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Change of Mechanical Properties of Polyethylene Film Materials during Their Modification by Technological Applications and during Aging

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Mechanical tests and studies of the structure of modified polyethylene film materials used as packaging elements of electronic devices have been carried out. The modification provided for the introduction of fillers of various types and technological additives that would facilitate the processing of raw materials and ensure a long service life. The peculiarities of changes in mechanical characteristics depending on the number and type of applications, as well as the course of processes under the influence of external factors are established. The relationship between changes in the structure and mechanical properties of polymeric materials is shown.

Key words: polymers, polyethylene films, mechanical characteristics, inhibitors, plasticizers, structure, aging.

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Introduction

Polyethylene is one of the most used polymeric materials, which is mainly used for packaging [1, 2]. Properties of polyethylene (massive, thin film) vary over a wide range. The high diffusion and good mechanical characteristics, resistance to outdoor weathering factors (atmospheric) environments are among these properties. Improving some of the characteristics of polyethylene by injection additives or creating composites is inevitably supplemented by changes in the structure, chemical and physical properties of the products.

This requires further studies to establish acceptable limits for the use of modified polyethylene material by mechanical, thermal and physical characteristics, as well as by operating time.

The purpose of the study was to investigate the mechanical characteristics of modified polyethylene film materials and to determine the directions of changing the surface morphology of the appropriate samples during different types of storage.

I. The experimental part

Polyethylene thin-film materials with additives were fabricated on an industrial sleeve-film aggregate. The granulate of low density polyethylene LDPE 15803 020 was used for the manufacture of film products. Modifying additives and some process ingredients (up to 4 wt. %) were blended directly into the granules before extrusion, providing the most uniform possible distribution this modifiers.

The additional supplementary of volatile inhibitor of atmospheric corrosion were selected primarily in terms of high efficiency of their action in protecting the metal surface, wide temperature range of application, saturated vapor pressure and low toxic properties, and only later – compatibility with other components and matrix.

The effect of the modifiers on the structure and mechanical properties of the polymer matrix was determined for the of hexamethylenediamine methanitrobenzoate $H_2N-(CH_2)_6-NH_2 \cdot HOOC-C_6H_4-NO_2$ (M-) known under the industrial name G-2, dicyclohexylamine nitrite $(C_6H_{11})_2NH \cdot HNO_2$ – NDA,

Cyclohexylamine benzoate (DCHAB – $(C_6H_{11})_2NH_2^+ \cdot (C_6H_5CO_2^-)$ – CHAB, Dicyclohexylamine benzoate $(C_6H_{11})_2NH_2^+ \cdot (C_6H_5CO_2^-)$ – DCHAB.

The plasticizers dibutyl phthalate $C_6H_4(COOC_4H_9)_2$ – DBP and dioctyl phthalate $C_6H_4(COOC_8H_{17})_2$ – DOP were injected in polymer matrix for facilitation processing and for combining with matrix material.

The thickness of the polymer films ranged from 45 μ m to 150 μ m.

Samples for research were selected and prepared in accordance with the requirements of GOST 12423-2013 (ISO 291: 2008) and ISO 527-3: 2018 [3, 4]. The test specimens were strips 10 \pm 0.2 mm wide with a clamping position 50 mm long.

Tensile tests were carried out by using testing machines ZT 4, which were equipped with measuring systems with automatic registration of tensile curves, and 2166P-5, according to standard GOST 14236-81 [5]. Multiple characteristics of mechanical properties were determined in the studies, but the main attention was rewarded to the fracture stress (tensile strength at break) σ_b and breaking strain ε_b [5-7].

The material was exposed to various external conditions in the artificial weather chamber III-1-3 and hydrostat Γ -4. The duration of certain external factors was 10, 21, 30 and 56 days, after which tensile tests were performed. In addition, the effect of outdoor weathering factors influence on the strength films characteristics was studied over two months between May and June, September and October.

These studies did not correspond the requirements of the standards in terms of time, but were supported to determine the directions of possible changes in the properties of polyethylene thin-films under the influence of meteorological conditions in open storage [8, 9].

Elektron-mikroskopy investigations were done on microscope UEMV-100K and EM-125 using the replica method. The samples were subjected preliminary ion etching and cut over with chromium and graphite coated. The resulting carbon replica, which retains the structure of the material, was torn off with gelatin.

