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Conductivity in Modified Polyethylene Films

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We have studied the influence of modifiers (inhibitors of corrosion and plasticizers) on the electrical conductivity of polyethylene films. A model of electrical conductivity provided the formation of several tunnel junctions characterized by own percolation parameters is proposed. The redistribution of carriers over channels will always take place in modified polymer materials because of the different concentration and temperature dependences of transport parameters of separate percolated pathways.

Keywords: conductivity; modifiers; percolation; polyethylene

INTRODUCTION

The development of modern techniques which are based on qualitatively new principles requires to search for nonconventional materials which not only will fit the needs of modern engineering, but also are accessible by the cost price. One of such materials is multifunctional polymeric films containing a considerable amount of components which present and ensure different consumer properties and characteristics, including electroconductivity [1–3]. The transport properties and characteristics of polymeric films are determined by their structure, levels of the crystallization and the orientation of supramolecular formations, and the sort and amount of components used in the modified polymer films.

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The aim of the present research is to study the influence of modifying components on the electrical conductivity of polymer films, which are intended for the protection of metal surfaces of details.

EXPERIMENTAL

As a polymeric matrix, high-pressure polyethylene PEHP (GOST 16337-70, brand 15803-020) was used. The components taken for a modification of the material were amine inhibitors of corrosion such as dicyclohexylamine benzoate (DCHAB) $(C_6H_{11})_2NH_2^+ \cdot (C_6H_5CO_2^-)$ and cyclohexylamine benzoate (CHAB) $(C_6H_{11})NH_3^+ \cdot (C_6H_5CO_2^-)$ and plasticizers dioctyl phthalate (DOP) $C_6H_4(COOC_8H_{17})_2$, dioctyl sebate (DOS) $H_4C_2OOC(CH_2)_8COOC_2H_5$, and di-2-ethylhexyl phthalate (DEHP) $C_{24}H_{38}O_4$.

Samples of the films were fabricated on a laboratory extruder. The inhibitors brought into a polymer matrix during the stage of a bloating near the zone of an exit film hose near the shaping head. The additional supplementary of a plasticizer into a polymer composition reduced the processing temperature and simplified the overlapping of inhibitors with a polymer substance.

The measurement of the surface and volume electrical resistances of polymer and composite films was performed with the use of a teraohmmeter E6-13A. The surface conductivity was measured in two directions for the samples obtained from a melt. The measurements were carried out by a four-contact scheme to avoid the influence of a contact resistance on the results [4,5]. Samples for measurements were obtained by extrusion on a polymer matrix by the size (20×5) mm² suitable for the mechanical fixing in a measuring cell.

The volume electrical conductivity was determined according to the procedure of the international standard ISO 1325, by clamping the samples between two copper electrodes with diameters of 25 and 40 mm which were installed on one axis.

RESULTS

It is established that the addition of amines inhibitors during the extrusion to a polymer matrix by all means predetermines a decrease of the initial value of the surface resistance. Even their inappreciable addition in amounts up to 0.5 wt. % gives noticeable aberrations in the resistance value, which is well determined on the use of inhibitor CHAB (Fig. 1). The addition of plasticizers, irrespective of their sort and amounts, operating on a polymeric matrix similarly to inhibitors from the transport viewpoint, decreases the initial surface resistance.

