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## Features of Time Characteristics of Diffusion Properties of Polymer Modified Film Materials for Technical Application

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The changes of the oxygen permeability of packings from polymeric film materials intended for prolonged storage of metal products have been investigated. High indexes of initial oxygen permeability were recorded due to insecure insulating properties of weld seams, as well as increased diffusion characteristics after the third year of exploitation. The most characteristic structural defects, which emerging in polyethylene modified materials during the period of prolonged storage, have been identified by means of electron microscopic studies.

**Key words:** polymer materials, polyethylene, oxygen permeability, surface structure.

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### Introduction

The diffusion properties, such as gas-, water- and water vapour transmission of polymer films (membranes) are considered in accordance with their technical usage. The most suitable for this aim materials and methods of control were used. The study of polymeric film packaging for technical purpose is difficult owing to the complexity of conducting research, the need for necessary comparison of results with another investigation of individual films properties, a large discrepancy in experimental methods and diffusion (permeability) characteristics units. Experimental data of the oxygen permeability in polyethylene film, obtained by different researchers, have a spread of data, which is mainly associated with the peculiarities of obtaining samples, as well as with modifiers and fillers used during polymeric materials reception. Transition of low-weight molecular substances in polymers are determined by the structure and properties of the matrix: the shape of the of macromolecule chains, the number of lateral groups and branches, the deviation of the chain from straightforwardness, the ability to exhibit the flexibility of macromolecules during mechanical and thermal load, and so on.

The transmission rates decreased with the increase of intermolecular interaction, the degree of crystallinity and orientation, which predetermined the growth of packing density. The diffusion characteristics of materials significantly changes with the use of different types of fillers, colorants, pigments, plasticizers, stabilizers,

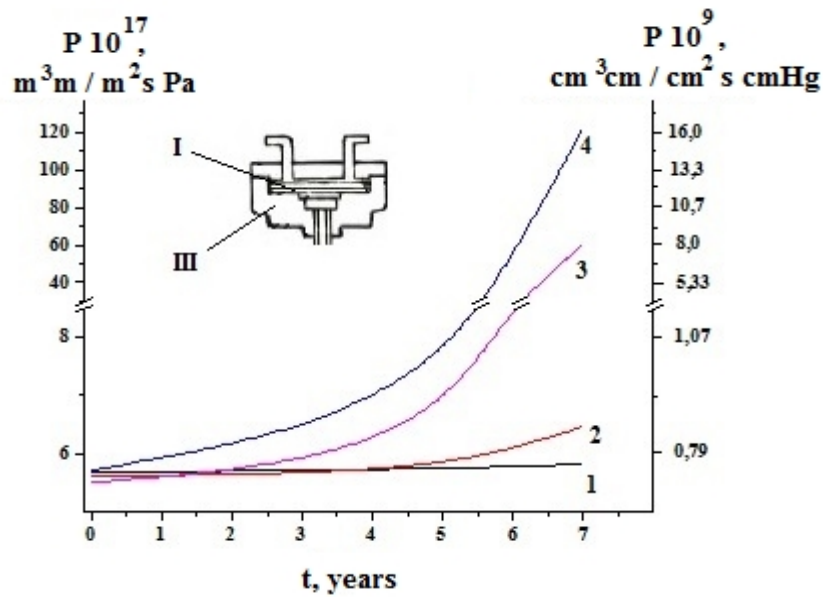
electromagnetic fields and ionizing radiation. Further and more detailed studies need to deal with the processes of transfer in modified polymeric materials and, in particular, their time characteristics in the long-term exploitation, despite the large number of diverse and large-scale studies on the flow of diffusion processes in polymeric materials by national and foreign scientists.

The aim of the research was to study the oxygen permeability of polymeric packaging made from modified film polyethylene, as well as comparison results with the corresponding studies for polymer films (membranes).

