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Conductive Characteristics of Thin-Film Composite Materials with Mineral Fillers

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The investigation of conductive characteristics and surface structure of polyethylene films modified by fillers was carried out. The dependence of changes in surface and volume resistivity on the quantity of non-metallic filler and time-based changes in structure and electrophysical characteristics for three years has been established.

Key words: polymers, polyethylene films, resistivity, structure.

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Introduction

The usage of polymer film materials for the needs of electronic equipment is mainly due to its minimization (creation of transistors, radiating devices, etc.) and the use as an auxiliary material (barrier laying's, flexible substrates and screens). Characteristics and properties of such materials should correspond to certain parameters of electronic products and provide the long lifecycle of devices. The main of the polymers materials used in the creation of various types of barrier and insulation

materials is polyethylene. The polyethylene composition is modified in dependence of needs and terms of usage.

The purpose of this research was to study the changes in the electrical conductivity of polyethylene films, modified by filled with inorganic non-conductive additives.

I. Experimental part

The object of research was the low density polyethylene (70-80 wt. %). The granulate LDPE 15803-

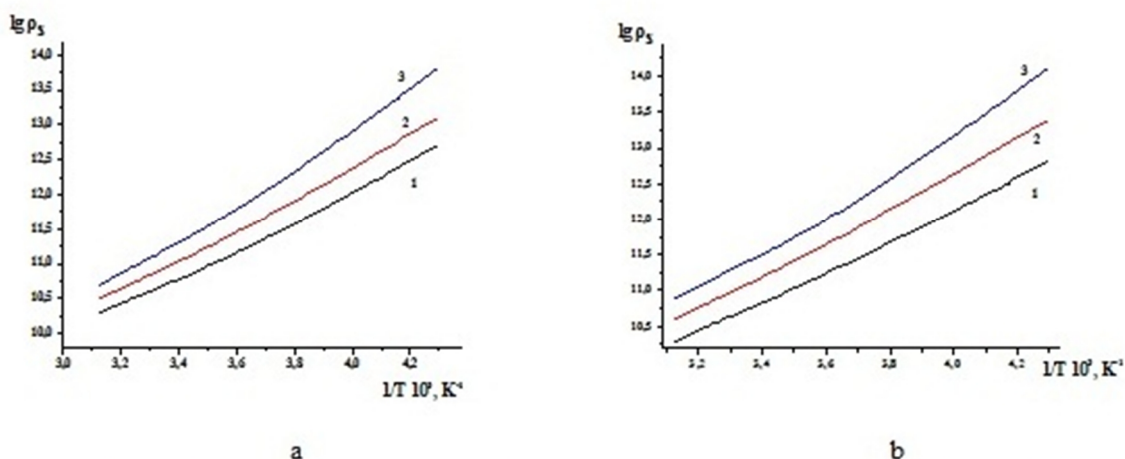


Fig. 1. The resistivity of polyethylene films: a – original samples; b – aging for 3 years; 1 – LDPE; 2 – LDPE+16.6 wt.% of mineral filler; 3 – LDPE+28wt% of mineral filler.

020 was used for the manufacture of film products. The mineral filler "Credolene" with a content of up to 28 wt. % was used as a supplement. Few additives up to 4 wt. % were blended into the polymer for various technological reasons (slip agents based on oleamide, antioxidants, light stabilizers, etc.).

The samples of films were manufactured on an industrial sleeve-film aggregate type LRP. The thickness of the polymer films was measured using the device MIR-12. The surface and volume electrical resistivity of polymeric and composite films were carried out using a teraohmmeter E6-13A. Surface resistivity was determined on samples by measuring in two directions. Measurement was carried out according to the four-contact circuit to avoid the influence of contact resistance on the results [1, 2]. Samples for conductivity measurements were obtained by extrusion of polymer mass with fillers and subsequent manufacture of a sample for mechanical fixation on a measuring cell.

Volume resistivity was determined by clamping the samples between two copper electrodes in diameter 25 and 40 mm, which were installed along the axis, according to the recommendations of the standards GOST 6433.2 and ASTM D 257.

Structure studies were done on a scanning electron microscope EVO 40XVP. The samples were exposed to ion digestion on the VUP-4 device, after aluminum was condensed on sample to ensure surface discharge and to increase the contrast of the microphotographs.

II. Results and discussion

It was established that the surface resistivity of polyethylene films without filler had value near $\rho_s \approx 2 \cdot 10^{10} \Omega \cdot m$. Additives of mineral filler (up to 16.6 wt. %) lead to slightly increasing ρ_s up to $2.5 \cdot 10^{10} \Omega \cdot m$. However, the next enrichment of the polymeric matrix by filler results to a more significant increase in the value of the surface electrical resistance (Fig. 1, a). Thermocycling of samples to low temperatures showed a fairly significant increase in the surface resistivity.

