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Obtaining a graft copolymer of polyethylene by electrodischarge synthesis

Abstract. *The article analyzes the mechanism of the impact of an electric discharge on the process of copolymerization of linear low-density polyethylene. Under the influence of electric discharges, a change in the electrophysical properties of materials occurs, thereby changing the property of materials in a given direction. The resulting material, due to the absence of a grafted monomeric homopolymer, has improved mechanical characteristics. The paper presents the results of dilatometric, and rheological studies of the graft copolymer obtained by the method of electric discharge synthesis, and it is shown that the resulting material has sufficiently high physicochemical characteristics. It can be argued that the development of the method of electrodischarge copolymer synthesis is an important step in solving the problem of achieving the efficiency, economy, and environmental friendliness of technological processes.*

Streszczenie. *W artykule przeanalizowano mechanizm wpływu wyładowania elektrycznego na proces kopolimeryzacji liniowego polietylenu małej gęstości. Pod wpływem wyładowań elektrycznych następuje zmiana właściwości elektrofizycznych materiałów, a tym samym zmiana właściwości materiałów w zadanym kierunku. Otrzymany materiał, ze względu na brak szczepionego homopolimeru monomerycznego, ma ulepszone właściwości mechaniczne. W pracy przedstawiono wyniki badań dylatometrycznych i reologicznych kopolimeru szczepionego otrzymanego metodą syntezy wyładowań elektrycznych i wykazano, że otrzymany materiał ma wystarczająco wysokie właściwości fizykochemiczne. Można stwierdzić, że opracowanie metody elektroerozyjnej syntezy kopolimerów jest ważnym krokiem w rozwiązaniu problemu osiągnięcia efektywności, ekonomiczności i ekologiczności procesów technologicznych. (**Otrzymywanie szczepionego kopolimeru polietylenu metodą syntezy elektroerozyjnej**)*

Keywords: high-voltage electrical discharges, uniform and non-uniform electric fields, modification of polyethylene, electrophysical properties of the polymer.
Słowa kluczowe: wyładowania elektryczne wysokiego napięcia, jednorodne i niejednorodne pola elektryczne, modyfikacja polietylenu, właściwości elektrofizyczne polimeru.

Introduction

The search for new, effective technological methods in all branches of production is a cardinal task of technical progress. One of the most important areas of these searches is the technological use of the energy of electric and magnetic fields [1,2].

The force action on electric charges, causing this or that form of movement, is the main manifestation of the electric field. In this way, it is possible to give whole streams of electrified material various kinds of ordered and purposeful movement. This allows for a wide range of targeted impacts on technological operations in various industries [3,4].

The interest of many researchers in studying the process of graft copolymerization is caused by the search for improving the electrophysical, mechanical, and chemical properties of polymers. The complex dependences of the properties of grafted polymers on grafting conditions and other factors gave rise to the search for new effective methods for obtaining such materials [5-7]. During electrical discharges carried out in gases, a large number of energetic particles arise, including excited atoms and molecules, ions, and fast electrons, which also affect the course of various chemical reactions [8,9]. For dielectric materials, it is best to use activation by low-temperature nonequilibrium electric discharges (corona, glow, and barrier), which share the property of requiring little energy to heat the material. The greater the degree of non-equilibrium, that is, the difference $Te - Ti$, the less energy is spent on heating the gas; that is, all of the energy received by "hot" electrons from the electric field is spent on the processes of ionization, excitation, and dissociation of gas molecules or atoms in the material's surface layer. It should be noted that nonequilibrium discharges develop in fields of high intensity.

Currently, the scientific and technical direction associated with the production of especially pure substances is actively developing. The presence of impurities of different chemical composition in the main raw materials leads to the complexity and rise in the cost of technological processes and worsens the physicochemical and mechanical properties of the resulting end products [10,11]. Appropriate technologies that pollute the environment, often do not meet modern environmental requirements. It should be noted that a successful technological solution to the problem of obtaining highly pure materials makes it possible, in some specific cases, to purchase additional raw materials in the form of isolated impurities. This turns a specific technology into waste-free production, and thus, at the same time, environmental cleanliness of production is ensured, and high economic indicators are achieved.

The impact of an electric discharge on chemicals depends on the nature of the discharge, which is primarily determined by the potential difference, the pressure in the discharge zone, and the current density. However, the use of a gas discharge is due not only to economic considerations; in some cases, it is the only possible way to carry out the reaction. An example is high-temperature chemistry, in which the activation of chemical reactions occurs when substances come into contact with the plasma of a high-voltage electric arc, the temperature of which reaches several thousand degrees.