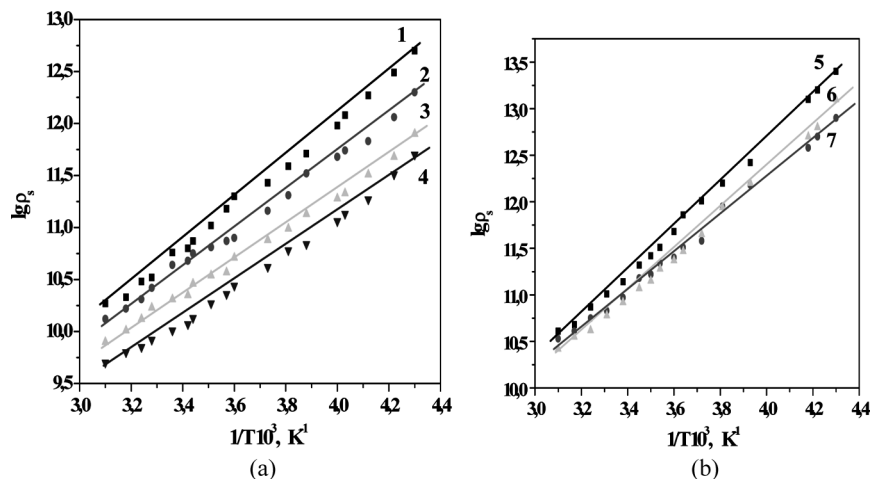


FIGURE 1 Temperature dependence of the surface resistance of polyethylene films containing the inhibitors and plasticizers, in wt. %: 1 – 0; 2 – 1% DCHAB; 3 – 10% DCHAB; 4 – 3% CHAB; 5 – 0.5% DEHP; 6 – 3% DOS; 7 – 1% DCHAB + 1% DOP.

We analyzed the temperature dependence of the specific resistance of modified films in the interval $T = 250\text{--}300\text{ K}$ by using the relation

$$\rho = \rho_o \exp\left(\frac{E_a}{2kT}\right) \quad (1)$$

where ρ_o is the preexponential factor, and E_a is the activation energy of charge transport [6]. In view of the linear character of the dependence $\lg \rho = f(1/T)$ (Fig. 1, a,b), the calculated values of the activation energy of conductance E_a lie in the interval 0.22–0.35 eV. The conductance of modified films has ionic character mainly. In this case, the current carriers are the modifying ionization admixtures, as it is possible to conclude from the calculated effective activation energy.

The surface conductivity of the inhibited films considerably increases during the storage (age-hardening) under natural conditions (atmospheric pressure and damp air) due to the migration of carriers to the film–gas (air) interface. That's why, during the age hardening from 3 to 5 years, the greatest changes of the resistance of the polymeric matrices with the equal amounts of modifying components are detected for inhibitor CHAB. Samples with the components of a plasticizer saved the initial transport parameters during this period (Fig. 2).

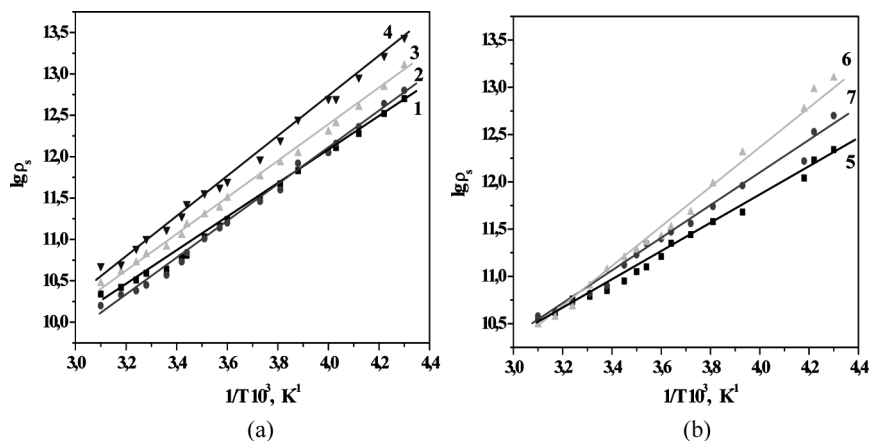


FIGURE 2 Temperature dependence of the surface resistance of polyethylene films containing the inhibitors and plasticizers (in wt.%) after the age-hardening under warehouse conditions during 3 years: 1 – 0; 2 – 1% DCHAB; 3 – 10% DCHAB; 4 – 3% CHAB; 5 – 0.5% DEHP; 6 – 3% DOS; 7 – 1% DCHAB + 1% DOP.

The volume resistance $\rho_v = 4 \cdot 10^{13}$ Ohm·m of polyethylene films, which do not contain modifying components, is by two orders higher as compared with the surface resistance. Nevertheless, the character of the dependence of the volume resistance on the nature and the amount of modifying components is similar, in common, as that from measurements of the surface resistance.