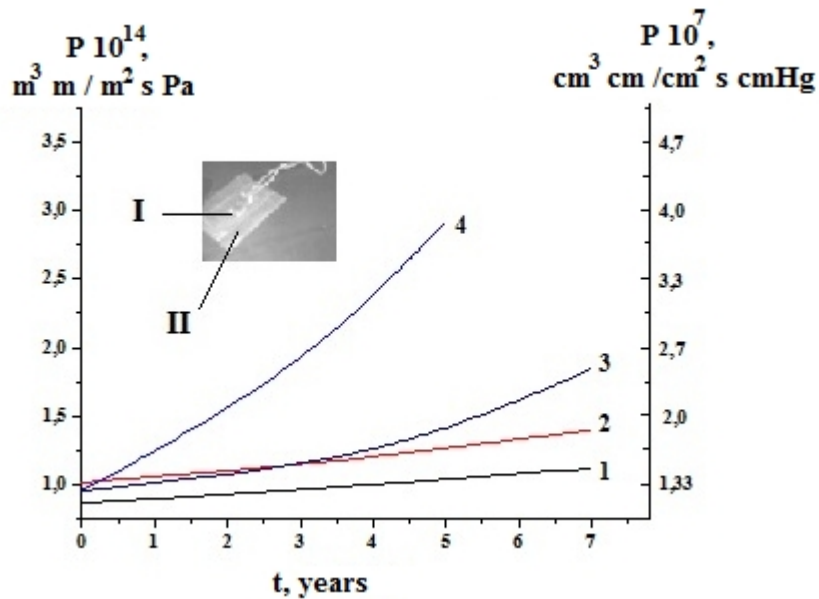
### I. Experimental part

The polymer matrix - low-density polyethylene (LDPE) has been chosen as the matrix of the research object. As an inhibitor with a content of 1.0 wt., percentage used dicyclohexylamine benzoate (DCHAB) as a plasticizer - dibutylphthalate (DBP). The introduction of the plasticizer into the polymeric composition reduced the processing temperature and facilitated the combination of the inhibitors with the matrix.

The samples of films were made on an extruder of model 4П 35x18 and an industrial sleeve-film aggregate of type JIPI. The inhibitors were introduced into the polymer matrix at the blowing stage in the outlet zone of the sleeve film from the forming head. The thickness of the films was  $h = 170 \pm 5$  microns.



**Fig. 1.** Changes in the oxygen permeability coefficient of polymer films in different storage conditions (manometric measurement method): 1 - LDPE + 1 weight. % DCHAB + 1 weight. % DBP (closed warehouse); 2 - LDPE (closed warehouse); 3 - LDPE + 1 weight. % DCHAB (closed warehouse); 4- LDPE + 1 weight. % DCHAB (open warehouse). At the insert - a measurable head (III) of the manometric method device for measuring the oxygen permeability for polymeric membrane materials (I).



**Fig. 2.** Changes in the oxygen permeability coefficient of polymer films in different storage conditions (measured using oxygen depolarization sensors): the designation of the material of the packages - corresponding to Fig. 1. At the insert - an oxygen depolarization sensor (I) in a hermetically closed polymeric bag (II).

The oxygen permeability of the polyethylene film material was determined by a manometric method in accordance with the requirements of international normative documents [1, 2].

The oxygen permeability of the polyethylene bags was determined after 6 daily exposures, guided by changes in the current of oxygen depolarization sensors placed inside single-layer packages. The sensor of oxygen depolarization represented two electrodes (carbon and zinc) between which a layer of filter paper impregnated with 1 n. solution of ammonium chloride was placed. The bags of standard sizes of 50x100 mm<sup>2</sup>

were used in these investigations. The bags sides were welded on device type Hanato NI.

The electron microscopy investigations were carried out using scanning microscope Tesla-250.

## II. Results

The initial oxygen permeability of modified and non-modified films is slightly different - in uninhibited films, the coefficient of oxygen permeability (P) is higher, compared to inhibited films (Fig. 1, 2). After 3-4 years of

closed warehouse, the diffusion characteristics of the studied materials increase within acceptable limits. However, the magnitude of deviations exceeded 15 % of the initial value in open warehouse films and those containing an inhibitor that actively interacts with a polymer matrix (Fig. 1).

It found large quantity of defects, which caused a sharp increase in the index of oxygen permeability, in such films after 5-6 years of storage

Considerably higher coefficient of diffusion characteristics revealed the measurements of the oxygen permeability of polymer films in the form of bags has significant increase in the penetration observed after three years of storage in the open warehouse (Fig. 2).

The DCHAB inhibitor significantly reduced the initial oxygen permeability coefficient. However, in the next, the oxygen permeability of inhibited films increases much faster than uninhibited ones. Additives of plasticizer DBP contribute both to the initial reduction and to stabilize the process of transition through polymeric bag.

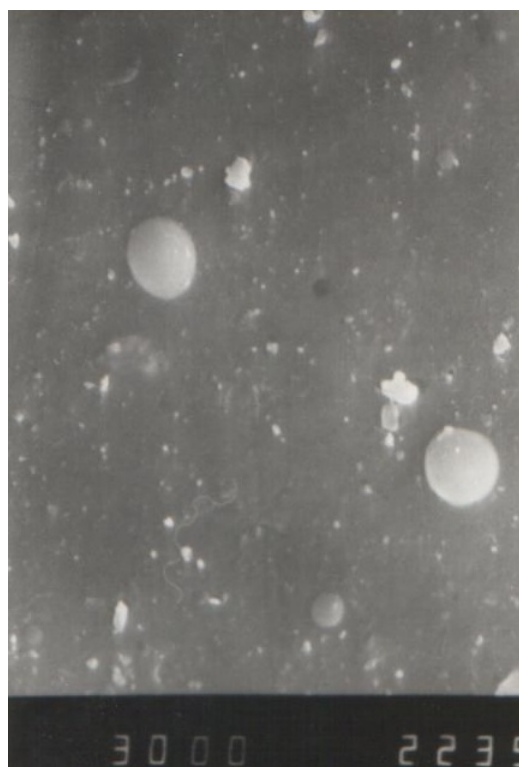
### III. Discussion

The existing discrepancies between the determined parameters of the oxygen permeability coefficient are due to several factors, among which two basic ones should be distinguished - the objects that caused the use of different research methods, and those materials that have a wide distribution of structure and properties.