Samples examined on a Tesla-250 scanning electron microscope were exposed to pre-ion ion etching, and cut over with Cu a60 Ag to ensure charge drainage for contrast.

II. Results

The effect of the percentage of different modifying components and fillers of different origin on polyethylene matrix properties was performed before and after modification over a long product life cycle.

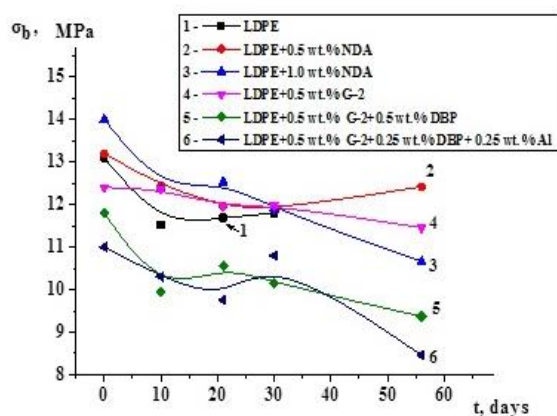
The mechanical characteristics of the initial polyethylene film materials containing small amounts of modifying additives are given in Table 1.

In general, there is a decrease in the mechanical characteristics of polyethylene films with the injection of a small number of volatile inhibitor of atmospheric corrosion, plasticizers and fillers. A similar dependence

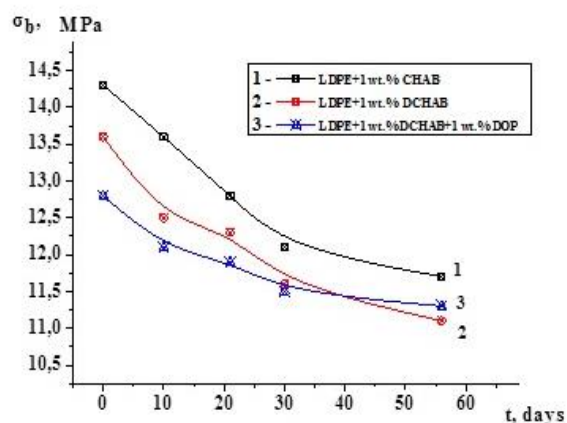
Table 1

Effect of modifying additives on the mechanical properties of polyethylene films

The composition	Fracture stress (tensile strength at break) σ_b , MPa	Breaking strain ε_b , %
LDPE	13.2	235.5
LDPE + 0.5 wt. % NDA	13.2	244.1
LDPE + 1 wt. % NDA	14.0	242.2
LDPE + 0.5 wt. % G-2	12.4	235.9
LDPE + 0.5 wt. % G-2+ 0.5 wt. % DBP	11.8	279.5
LDPE + 0.5 wt. % G-2 + 0.5 wt. % DBP + 0.25 wt. % Al	11.0	250.2
LDPE + 1 wt. % CHAB	14.3	247.2
LDPE + 1 wt. % DCHAB	13.6	241.4
LDPE + 1 wt. % DCHAB +1 wt. % DOP	12.8	264.2



a



b

Fig. 1. Changes in tensile strength of modified polyethylene films after the high temperature (333 K) exposure.

is observed with the injection into the polyethylene matrix of a small amount of atmospheric corrosion inhibitors of metals such as KCA, HCA and IFHANGAS.

The effects of outdoor weathering factors (temperature, humidity, UV radiation, and their compatible action, etc.) lead to changes in the mechanical characteristics of polyethylene modified films. It was found that raising the temperature to 333 K reduces the tensile strength during the first 10 days of testing (Fig. 1). Over the next 20 days, the raised temperature exposure showed tensile strength stabilization in all samples except those containing CHAB and DCHAB inhibitors. While, small additives of plasticizers (DOP or DBP) tend to reduce σ_b gain. Attention is drawn to the sharp decrease of σ_b values in films containing negligible additives of aluminum

(Fig. 1a).

Increased humidity ($\varphi = 95\%$ at $T = 293\text{ K}$) is a much smaller tool for influencing the mechanical properties of polyethylene film than the increased temperature (Fig. 2). The value of the σ_b decreases slightly in the first 10 - 20 days exposure, after which the indexes stabilize. The exception is the rates of samples with plasticizers, which are marked by some instability in the changes.