Another and, possibly, major factor defining the transport properties of polymer films alongside with charge carriers is the structure of the polymer matrix, in particular, the presence of voids, density of crosslinks, and mobility of polymer chains. All factors resulting in a lowering of the mobility of macromolecules promote a diminution of the ionic conductivity. By the spectral and electron-microscopic investigations, we have established the increase of the amount of fine-crystalline formations in the initial samples of modified films at the use of amines inhibitors, which is caused, probably, by increasing the amount of short ethyl branches in the polymer matrix and the matrix crystallinity [7–10]. Accordingly, the electrical conductivity of films with the components of inhibitors will be higher as compared with samples without the components, which is caused by the increase of the matrix crystallinity and the corresponding increase of the density of clusters on percolation channels. A high imperfection of inhibited films and their oxidation susceptibility during the

age-hardening induce the processes of destruction which become much more intense as compared with those in nonmodified films. Thus, the electrical conductivity of inhibited films during the age-hardening will be reduced. Changes in the resistance of the plasticized films during the 5-yr age-hardening were inappreciable, which is related to a low imperfection and a high time stability of their structure.

The electrical conductivity of modified polyethylene films at the age-hardening is determined by features of a change of their physico-chemical properties. The increase of the resistance of films with inappreciable admixtures of an inhibitor is observed at the age-hardening, which corresponds to the processes of destruction (the crosslinking of polymer chains and the formation of a rigid network) which occur in the polyethylene substrate. The electrical characteristics of the plasticized samples are stabilized, owing to inappreciable structural changes in the polymer compound.

The necessity of theoretical justification mechanisms of the transport process arises, when we consider the time of changes of the transport characteristics in polymer structures and the various influences of catalysts and passivants on transport processes, which involves the modifying components. The transport phenomena in modified polymer systems demand the development of model approaches, since modified polymeric matrices have different characteristics of the distribution of local capture centers of carriers and different conductances. It is possible to detect many types of conductance related to changes of the structure and the imperfection of a substrate, which are initiated by a change of physical properties of the modified polymeric materials, as compared with pure "classical" polymeric materials, the electrical phenomena in which are simplified and described by one dependence.

In order to explain the features of random walks of electrons and holes in disorder materials, we will use the percolation model [11]. The theory of percolation carrier transport is based on the conjecture of the existence of infinite very large tunneling clusters which penetrate the whole space of a polymeric matrix. It is considered that the clusters have an identical density and are spatially on particular distances from one another [12]. The existence of such conduction element as an infinite cluster with the identical density is supposed by viewing the homogeneous surrounding (for example, the polymerization of a melt with complete removal of a solvent). The viewing of inhomogeneous modified polymeric materials (for example, those generated on a ground of a polymeric compound with modifying components) does not allow approving about the homogeneity of the density of clusters. It is possible to assume that one-type imperfections

in the matrix create homogeneous clusters of the same type with relevant tunnel junctions. As a matter of fact, this means that the carrier transport occurs on different channels, and they correspond to the own densities of clusters, percolation thresholds, and transport indices [12]. The percolation process of carriers is described by the identical formulas with different critical indices. Therefore, the common formula which describes the transport phenomena in disorder inhomogeneous systems should take into account the carrier transport on different channels with different densities of clusters (similarly to Matthiessen's rule at the calculation of a resistance of crystalline systems).

The electrical conductivity of a homogeneous material can be described through the effective radius of capture r :

$$\sigma \sim r^t. \quad (2)$$

The value of r is selected from the tests of the sufficiency for the percolation channel to be formed, and the transport threshold will be determined by the percolation radius $r=r_c$. For the conductivity of polymer compounds, r can be approximately defined from the thermodynamic criterion for the formation of a matrix due to the Gibbs thermodynamic potential. So, in [13], the value of r calculated through Gibbs energy (by equating the effective radius of capture to the size of crystalline grains) is determined to be in the range $8 \cdot 10^{-9}$ – 10^{-7} m. The value of r determined from the structural and spectral studies executed earlier is 1.1 – $4.5 \cdot 10^{-10}$ m. It will be used in calculations concerning polyethylene.

