic or molecular state - oxygen, hydrogen, carbon monoxide, nitrogen, their mixtures, as well as vapors of various organic compounds and water vapor. Contact of a small amount of the above substances - agents of influence on the defect-free operation of devices, leads to the activation of oxidation processes on metal components, damage and blockage of conductive paths, changes in the electronic structure of materials etc. For this reason, the study of diffusion processes in polymeric protective materials used for storage of electronic products is inevitably associated with ensuring their high quality work and long life cycle. The use of specific substances (volatile inhibitor of atmospheric corrosion, plasticizers, fillers) to improve storage conditions, which has become quite common, can reveal unexpected aspects of the process, as increased anti-corrosion characteristics often lead to changes in the barrier properties of the material.

The purpose of the research was to determine the influence of UV radiation and outdoor exposure on the diffusion characteristics (vapor permeability) of barrier polymer modified materials and to establish the time of their possible use during operation in extreme conditions of radiation exposure.

I. The experimental part

Polyethylene thin-film materials with additives were made on on an industrial sleeve-film aggregate. The initial materials for the manufacture of products were granules of low density polyethylene LDPE 15803-020. Modifying additives and some process ingredients (up to 4 wt. %) were injected directly into granulate before extrusion, ensuring the most uniform distribution of the modifying components in the polymer matrix. Hexamethylenediamine methanitrobenzoate $H_2N\text{-}(CH_2)_6\text{-}NH_2\cdot HOOC\text{-}C_6H_4\text{-}N0_2$ (m-) known under the industrial name G-2 and dicyclohexylamine nitrite $(C_6H_{11})_2NH\cdot HNO_2$ - NDA was used as atmospheric corrosion inhibitors. To facilitate the processing and promote the combination of inhibitors with the base in the composition of the polymer matrix were injected plasticizers dibutylphthalate $C_6H_4(COOC_4H_9)_2$ – DBP and dioctyl phthalate $C_6H_4(COOC_8H_{17})_2$ – DOP.

The thickness of the polymer films ranged from 145 μm to 160 μm.

The researches of films vapor permeability were performed by weight method (dry cup method), using metal cups, according to international documents ISO 7783, ISO 2528 and ASTM D 1653 [4]. The investigation was performed for 30 days with recording of intermediate data every 5 days.

The research of modified polymer films to the action of UV radiation was done in the artificial weather chamber ИП-1-3 with a lamp ПРК-2. Samples of polymer films were installed on a frame that rotated around the lamp at a distance of 30 cm from its center and irradiated at different time intervals. The surface temperature of the samples was maintained at 303 K, the average relative humidity was close to 55 %. In addition, the change in barrier properties after exposure to atmospheric factors during September-October and May-June was studied (at an average daily temperature of 285.4 K and 295.4 K, and precipitation of 113 and 206 mm). These investigations did not meet the requirements of the standards for testing the effects of UV radiation and outdoor weathering ASTM D1435 and ASTM D 4364 and were carried out to determine the direction of possible changes in the properties of modified polyethylene thin film materials under the influence of meteorological conditions in open storage.

Samples of 0.4 grams of crushed polyethylene were prepared for polarographic studies, which was flooded into 10 ml of 0.25 N. alkaline solutions and heated in a water bath in reflux flasks at 373 K for 30 min. The obtained extracts were cooled to room temperature and placed in a polarographic cell, spent 10 minutes purging with nitrogen to remove oxygen, and then determined the polarograms from 0.4 V to 2 V.

II. Research results

Vapor permeability of polymer films is largely determined by their structure and composition (presence of modifying components, fillers, additives), thickness, conditions of diffusion processes (adsorption-diffusion-desorption), technological conditions of manufacture, and for samples that were in operation – by the quantity and action time of influencing factors [5, 6]. The most important external factors include UV radiation and atmospheric factors.

The initial vapor permeability of unmodified polymer films, defined as “water vapor transfer rate”, was set at WVTR = 0.24 - 0.25 mg/m^2·s, which in terms of water vapor transfer coefficient was $P_{WV} \approx 1.8$ g·mm/m^2·day. The exposure of the film for 30 days significantly reduced and stabilized the vapor permeability at the level of WVTR = 0.12 - 0.13 mg/m^2·s ($P_{WV} \approx 0.97$ g·mm/m^2·day, respectively) [7].