The combined influence of high temperature ($T = 313\text{ K}$) and humidity ($\varphi = 95\%$) led to a greater convergence of the σ_b values (Fig. 3). However, the tendency for a steady decrease in the tensile strength during the investigation was maintained only in films modified by the CHAB inhibitor (Fig. 3b).

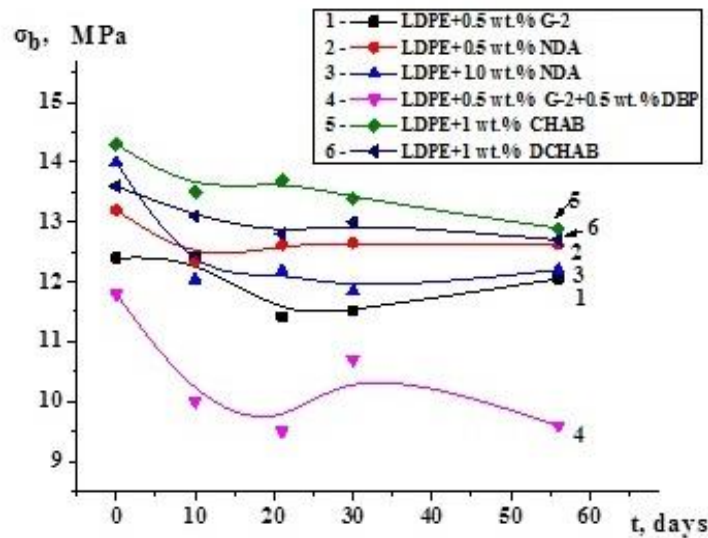


Fig. 2. Changes in the mechanical characteristics of modified polyethylene films after exposure to high humidity $\varphi = 95\%$ ($T = 293\text{ K}$).

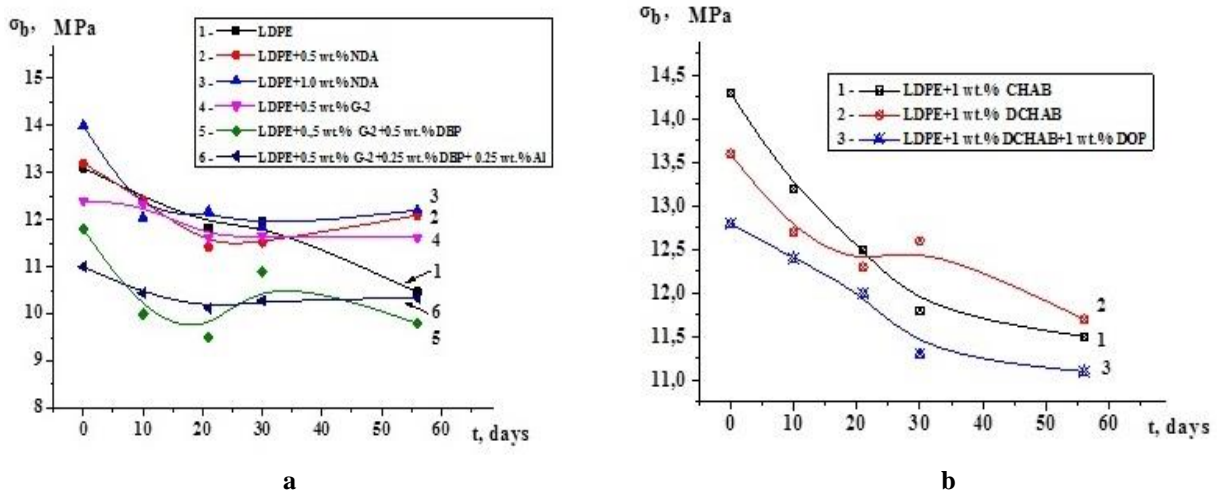


Fig. 3. Changes in tensile strength of modified polyethylene films after combined high temperature ($T = 313\text{ K}$) and humidity ($\varphi = 95\%$) exposure.