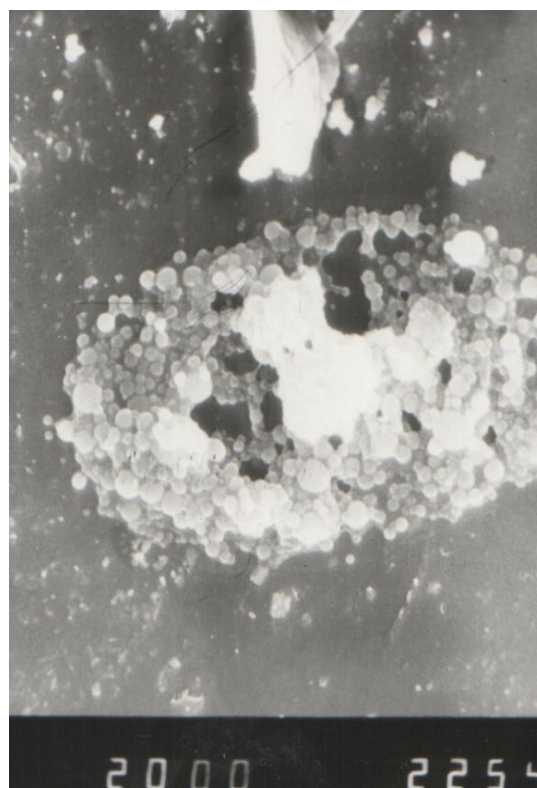
In some cases, indirect, tactical research methods are used, since there is a need to obtain general characteristics of the combined protective agent. Thus, the usage of weight testing methods or some oxygen depolarization sensors to determine the permeability of polyethylene bags or medical polymer vials can sometimes be used only to establish the overall dynamic characteristics of the penetration process. Such investigations are also necessary to establish the barrier characteristics of individual parts of the package [3]. Manometric studies are used as classics, which help to assess the permeable characteristics of the main component of the package - a polymeric barrier film.

It is known [4, 5, 6], that the transition of low-weight molecular substances in polymers is determined by the flexibility and peculiar nature of the thermal movements of the matrix chain molecules, by the change in the polymer molecules symmetry, by the increase in density, by the creation of additional bonds, by the formation of layer and spiral structures. The permeability coefficient of a polymer film is also dependent on the degree of polymer dispersion in the presence of low-weight molecular fractions and on the chain form of macromolecules (an increase in the number of lateral groups, branches, and deviations of the chain from straightforwardness) [7, 8].

The parameters of the permeability of the polymer films are always depending on the type of polymer (structure, orientation and density of laying fibrils, which also implies the density material, physical state, id est degree of crystallinity, the presence of bonds, stitching or conjugation between polymer chains, etc.) [9, 10]. The



**Fig. 3.** Microphotography of polyethylene film, modified by inhibitor DCHAB (1% weight) and plasticizer, in initial storage (x 3000).



**Fig. 4.** The semi-crystalline growths on a crystalline region of a polymeric film modified by a DCGAB inhibitor and plasticizer subjected by aging up to 10 years (x 2000).

permeability is also influenced by the composition and characteristics of penetrant substances (especially the sorption characteristics relative to the membrane material), their concentration and the pressure difference that arises during the permeability through the polymer partition. In addition, the measured parameters of polymeric permeability are largely corrected by the measurement methods and characteristics of the equipment used for this purpose, as well as the external conditions of conducting experiments (temperature, humidity, deformation efforts, etc.).

Manometric studies have found that some thin polymer films used for packaging had initial oxygen permeability coefficient that were consistent with studies by other researchers [4, 6, 11]. In this case, the initial values  $P$  of films with inhibitors were slightly lower, which was associated with increased crystallinity of the polymer matrix under the influence of inhibitors. The permeability further reduced during introduction of a plasticizer in the composition, although an increase in permeability was expected due to increased mobility of polymer chains. Obviously, the processes of increasing crystallinity under the influence of the inhibitor at the initial stage of the matrix formation were over the processes of increasing the amorphization under the action of a plasticizer. May be a part of the plasticizer play the role of the defect eliminator, filling the pores and cavities, and decreasing the permeability coefficient.