The need to save energy and reagents makes technologists pay more and more attention to the processes occurring in electric fields and low-temperature discharge, in which the temperature of atoms and molecules is close to the ambient temperature while electrons have energy sufficient to excite, dissociate, and ionize atoms and molecules. As a result, the yield of reaction products in a low-temperature gas-discharge plasma is much higher than the thermodynamic equilibrium calculated only on the basis of the gas temperature. Therefore, in discharges, it is possible to carry out many processes much more efficiently (with less energy and reagents) compared to traditional thermal, gaseous, and liquid chemical media, such as

plasma-chemical deposition of polymeric and inorganic films, etc. [12].

Problem setting

Thus, the analysis of the literature on the electric discharge effect on chemical processes indicates the effectiveness of the effect of electric discharges on the processes of polymer modification and the possibility of controlling these processes. However, at present, a limited number of theoretical and experimental results have been obtained that characterize certain aspects of the grafting of various monomers to polyethylene under external influences, and there are practically no data on the impact of strong electric fields and discharges [13].

Each chemical reaction requires a certain amount of energy from the reacting particles, the so-called activation energy of this reaction. In addition, chemical reactions require the activation of reactants to begin. Studies show that the parameters and conditions of electrical influences have a certain effect on the course of the reaction. In chemical reactions in a discharge, the role of molecules in which high vibrational levels are excited is especially important. The absence of thermodynamic equilibrium in the discharge causes a significant excess of the average energy of some electrons over the average energy of other electrons. These electrons transfer their kinetic energy to molecules, initiating the detachment of atoms [14].

Despite the fact that polyethylene is a nonpolar dielectric, under the influence of an electric field, the electronic and ionic polarizations of its molecules occur, which also increases their reactivity and, accordingly, the rate of initiation of graft copolymerization by the radical mechanism [15].

The purpose of this work is to study some features of the efficiency of nonequilibrium electric discharges in relation to the processes of polymer modification in order to improve the electrical and mechanical properties.

Solutions to the problem

The development of methods for the synthesis of graft copolymers significantly expands the possibilities of obtaining polymeric materials with various properties. Unfortunately, most of the chemical methods for the synthesis of graft copolymers currently used allow you to get a mixture of graft copolymers and homopolymers, which degrades the quality of the final product. The separation of such a mixture is rather difficult and, as a rule, is associated with the consumption of a large amount of organic solvents. In addition, the separation of the homopolymer requires additional costs.

It is natural to expect that an electric discharge, leading to the formation of a significant number of excited particles in a gas, can have a great influence on the course of chemical reactions that require a certain amount of energy for the reacting particles, that is, the activation energy of this reaction.

Experiments on electrical effects were carried out using a laboratory universal high-voltage setup, which made it possible to obtain regulated alternating voltage up to 100 kV and direct voltage up to 140 kV and control the discharge parameters. The installation was powered by alternating voltage at industrial frequency. Experiments on the electric-discharge modification of low-density polyethylene without the use of traditional reaction initiators were carried out on special installations, the main components of which were glass reactors [16].

To study the effect of barrier-type electric discharges on liquid-polymer systems in sharply inhomogeneous and weakly inhomogeneous fields, the reactors had the corresponding forms of interelectrode gaps, the geometry of which was selected after an appropriate calculation of the electric field.The experiments were carried out at room temperature, except for those cases when heating of any component was required [13]. When studying the electric discharge effects on the system, the voltage range was chosen and the discharge ignition voltages were determined in sharply inhomogeneous and weakly inhomogeneous fields.

The initial voltage of the electric discharge in each case was determined from the experimentally obtained current-voltage characteristic by changing the course of the $I(U)$ dependence towards a sharp increase in the current growth rate. In some cases, the initial voltages were determined directly using an electronic oscilloscope and recorded with a kilovoltmeter.

Figure 1 shows the current-voltage characteristic of the interelectrode gap with sharply inhomogeneous (1) and weakly inhomogeneous (2) fields in the presence of copolymers in the reactor. It can be seen from the current-voltage characteristic: $U_{sh.inh.} = 11\ kV$; $U_{w.inh} = 17\ kV$.

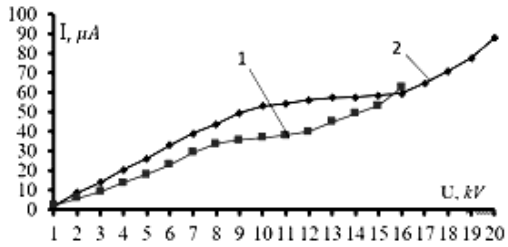

Fig. 1 Current-voltage characteristics of an electric discharge in sharply inhomogeneous (1) and weakly inhomogeneous (2) fields in a viscous liquid

As a starting material for the graft copolymerization reaction, linear low density polyethylene obtained by the traditional method of copolymerization of hexene-1 monomer and ethylene was used. The copolymerization reaction was carried out at a pressure of $4 \times 10^6\ Pa$ ($\sim 40 atm.$), a temperature of $413\ ^{\circ}K$, and a hexene-1 concentration of up to 3-5% mol.