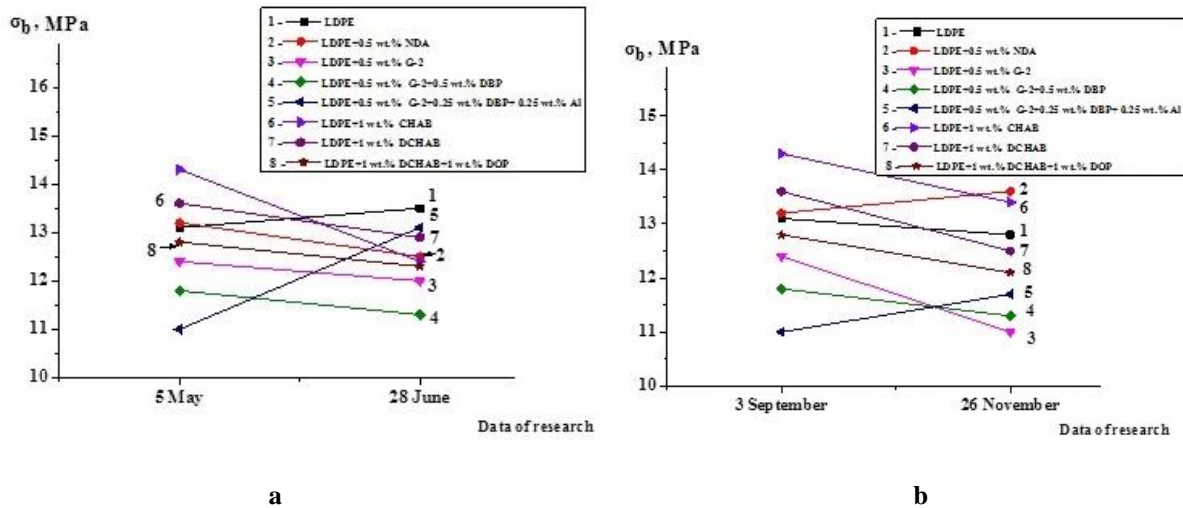


Fig. 4. Changes in tensile strength of modified polyethylene films after exposure to spring-summer (a) and autumn (b) outdoor weathering factors.

Testing of films after influence of various factors of outdoor weathering factors (2 months) in the spring-summer and autumn period showed similar results (Fig. 4). Small differences in results can be attributed to the variety of factors at different times.

Some specimens with increasing tensile strength were distinguished. Those samples had such additive as NDA atmospheric corrosion inhibitors and combined additive of G-2 inhibitors, DBP plasticizer and aluminum. Moreover, the growth of the σ_b of the two samples was insignificant and concerned a one test period. Instead, the aluminum specimens (sample 5, Fig. 4, a, b) showed a steady increase in the tensile strength over the two test periods.

III. Discussion

The change in tensile strength at break of polyethylene is completely in line with previous scientific studies that have been performed to study structure changes in films with the injection of additives, different external influences, or during certain periods of the life cycle during aging.

The main factors affecting the structure and properties of polymer materials are temperature, time, pressure, type of stress, the external environment (reactive substances, ionizing radiation, etc.) or their compatible action [10]. The influence of the research methodology (time, speed and conditions of the research), as well as the influence of design and technological factors of matrix material creation (molecular weight, degree of orientation of polymer chains, branching and cross-linking, copolymerization, crystallinity, plasticization, action of additives, etc.), which can lead to changes of mechanical characteristics [11, 12].

In some cases, the influence and effect of the external environment - temperature and humidity during storage and using of the material, time and action value

of the factors, type and size of deformation, combination of different types of harmful influences, play a decisive role in determining the mechanical properties, in addition to the above structural and molecular factors. [11, 13].

The decrease in the mechanical characteristics of polyethylene films with the injection of a small quantity of modifiers is quite predictable, given that the addition of any component in the polymer matrix inevitably leads to a change in the structure, increase its defect. In this case the actions to prevent the decrease of characteristics by adding other technological components and stabilizers were insufficient due to small amount of adds.

A slight increase in the crystallinity of polyethylene films under the influence of inhibitor of atmospheric corrosion (> 1 wt. %) led to a small increase in (Table 1). The surface structure of the modified samples lost the homogeneous and undefect characteristic which were peculiar to unmodified and more amorphous specimen (Fig. 5).