Films modified with atmospheric corrosion inhibitors, plasticizers and Al additives had an initial vapor permeability, usually less than unmodified samples - WVTR = 0.16 - 0.21 mg/m^2·s, and after 30 days of stabilization - WVTR = 0.09 - 0.13 mg/m^2·s. The films with chemically incompatible components - amine inhibitor and plasticizer based on dibutyl phthalate were singled out. They showed greater initial vapor permeability before and after 30 days of stabilization at the level of WVTR ≈ 0.3 mg/m^2·s.

The vapor permeability coefficient of UV irradiated films may differ due to changes in the intensity of structural processes as under the internal influence (composition, type and quantity of additives) and external (intensity and time of radiation, outdoor exposure so on) factors. UV irradiation for 200 hours inevitably led to a slight increase in vapor permeability. For films in which only one component was injected – a volatile inhibitor of atmospheric corrosion, the growth of WVTR could be Δ ≈ 0.07 mg/m^2·s (Fig. 1).

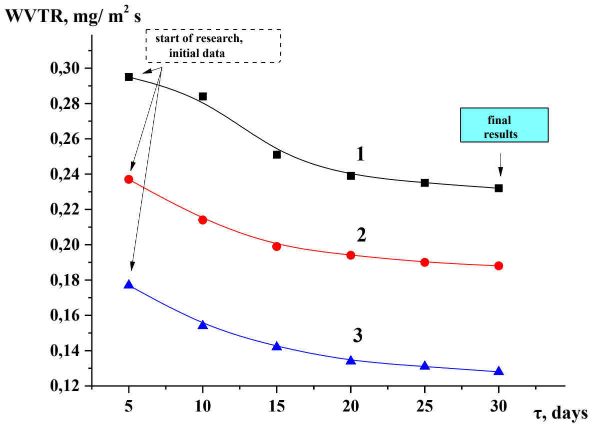

Fig. 1. The vapor permeability of polymer films after exposure to UV radiation for 200 hours: 1 – LDPE; 2 – LDPE + 0.5 wt. % G-2; 3 - LDPE + 1.0 wt.% NDA.

However, there is an ambiguous dependence of vapor permeability on irradiation with a wider modification and the injection of other additives and fillers. There was a tendency of a slight increase in vapor permeability during prolonged UV radiation exposure and the combined effect of the injected plasticizer DOP (Fig. 2).But the presence of the plasticizer DBP led to an intensive increase in vapor permeability at 200 hours UV radiation. Instead, the presence of DOP plasticizer, G-2 inhibitor and aluminum filler in the film composition leads to a slight increase in vapor permeability even at longer irradiation periods (up to 500 hours).

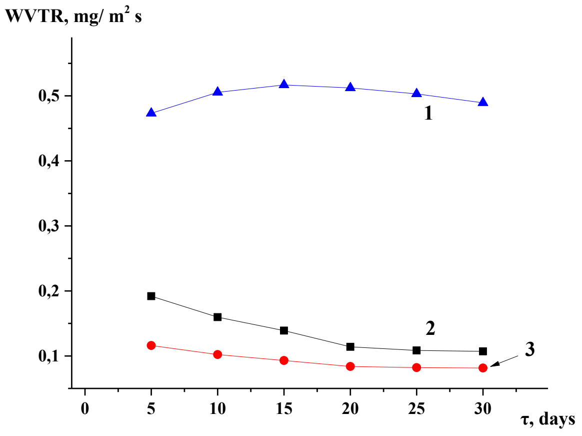

Fig. 2. The changes in vapor permeability of polymer films after exposure to UV radiation for 200 hours:
1 – LDPE + 1.0 wt. % G-2 + 0.2 wt.% DBP;
2 - LDPE +1.0wt.% G-2 + 0.5wt.% DOP +0.25 wt. %Al;
3 – **LDPE** +2.5wt.% G-2 +0.2wt.% DBP + 0.25wt. %Al.