To implement the process of grafting nitrile-acrylic acid to linear low-density polyethylene, electric discharge effects were carried out in two different modes:

1) during the graft reaction process;

2) by pretreatment of the reagents before the grafting reaction.

The optimal grafting conditions were determined using the experimental design method. The liquid hexene-1 monomer was subjected to electrical discharges and adsorption purification from oxygen-containing compounds before the copolymerization reaction [17].

Many important properties of polymers are determined by and related to their density. Particularly great information is provided by the temperature dependence of the density of polymers, that is, their dilatometric characteristics. According to dilatometric curves obtained in a fairly wide range, one can judge the expandability and compressibility of polymers at various pressures, compose the equations of state of the polymer, and judge the presence of phase transitions. In addition, the dilatometric characteristic of the polymer also solves a number of technological issues: refinement of processing modes, determination of the parameters of a number of special processing methods (orientation, calibration, heat setting, etc.), and, finally, finding the optimal temperature range for additional heat treatment of finished products [4]. Dilatometry was carried out in the mode of slow stepwise heating and subsequent stepwise cooling in the range 293-573K. The change in the volume of

the sample with a change in temperature was recorded by a dial indicator with a division value of 10-3 mm.

Figure 2 shows the dilatometric crystallization curves of linear low-density polyethylene (curve-1) and the graft copolymer of linear low-density polyethylene with acrylonitrile (curve 2). Figure 2 shows that nitrile-acrylic acid grafting changes the nature of the dilatometric linear low-density polyethylene crystallization curve. The crystallization onset temperature of the graft copolymer rises to 399 K. The specific volume decreases over the entire temperature range studied.

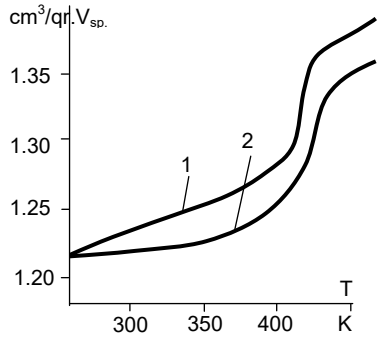

Fig. 2 Dilatometric crystallization curves: 1- linear low-density polyethylene; 2-graft copolymer

Figure 3 shows the dilatometric characteristic of the polymer in the form of V-T dependence, where T is the _absolute temperature K. With such processing of dilatometric data, it is possible to estimate and determine the values of the specific volume at 0K (V_{to}), that is, the occupied volume [16]. And, then, at any temperature, calculate the value of the so-called "free" specific volume as the difference $V_{sp.free} = V-V_{to}$.

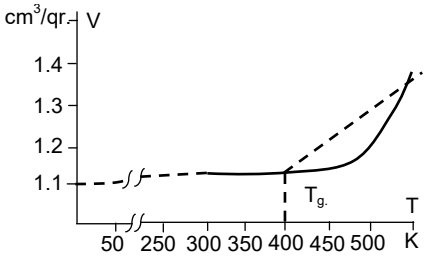

Fig.3 V(T) dependences for the graft copolymer upon crystallization

It is known that the exact determination of Tg (glass transition temperature) for crystalline polymers is associated with great difficulties. In the Tg region, only amorphous polymer chain segments are mobile. Usually, this mobility does not affect the character of the dilatometric curves in any way, and no break in the V-T dependence is noticed on them at Tg. Therefore, in this work, Tg is determined by extrapolating the V–T dependence from the temperature range in which the polymer is in the fluid state to the same dependence in the solid state [16].

A comparison of the main mechanical and electrical characteristics of the copolymer of linear low-density polyethylene obtained by the method of electric discharge characteristics grafting with similar characteristics of conventional industrial linear low-density polyethylene revealed the high quality of the obtained copolymer.

At Tg, the "free" volume is calculated. It turned out to be equal for linear low-density polyethylene at Tg = 341 K (V-Vto) = 0.050 cm3 / g, that is, the graft copolymer has a “free” volume by 0.029 cm3 / g (050-0.021 = 0.029) less than linear low-density polyethylene. The decrease in the "free" volume of linear low-density polyethylene as a result of grafting with nitrile-acrylic acid is associated with the introduction of acrylonitrile groups at the site of the tertiary carbon atom. An analysis of another universal quantity inherent in most of the studied polymers leads to the same conclusion. This is the so-called "free" volume fraction fg of polymers at the glass transition temperature Tg. As is known, this value is universal and equals ~0.025. For the graft copolymer linear low-density polyethylene, it turned out to be equal to 0.02, that is, when it crystallizes, it really loosens [5].