Such changes in the mechanical strength value can be completely compensated by a small amount of plasticizers.

The most resistant to the effects of humidity were polyethylene films modified by inhibitors of NDA and CHAB, which noted minimal changes in mechanical characteristics during 56 days of research (which contrasts with changes caused by high temperature). This is due to the active crystal-forming function of these components, which in a short time formed a structure with higher mechanical properties than in films with other additives. The plasticizer injection in the polymer matrix led to lowers σ_b , the change of which during this test is stochastic.

The simultaneous action of humidity and high temperature steered to the initial (within 10 days) decrease in the σ_b . Such changes in the mechanical characteristics under the influence of these external factors is associated with a slight change in the structure, namely a greater increase in the crystallinity of the

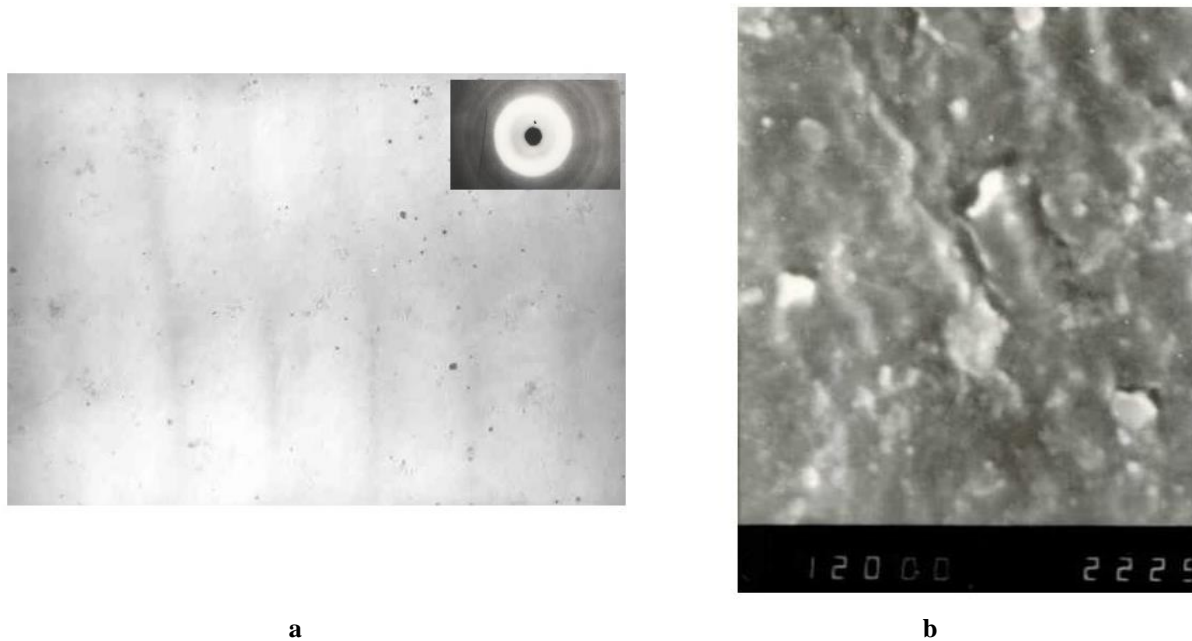


Fig. 5. The surface structure and X-ray diffraction (inset) of a polyethylene film without additives (a, X 10700) and a film modified by the inhibitor of atmospheric corrosion DCHAB (0.5 wt.%) (b, X 12 000).

polymer matrix under the action of temperature without humidity (Figs. 1, 3). Aluminum are the component that stabilize the σ_b values help to preserve the phase composition of the polymer matrix, during injection other components or under stated outdoor weather conditions.

In [14] investigated the effect of Al nanoparticles on the mechanical properties of a thin-film LDPE matrix grown from solution. Characteristically, insignificant additions of Al (0.5 - 5 wt.%) lead to an increase in the ultimate stress σ_u and the elongation at break ϵ_b , although the tensile strength σ_b increases slightly.

The influence of humidity on the polymer matrix covers many more aspects than a single action. In our opinion, this is due to the multi-vector affect of humidity on the matrix, which includes a number of processes (sorption, diffusion, saturation of moisture, chemical interaction with additives, influence on the rate of defect formation in a polymer matrix, etc.), each of which contributes to lowering of ultimate strength characteristics. Of course, the effect of humidity on the strength indices is specific, although in the case of thin film specimens it has the same orientation with the effect of temperature - it leads to a decrease in tensile strength at break.