Researches to determine the impact some factors were necessary, as these data determine the changes in the protective properties of the studied anti-corrosion polymer films during open storage. The obtained results show that there is an increase in vapor permeability under the influence of external factors in September-October (Fig. 3).

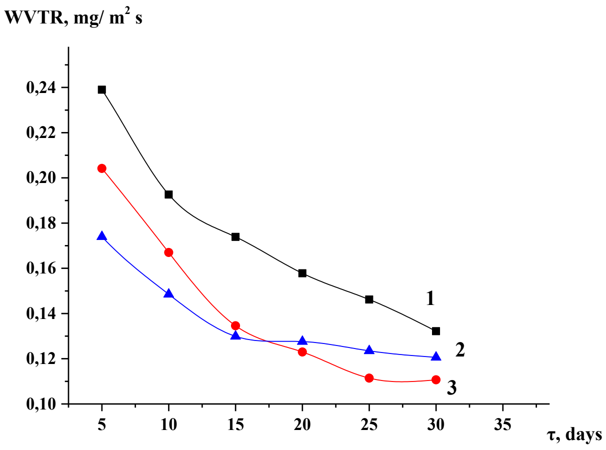

Fig. 3. The changes in vapor permeability of polymer films after the action of atmospheric factors during the autumn period: 1 **-** LDPE**;** 2 **-** LDPE + 1.0 wt. % NDA; 3 **-** LDPE +0.5wt.% G-2 +0.5wt.% DOP + 0.25 wt.% Al.

The WVTR remains lower for polymer films with modifying components, than that of unmodified polyethylene film. This indicates about of a slight positive effect of modifiers on increasing the barrier characteristics of the polymer matrix. The presence of a complex of modifiers in the polymer film (DOP plasticizer, G-2 inhibitor and Al filler) more effectively reduces the rate of vapor penetration through the coating. The value of WVTR is much lower than that of unmodified film that has been showing to autumn outdoor exposure tests for two months.

Similar studies on the influence of external factors during May-June showed an increase in the vapor permeability of polymer films. However, this value changes slightly in polymer films with NDA corrosion inhibitor (Fig. 4). Instead, the combination of G-2 inhibitor and DBP plasticizer in the film increases the vapor permeability. Similar changes in the WVTR cotfficient were observed for the film of this composition under the action of UV irradiation (Fig. 2).

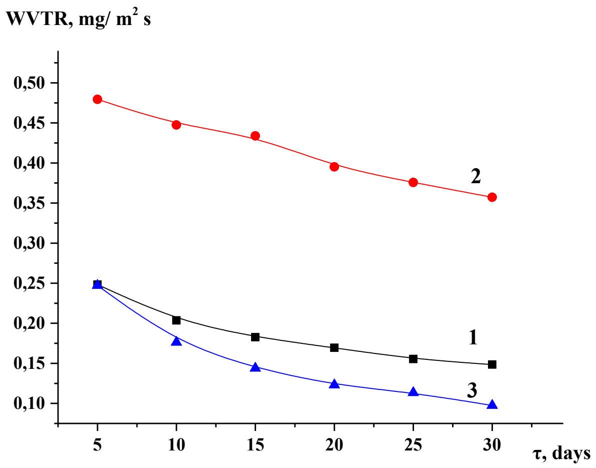

Fig. 4. The changes in vapor permeability of polymer films after the action of atmospheric factors during the spring period:
1 – LDPE; 2 – LDPE + 1.0 wt. % G-2 + 0.2 wt. % DBP;
3 – LDPE + 2.0 wt. % NDA.

In general, it was found that for polyethylene films that were exposed to UV radiation for 200 hours. vapor permeability increases (Fig. 5).