The surface resistivity of polyethylene films without filler has practically not changed during aging for 3 years in warehouse conditions. But the addition of mineral filler significantly increases ρ_s of aging samples (fig. 1, b).

The volume resistivity of polyethylene films that do not contain filler has a value more than two orders larger in comparison with the surface resistivity - $\rho_v = 4 \cdot 10^{13} \Omega \cdot m$. However, in general, the nature of the dependence of the volume resistivity on the amount of the filler is similar, as in the measurements of the surface resistivity (Fig. 2).

An increase in the content of mineral filler in the polyethylene film leads to unequivocal increase in the values of both resistivity. However, changes in the value of volume resistivity are more noticeable. An increase in the amount of mineral filler necessarily leads to a corresponding increase in the resistivity. This assertion is in contrast to the similar dependencies with mixing into

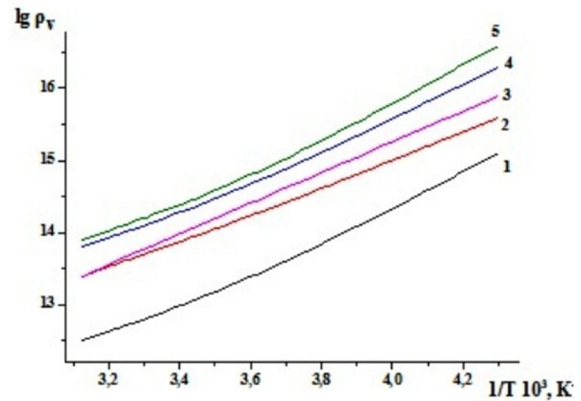


Fig. 2. Temperature dependence of volume resistivity of polyethylene films: 1- LDPE; 2 - LDPE+16.6 wt.% of mineral filler; 3 - LDPE+16.6 wt.% of mineral filler (aging 3 years); 4 - LDPE+28 wt% of mineral filler; 5 - LDPE+28 wt% of mineral filler (aging 3 years).

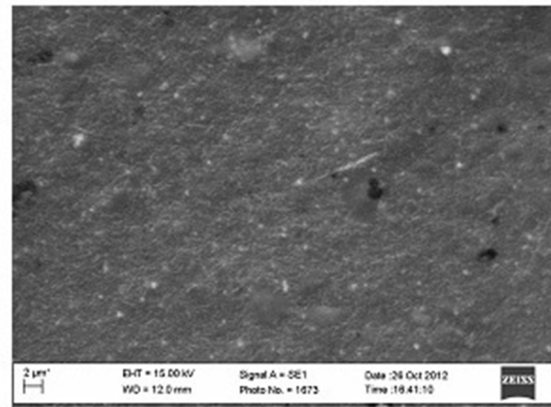


Fig. 3. Structure of the surface of the initial polyethylene sample. X 2000.

composition inhibitors and plasticizers, where such uniqueness is not observed [3]. Such changes may be related to deviations in the mobility of carriers, which was as discovery of two different actions of modifiers [4, 5].

Mineral filler additives lead to changes in the structure of the polymer matrix, causing an increase in crystallinity. Crystallization of the polymer leads to a decreasing in the mobility of segments of macromolecules and the diffusion coefficient. Therefore, conductivity also decreases during crystallization, which is typically for ionic conductivity. It is known, that increasing of crystallinity of polyethylene terephthalate by 20 - 40 % leads to a growth of resistivity by 2-4 orders.

So, two differently directed processes are indicated on passing of processes of transfer of carriers in films with additives of inhibitors and plasticizers. A certain number of modifiers leads to an increase in carrier transfer channels (in terms of percolation theory), cluster