Increasing the temperature (up to 333 K) leads to growth of crystallinity of the samples, and in the case of the injection of amine-based corrosion inhibitors tips to a significant increase in crystallization and as result – to a decrease in the strength characteristics while reducing the relative elongation at break. Instead, the effect of humidity is determined by the sufficiently high saturation levels of the samples with water, which hints to the effect of imaginary plasticization. The consequence is a decrease in tensile strength when the value of and breaking strain ϵ_b increases.

As is known, the influence of humidity on polyamide 66 was marked by a decrease in such strength characteristics as the Young's modulus, yield stress, tensile strength at break σ_b , although the plasticity of the sample (breaking strain ϵ_b) increased [15].

It should be noted that the influence of temperature, as well as the effect of humidity, in the modified samples could both enhance and reduce the strength characteristics, depending on the specific action of the modifier on the matrix. However, during the prolonged influence of humidity anybody should take into account the effect of "displacement" and "leaching" components of the base material.

The combined influence of temperature and humidity is more damaging to a polyethylene film if it is to be tested for strength. For films with an active crystalline-forming agent, which acted as inhibitor of atmospheric corrosion (NDA, CHAB, DCHAB), the indexes of fracture stress were reduced under both influence factors – temperature and humidity. The nature of the changes in mechanical characteristics at a given lifecycle may be determined as a result of the interaction of injected and unbound inhibitor and an adsorbed water vapor with polymer matrix which have sufficiently high permeability [12].

This contributed to the active destruction of the polymer structure with an increased defect at the boundary of the "crystalline-amorphous phase", which was enhanced by the permeability of water vapor to the formed imperfections of the matrix [16]. It was confirmed [15] that the strength characteristics of polymers undergo much greater deterioration under hydrothermal conditions, since the degree of moisture absorption by the matrix accelerates with temperature. Of course, the effect of moisture in the work had to be greater, since there are sudden significant changes in the

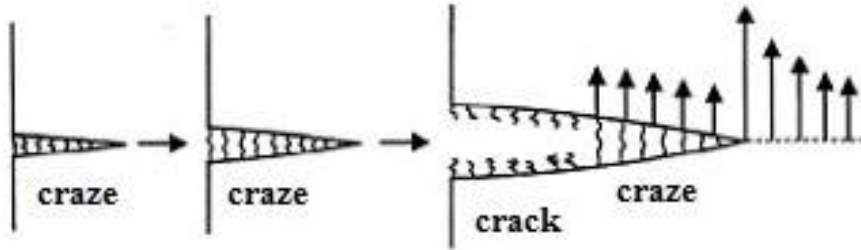


Fig. 6. Continuous craze growth and formation of a crack, which cannot support load [17].

matrix.

With larger exposures in the studies, such a moisture action was more pronounced due to the manifestations of the plasticizing effect, but this requires a saturation of the wet matrix.

In general, these studies confirmed the scheme of ultimate destruction of amorphous-crystalline polyethylene thin-film material, established in due time for amorphous elastomers [17]. However, most clearly this pattern of destruction is demonstrated in thin-film polyethylene, which has a greater propensity for crystallization – either by the injection of modifying components, or by the action of under weather and operational conditions for a specified period of time.

Cracking is a phenomenon that often precedes fracture in many glassy polymers and occurs in areas with high stress, acquired during storage or operation [17]. This leads to the formation of micro-voids and a reduction in the fibrils size. Such small cavities can occupy sufficiently large volumes of the matrix and allocated into a separate category of microcracks under the name of craze. Their appearance precedes the formation of large-scale cracks, and the presence of their large quantities in polymers under loadings has been called "silver cracks" because of the characteristic coloring of such damage on microphotographs [18].

Such microcracks appear, first of all, in polyethylene as its life cycle increases, even when the material is not under load. Crazing occurs mainly in brittle regions of polyethylene and along the line "amorphous-crystalline phase", similar to the destruction in polymers such as polystyrene and poly (methyl methacrylate). With the aging of polyethylene, such microcracks are particularly common appears in places of mechanical damage, obtained during films extrusion.