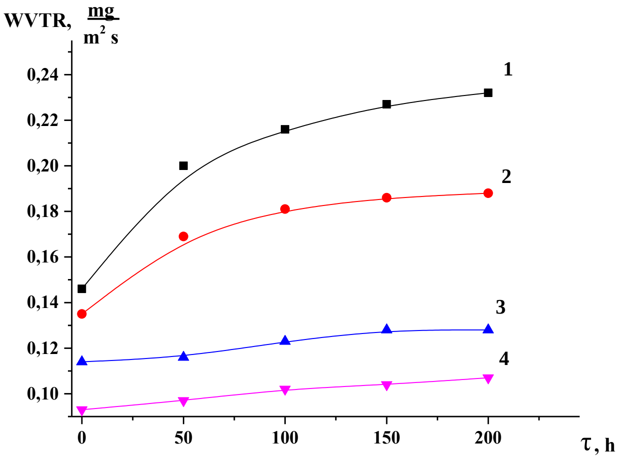

Fig. 5. The vapor permeability of modified polymer films from the duration of UV irradiation (final measurements on the 30th day of stabilization): 1 - LDPE; 2 - LDPE + 0.5 wt. % NDA;
3 - LDPE + 0.5 wt. % G-2; 4 – LDPE + 0.5 wt. % G-2 +
+ 0.5 wt. % DOP + 0.25 wt. %Al

Exposure to UV radiation for a long time (more than 50 hours) leads to an increase in the vapor permeability of polymer films, which is due to the combined processes, which in general have different directions in relation to changes in vapor permeability. However, if the WVTR coefficient increased by 46% for unmodified samples, then for modified ones - on average by 9 – 16 % depending on the content of modifying components (except for films with DBP plasticizer).

III. Discussion

It can be confirm, based on the analysis, that influence of of UV radiation leads to a decrease in vapor permeability in the films with presence of corrosion inhibitors (Fig. 5, curves 2 and 3). The presence of aluminum filler (along with a corrosion inhibitor and a plasticizer) in the composition of the modified film (Fig. 5, curve 4) has an even greater effect on the decrease in the WVTR coefficient.

Evaluation of diffusion processes of modified polymer films is carried out, first of all, on that modifying component which in the end leads to essential changes. For polymer films with mineral fillers, these are changes in the structure and increasing over time defect along the line "polymer-filler", as well as the initial decrease in the permeability of the penetrant due to the overall decrease in the diffusion coefficient of the composite (compared to pure polymer). In films with organic additives (as well as organic initiators of various processes) a number of diverse processes play the leading role in penetration changing. This processes describing the entire path of penetration - from adsorption through diffusion to desorption [5, 6]. The regularity of such processes at the level of adsorption are satisfactorily described by Henry's law and the theoretical works of a number of authors and are known as BET theory, which got its name from the initials of its authors - Brunauer S., Emmet P.H., Teller E. [8, 9]. Already at the level of adsorption consideration it was shown how important it is to take into account the interaction of the penetrant or organic additive with the polymer matrix and to predict the course of penetration processes. In turn, it can be foreseen that the interaction of the organic additives with the polymer matrix can change the diffusion processes much more effectively. But the effect of organic additives on the polymer matrix may have some uncertainty in the passage of diffusion processes. Any chemical interaction between the additives and the matrix leads to a redistribution of the quantity of amorphous and crystalline phases in the polymer (the crystalline phase usually has a lower diffusion coefficient). In addition, under the action of organic additives, plasticization can occur, which leads to changes in the flexibility of the polymer units. However, the application of known plasticizers can also have different effects on diffusion processes in the polymer matrix. Even a small amount of plasticizer can both facilitate the passage of the penetrant by increasing the flexibility of the polymer units, and reduce the possibility of penetration of gas atoms or molecules by blocking the pathways (which is typical for plasticized samples subjected to aging).

All the above processes are taking unusual forms of detection in modified polymer thin-film structures under the action of external factors - UV radiation and sunlight during outdoor exposure tests. After all, such operation or researches necessarily reveals additional processes of intensive evaporation of components from the polymer matrix, expansion and leakage of additives through pores, cracks and channels (which has a dual nature in terms of vapor permeability - increased volume of the additives can "clog" the penetration pathways and, as a consequence, to reduce the rate of WVTR, or, otherwise, with intensive phase transformation of additives – to increase the size of pores and holes, which would lead to increased vapor permeability. In addition, all this is necessarily superimposed on the aging processes of the polymer matrix with a change in phase composition and an increase in structural defects [10-12].