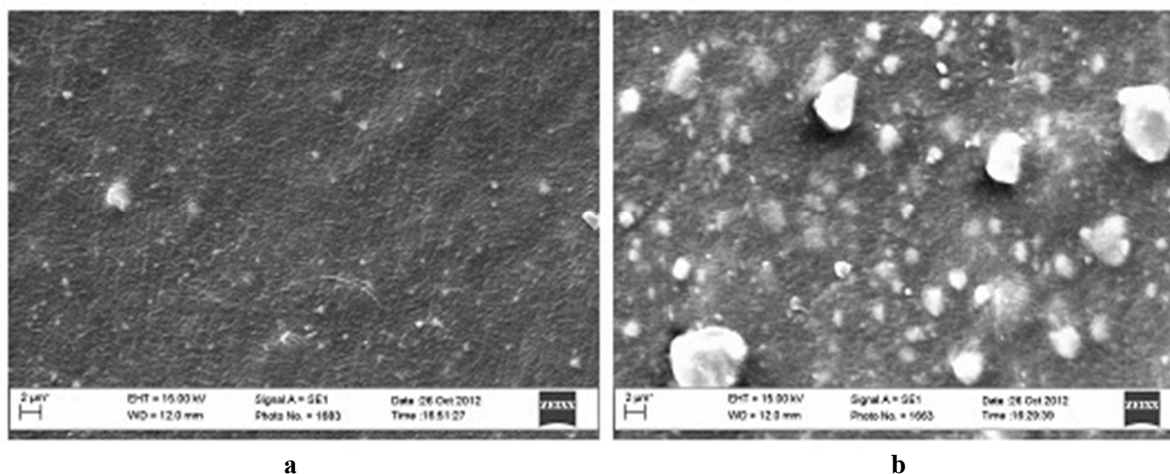


Fig. 4. Morphology of the surface of polyethylene films with additives of the mineral filler: a - 16.6 wt.%; b - 28 wt%. X 2000.

density growth, decreases in percolation thresholds and changes in transfer indexes, on the one hand [6]. Also the changes in the characteristics of the polymer matrix modified which must be taken into account, on the other hand. That's why; the initial electrical resistance of the inhibited film is much less compared with unmodified samples [3].

Low molecular weight materials blended into the polymer reduce intra-molecular interaction, which leads to an increase in the mobility of macromolecules and low molecular weight ions. Therefore, electrical conductivity of plastificated polymers sharply increases, also.

The electrical conductivity of polyethylene films with mineral filler during aging is determined by the peculiarities of the change in their physical and chemical properties and caused by the corresponding structural transformations that are associated with the mixed modifier. Basically, changes in the carrier transfer occur due to an increase in the crystallinity of the matrix (both due to an increase in the amount of crystalline filler, and due to the growth of the crystallinity of the own matrix, and, accordingly, the decrease of the channel passage), and due to increasing in of matrix defect, which corresponds to a changes in the density of clusters, and lead to decreasing in the efficiency of the carrier's passage.

It is interesting to note that minor inhibitor additions caused increasing of the electrical resistance polymer film during aging. This associated with the destructive processes that arise in the matrix under the influence of the modifier. In the early stages of aging, this is determined by the processes occurring in the matrix of polyethylene – by cross-linking of chains, formation of a rigid spatial grid, and only later – by crystallization processes and destructive process in the matrix [7]. Instead, the electrical characteristics in the plasticized samples are stabilized, due to insignificant structural changes in the polymer.

Electron microscopic studies of the surface of the samples revealed slight defects in the surface of the initial samples, which is associated with the technology of their production (Fig. 3). Initial centers of

crystallization are formed on the surface. The overall crystallinity of the original sample is negligible.

Adding inorganic filler increases the overall crystallinity of the material (Fig. 4). The structure of the surface of the modified polymer film is defect-free, with the uniform placement of the mineral filler by the volume of the matrix, but the crystallinity of this material has increased. Of course, there is no major difference between the conductivity of film materials with and without fillers [8]. However, short-lived aging, over 3 years, revealed a significant increase in the values ρ_s and ρ_v , which may indicate as initial stages of structural changes caused by the incompatibility of the components.

It should be noted that the materials used in the research were not completely clean, since they were accompanied by technological additives based on low molecular weight materials (blind, antioxidants, plasticizers, etc.). Of course, the blending of such ingredients into a polymer matrix reduces intra-molecular interaction and leads to an increase in the mobility of macromolecules and low molecular weight ions. Accordingly, the electrical resistance of such samples is significantly reduced. For example, the specific volumetric electric resistivity of the purified polyethylene should be $\rho_v = 10^{16} - 10^{20} \Omega \text{ m}$ [9-10].

Conclusion

Including of mineral filler in the composition of the polyethylene film does not lead to particularly significant changes in the indicators of surface and volume specific electrical resistance. More noticeable changes in these quantities occur when the aged films, when the filler initiates an increase in the crystallinity of the polymer matrix, lowering the overall electrical conductivity of the sample.

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Провідні характеристики тонкоплівкових композиційних матеріалів з мінеральними наповнювачами

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Проведено дослідження провідних характеристик і структури поверхні поліетиленових плівок, модифікованих наповнювачами. Встановлено залежність зміни поверхневого і об'ємного питомого опору від кількості неметалевих наповнювачів і часових змін структури і електрофізичних характеристик за три роки.

Ключові слова: полімери, поліетиленові плівки, питомий опір, структура.