The crazes tend to increase in the direction perpendicular to the main stress at loads of polyethylene films [17, 19]. The polymeric material is elongated, and the crazes move into a new category - cracks, unable to withstand the loads, the space of which is completely hollow if the applied load is sufficient large (Fig. 6).

In modified polyethylene specimens, which underwent aging without additional mechanical stress, the transition from craze to cracks in the matrix was always accompanied by certain, depending on the type of additives, fractures of the surface, which were clearly recorded in the micrographs. We watched the formation of magistral cracks in materials with crystalline-forming

additives and observed the mass exit of the plasticizer to the surface in plasticized samples.

In the strength studies of such samples, this effect was manifested in the shift of the stress curves along the abscissa ($\frac{\Delta \ell}{\ell}$) – in the inhibited samples in the direction of decrease, in plasticized – growth (Table 1, Fig. 7). A small amount of modifier (up to 6 wt. %) slightly changes the value of fracture stress σ_b , however, the value breaking strain ϵ_b is extremely sensitive to the type of modifier and its influence on the matrix. Such displacement is not always recorded, because the polyethylene matrix is extremely sensitive to another influence as the conditions during obtaining and the first structural changes are noted precisely as the technological process changes.

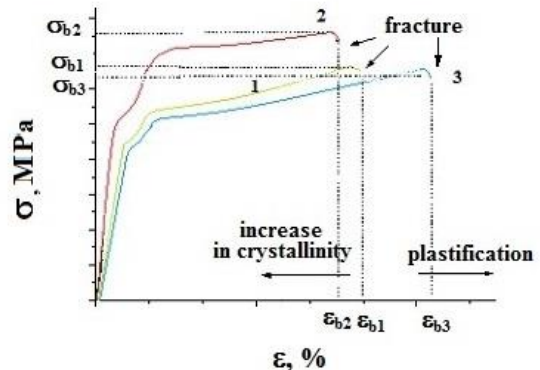


Fig. 7. Scheme of displacement of the breaking strain ϵ_b in stress-strain graph $\sigma = f(\epsilon)$ of polyethylene films at various types of modifiers: 1 – without modifier, 2 – with crystallizing component, 3 – with plasticizer.

In fact, these results are consistent with those obtained by Smith Th. L., when the similarity and the possibility of shifting the value of fracture stress σ_b in polymer materials by time-temperature dependence was indicated, which allowed them to coincide by introducing a certain shifting temperature-dependent factor α_T [20]. However, in the case of these studies, a more useful factor of minor technological regulation of some strength characteristics by injection additional ingredients into the polymer matrix was found.

Separately, there is the question of outdoor weathering factors influence on the mechanical characteristics of polyethylene films. The similarity of

changes in the mechanical characteristics of modified polyethylene films under the influence of weathering factors has been established, despite the different meteorological conditions were in the autumn and spring-summer periods of investigation. The results from the growth of σ_b for unmodified films in the spring-summer period (line 1, Fig. 4, a), in the modified samples with aluminum additives (line 5) and the samples with the NDA inhibitor in the autumn are distinguished.

This may be due to the increase in crystallinity of the samples with a general slight defect in the polymer matrix. However, such a passage of the process could not be last long, due to the destruction that weathering factors influence bears – leaching of the composite components by precipitations, changes in structure under the action sun ultraviolet (UV) and longer-wavelength radiation, accelerated temporal destabilization of the structure (Fig. 8) [21]. The surface structure of films that have been exposed to weathering factors during the year is more relief, with breaking polymer chains, and with significant damage of surface integrity.