The polarographic studies of the content of the atmospheric corrosion inhibitor, which was injected as a factor of protective anticorrosive action of the coating, were done for determine the changes in the modified polymer matrix under the action of UV irradiation [13]. It was found that the decrease in the content of G-2 inhibitor occurred during the first 100 hours of UV irradiation. Further reduction of the inhibitors content in the film is less intense (Table 1).

Table 1

The polarographic determination of substances changes in the LDPE + 0.5% G-2 film, which was subjected to UV irradiation.

UV irradiation time, h	Polarographic wave height, cm	Defined group	The content of groups that are determined by polarography, in
0	64	hexamethylenediamine	$3.2 \cdot 10^{-3}$
100	17	hexamethylenediamine	$8.5 \cdot 10^{-4}$
200	14.5	hexamethylenediamine	$7.2 \cdot 10^{-4}$
300	12	hexamethylenediamine	$6.0 \cdot 10^{-4}$

The consequence of content reducing of corrosion inhibitors in the film during prolonged exposure to UV radiation is a deterioration of its structure and an increase in WVTR, although the minimum necessary barrier and protective properties of the film are preserved.

Unfortunately, there is no such unambiguous simplification in the interpretation of measurement results when determining the vapor permeability during outdoor tests as it was at UV radiation exposing. Because the additional factors such as wind and precipitation are imposed, this leads to increased defects in the matrix structure due to leaching and deflation. However, there is some regularity that is inherent in the modified films exposed to UV radiation. First of all, this is a slight increase in the vapor permeability of most modified films, which is associated with growth in the overall crystallinity of the samples. Previous structural studies confirm this thesis, and also indicate the next course of dependence - a sharp increase in vapor permeability due to the catastrophic destruction of the modified film caused by the action of additives, external factors and aging processes [12].

In addition, it has been found that exposure of polyethylene to ultraviolet light causes eventual embrittlement of the polymer. This is believed to be due to the absorption of energy by carbonyl groups injected into the chain during polymerisation and/or processing [14]. However, the presence of a corrosion inhibitor in the film inhibits the oxidation of the polyethylene film both in its manufacture and in the initial stages of operation - in the absorption spectra of modified coatings no valence oscillations of C = O ketone at 1720 cm^{-1} [15]. Slowing down the process of photooxidative degradation has a positive effect on the change in vapor permeability in the initial stages of operation. At the same time, the increase in the crystallinity of the films slows down the initial stages of oxidative degradation processes, as the crystallites can play the role of "traps" of free radicals [16].

But, small concentrations of additives significantly affect the change of structure, which is especially evident during long-term operation (more than 4 years) of coatings in open areas [10-12]. The photooxidative destruction was intensified, the rupture of polymer sections and leaching of the inhibitor were imposed in the modified films exposed to the sun. Destructive processes in modified coatings under conditions of changes during atmospheric factors develop much more actively than in previously studied films in the climate chamber.

Another common feature is the positive effect of the aluminum additive, which inevitably lowers the WVTR. The increasing in the WVTR coefficient by action of the DBP plasticizer additives was determined by two types of researches.

Conclusions

It can be entered that the action of UV radiation and atmospheric factors leads to a deterioration of the barrier properties of the studied polymer films, and the injection of modifying components has a positive effect on the films stability to external factors at short terms of operation. However, the magnitude of vapor permeability of the modified films is significantly affected by the quantity and compatibility of the components injected into the matrix - inhibitor, plasticizer and filler.

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Вплив УФ-випромінювання та атмосферних факторів на паропроникність тонкоплівкових модифікованих поліетиленових матеріалів

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Проведено дослідження паропроникності модифікованих поліетиленових плівок після тривалої дії УФ-випромінювання та атмосферних факторів. Встановлено залежності змін дифузійних характеристик від виду модифікуючих додатків та тривалості дії зовнішніх факторів. Показано, на основі проведення полярографічних досліджень, зменшення кількісного складу летких модифікуючих компонент модифікованої плівки при дії УФ-випромінювання.

Ключові слова: полімери, поліетилен, модифіковані плівки, УФ-випромінювання, атмосферны фактори, паропроникність, полярографія.