Crystalline accelerated formation took place in the matrix of the inhibited films during 1 - 2 years aging. This process contributed decreasing of oxygen permeability. However, the destructive processes, activated on 3 - 4 years along the boundary "amorphous - crystalline phase", led to increasing of matrix defect that's why gas permeability also rise. This is confirmed by spectroscopic measurements of the optical density methyl region on  $1378\text{ cm}^{-1}$  in inhibitor-containing preservation-packing materials when increasing in the number of methyl groups ( $\text{CH}_3$ ) is detected. The activation of crystallization processes characterized by a structure with significant content of the small crystalline phase took place during with subsequent aging of such films. In turn, the defect at the boundary between the amorphous and crystalline phases of such films is greater in comparison with uninhibited films, which is especially noticeable in the later stages of operation [13]. This was especially noticeable on inhibited films at open storage films that showed a mass defects which led to the complete loss of protective properties (Fig. 1).

Plasticization of uninhibited polyethylene films led to an unexpected result - the processes of gas permeability were actually fixed at the baseline level throughout the research time, which was associated with the stabilization of the structure [14]. The disadvantage of plasticization of polyethylene films with prolonged storage were loss of transparency and aesthetic appearance. The films became greasy to the touch, due to the diffusion of plasticizer to the surface of the coating (Fig. 3). Such behavior could take place after half year of closed storage - a large number of small spherulites with diameter  $d \approx 2 \cdot 10^{-7}\text{ m}$  were observed on the film surface, but the general defects (pores, cracks, crazy) were significantly smaller (Fig. 3).

The specific feature corresponds for to polymer films plasticization - the permanent displacement and allocation of the plasticizer and other related components from the polymer matrix. It was found by investigations that such secretions may have a double adventure. The unbound plasticizers diffuse through the amorphous regions (it is easily washed off by a degreasing agent when cleaning the film), and other plasticizers displaced to the surface and forms semi-crystalline formations associated with the inhibitor and polyethylene within the crystalline regions (Fig. 4).

It was fixed, due to measurements of the oxygen permeability of thin polyethylene film materials in the form of bags, using the change in the current of oxygen depolarization sensors, the same time periods for changes in the passage of gas permeability processes, as in measurements by a manometric method. However, the penetrant activity in product is two orders higher owing to the defectiveness of welding and to the occurrence of significant defects under the influence of high temperatures in the welding places (Fig. 2). The inhibitor-containing films with plasticizer applications were characterized by increased gas permeability throughout all time of aging, compared to single films. Although the processes of gas transition in such films are lowered. Mainly, this situation is due to the passage of two-linked processes with opposite effects, that caused by the introduction of the inhibitor and plasticizer. An increase in crystallinity at the initial stage of aging with the introduction of the inhibitor was offset by the influence of the plasticizer, which ultimately led to the small crystallinity of the matrix. Subsequently, there appeared a metastable structure, which, due to the limited action of external factors (UV irradiation, washing, etc.), was characterized by a lowered the oxygen permeability coefficient.

It should be noted that the application of different methods for measuring the permeability of polymer films is justified in the case of investigations of complex protective devices and packages.

## Conclusion

The necessity of using various studies in determination of parameters of gas permeability of complex protective devices and packages is established. It is possible to forecast time changes in the properties of protective packaging materials and to predict the direction of modifications of their barrier functions for the long-term improvement, using different measurement methods and additional studies.

Introduction to the coating composition such components as gas-corrosion inhibitors increased the anticorrosive protection of metal products in packages, but the crystallinity of the polymeric base are increased too. The initial intensity of the diffusion transfers of oxygen through the film also decrease, that's why the activation of destructive processes, the formation of transverse pores and the destruction of the coating integrity increase with prolonged exploitation of the packaging takes place.

The diffusion processes in the material throughout

the life of the exploitation stabilized during simultaneous introduction plasticizer and inhibitor into the polymer matrix during the manufacture.

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## **Особливості часових характеристик дифузійних властивостей полімерних модифікованих плівкових матеріалів технічного застосування**

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Досліджено зміни киснепроникності упаковок із полімерних плівкових матеріалів, призначених для тривалого зберігання металевих виробів. Зафіксовано високі показники початкової киснепроникності з-за ненадійних ізоляційних властивостей зварних швів пакетів, а також встановлено зростання дифузійних характеристик після третього року експлуатації. За допомогою електронно-мікроскопічних досліджень визначено найбільш характерні структурні дефекти, що виникають у полімерних матеріалах у період тривалого складування поліетиленових модифікованих матеріалів.

**Ключові слова:** полімерні матеріали, поліетилен, киснепроникність, структура поверхні.