It is worth to note that the total electrical conductance through tunnel junctions with different percolation radii in case of modified inhomogeneous polymer systems is given by the relation

$$\sigma \sim r_1^{t_1} + r_2^{t_2} + \dots + r_n^{t_n}. \quad (3)$$

The calculated electrical conductivity of a pure polymeric material according to formula (2) well agrees with the observed and reference data [4–6]. In view of the results of structural studies and the data in [13,14], the nominal value of the index t is determined as 2.3 (in common, t varies in the range from 0.973 up to 6). So, for a polyethylene film without components and fillers at $r = 0.8 \cdot 10^{-10}$ – $4.5 \cdot 10^{-10}$ m and $t = 2.2$ – 2.5 , the conductivity $\sigma \approx 10^{-21}$ Ohm $^{-1}$ m $^{-1}$ (Fig. 3).

The calculation of the electrical conductivity of modified films yields a good agreement with the data of practical measurements with regard for the sort and amount of the components (fillers) and the

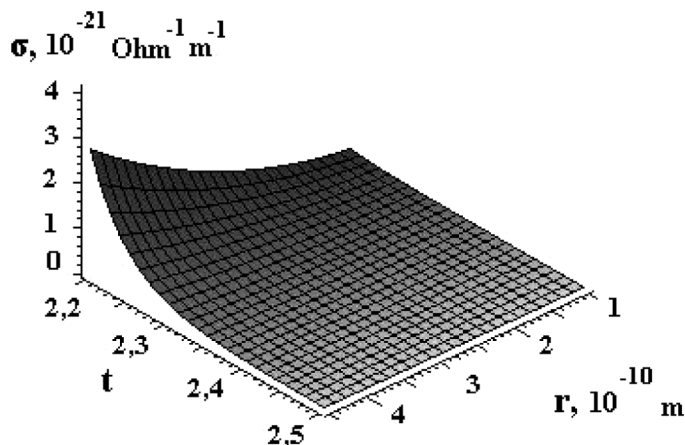


FIGURE 3 Calculated conductivity σ of a polyethylene film for different values of transport parameters.

efficiency of the carrier transport through percolated pathways. Thus, as shown by the calculations, the electrical conductivity of modified materials can vary not only due to the introduction of components, but also at the expense of a change of the characteristics of the polymeric matrix during the modification, which should be accounted as the increasing percolation radius (Fig. 4).

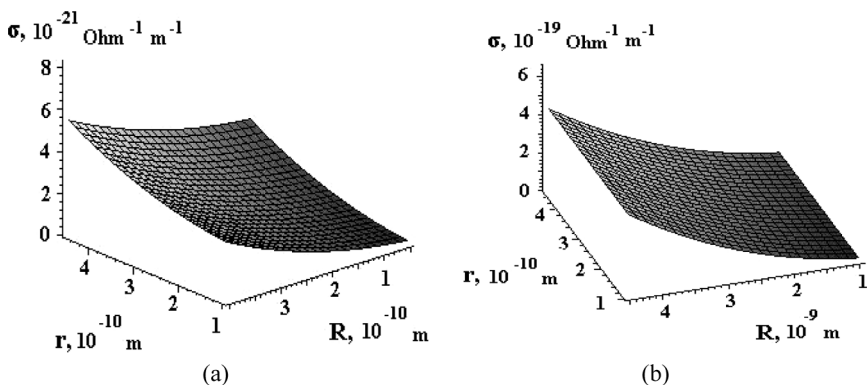


FIGURE 4 Dependences of the conductivity σ of the model problem on the effective percolation radii of carriers in a polymer matrix which contains tunnel junctions of two types ($t = 2.2$): a) $r = 1 - 4.5 \cdot 10^{-10}$ m; $R = 1 - 4.5 \cdot 10^{-10}$ m. b) $r = 1 - 4.5 \cdot 10^{-10}$ m; $R = 1 - 4.5 \cdot 10^{-9}$ m.

CONCLUSION

Thus, the volume and surface resistances of modified polymer films are changed in the presence of such modifiers as inhibitors of corrosion or plasticizers. We have proposed a model of electrical conductivity involving the formation of several tunnel junctions characterized by own percolation parameters. The redistribution of carriers over channels will always take place in modified polymer materials because of different concentration and temperature dependences of the transport parameters of separate percolated pathways.

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