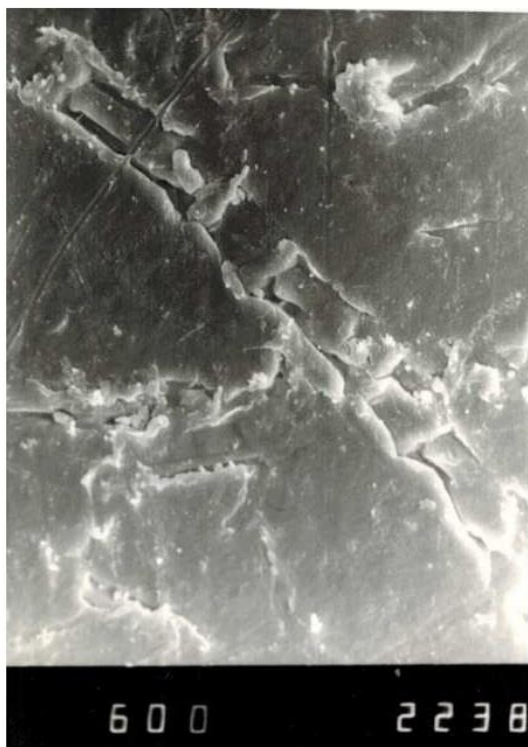


Fig. 8. Accelerated destabilization of the polyethylene film structure with the addition of a DCHAB inhibitor (1 wt. %) during operation for 12 months on an open platform (X 600).

In open storage or operation of polyethylene films, this defect is detected early than 5 months, depending on the activity of the structure-forming components, the main of which are some inhibitor of atmospheric corrosion. The passage of such processes leads to a decrease in the mechanical characteristics of the films.

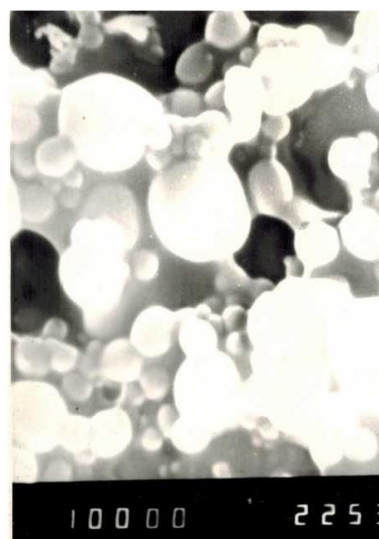
Of course, the degradation processes in polyethylene films with inhibitor of atmospheric corrosion, which will actively have marked themselves during the growth of external influences, can be offset by the injection of other additional components in the polymer matrix. In

particular, this applies to plasticizers that tend to amorphized of the polymer matrix.

This is manifested in the initial decrease in tensile strength at break σ_b (Table 1), a decrease in the strength characteristics during first 10 days influence of high temperature (Fig. 1), humidity (Fig. 2), their combined exposure (Fig. 3), or weathering tests (Fig. 4). The exceptions were samples with aluminum additives, where plasticization did not produce similar results. In addition, plasticization helps to stabilize the structure and to safeguard the stability of mechanical performance when long-lasting external forces are exerted on the specimens. Such stabilization was expressed in a slower time dependence of σ_b under the influence of various external factors, and in a certain variation of the measurement results.



a



B

Fig. 9. The plasticizer secretion on the surface of film LDPE + 1 wt. % DCHAP + 1 wt. % DOP: a) after 2 days of high temperature ($T = 338$ K) exposure (X 4000); b) after 10 years aging (X 10000).

Negative exhibition of plasticization was the plasticizer secretion on the sample surface, noted at the initial stages of temperature studies, as well as during long-term closed storage (Fig. 9) [22, 23].

decisive in determining strength. Minor enhancements to the tensile strength are observed in some composites over a limited period of investigation and may be leveled when long-term usages of such materials are in inclement weathering condition.

Conclusions

Injection additives and technological process components during manufacture of matrix material reduce the strength of the polyethylene thin film. This is due to certain structural transformations that occur in the matrix material when high-activity components are injected.

The long-lasting influence of external factors is

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Зміна механічних властивостей поліетиленових плівкових матеріалів при їх модифікації технологічними додатками та під час старіння

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Проведено механічні випробування та дослідження структури модифікованих поліетиленових плівкових матеріалів, що використовуються як елементи пакування електронних пристроїв. Модифікування передбачало введення наповнювачів різного виду та технологічних добавок, які б полегшували переробку сировини та забезпечували тривалий термін експлуатації. Встановлено особливості змін механічних характеристик залежно від кількості та типу додатків, а також перебіг процесів під дією зовнішніх факторів. Показано взаємозв'язок змін структури та механічних характеристик полімерних матеріалів.

Ключові слова: полімери, поліетиленові плівки, механічні характеристики, інгібітори, пластифікатори, структура, старіння.