Considering the foregoing, as well as the fact that the resulting material, due to the absence of a homopolymer of the grafted monomer, has improved mechanical characteristics and increased resistance to aggressive environments, and that a traditional initiator was not used in its synthesis, it can be argued that the development of a method for the electrical discharge synthesis of a copolymer seems to be an important stage in solving the problem of achieving efficiency, economy, and environmental friendliness of technological processes.

In this work, a theoretical analysis of the influence of the degree of inhomogeneity of the electric field under electric discharge effects on the efficiency of the grafting process, as well as the conditions for the reaction of copolymer synthesis depending on the energy expended by the electric field and the discharge to activate the reaction, is carried out.

It has been established that a sharp difference in the distribution of the electric field strength in the gaps between the cylindrical electrodes of the reactors in which the copolymer synthesis was carried out under the influence of a barrier discharge, that is, under conditions of sharply inhomogeneous and weakly inhomogeneous fields, respectively, leads to the fact that in the first case, the excitation and activation of macromolecules have place only in a small part of the interelectrode gap near the inner electrode, and in the second, that is, in a weakly inhomogeneous field, in the entire gap between the electrodes. This, accordingly, causes a higher efficiency of the effects of a barrier discharge in a weakly inhomogeneous field on the synthesis process.

As is known, the reaction process, graft copolymerization, requires a certain amount of energy from the reacting particles, the so-called activation energy of this reaction. We have found that the parameters and conditions of electrical influences have a decisive influence on the course of the reaction.

Theoretically, the processes occurring in the reactor during the synthesis of the copolymer and the action of an electric field in the absence of any discharge and an electric discharge at a voltage significantly exceeding its ignition voltage are considered separately. It was found that both in a sharply inhomogeneous field in the "wire-cylinder" system and in a weakly inhomogeneous field in the "cylinder-cylinder" system, at voltages lower than the initial voltages (i.e., ignition voltages) of the discharge in the corresponding field configurations, the grafting process was practically not visible. Apparently, this is due to the insufficient amount of energy transferred by the electric field to the monomer.

The literature data [18], as well as the calculated values of the reduced electric field strength E/p (E is the electric field strength, p is the pressure), for both configurations, indicate that in both cases the energy received by electrons from the electric field is clearly not enough to break the C-H bond (bond energy of 3.4 eV) and, therefore, for the grafting process to proceed. In the polymer chain, the atoms are linked by covalent bonds. Under normal conditions, chain links are in thermal motion. In a chain with a fixed value of bond angles, the position of

each subsequent link turns out to be dependent on the position of the previous one. Indeed, the bond energy between $C–H$ is 3.4 eV (80 $kcal$), and the bond energy between $C–C$ is 3.6 eV (83 $kcal$) [16]. In addition, given that the carbon atom in the chain is bonded on both sides, it is obvious that it is much more resistant to bond breaking than the hydrogen atom.

In the case of exposure to electric discharges at voltages significantly higher than the initial ones, the reaction conditions change significantly since the energy of electrons in the discharge channel is much higher than the energy of electrons at pre-discharge voltages [19], i.e., voltages below the initial. In this case, the absence of thermodynamic equilibrium in nonequilibrium discharges causes a significant excess of the average energy of some electrons over the average energy of other electrons. These electrons transfer their kinetic energy to the molecules of linear low-density polyethylene, initiating the detachment of hydrogen atoms and the reaction proceeding by a radical mechanism.

According to [20], the average energy of electrons bombarding the mixture $W_{e.med}$ in electron volts can be approximately calculated by the formula:

$$W_{e.med} = 8.63 \cdot 10^{-4} \cdot T\,(21+33lg\,(0.5/d+44)),$$

where d is the length of the discharge gap, cm; T is the air temperature in the discharge channel, K.

Under our conditions, if the distance between the electrodes is $d=0.5\ cm$ and $T=300\ K$, then we get $W_{e.med} \approx 20$ eV. The calculated electron energy is quite sufficient to break the $C–H$ bond (the $C–H$ bond energy is 3.4 eV) and, therefore, the process can proceed.

Thus, our theoretical analysis showed that the course of the reaction of the electrical discharge synthesis of a copolymer primarily depends on the energy expended by the electric field and the discharge to activate the reaction.

Conclusions

As a result of the studies carried out, the effectiveness of applying the effects of non-equilibrium electric discharges to various chemical processes has been established. A technological regime of the chemical reaction of polymer grafting activated by an electric discharge has been developed and studied, which makes it possible to obtain a polymer product with improved properties without the use of chemical catalysts. The theoretical analysis revealed that the course of the reaction of the electrical discharges leading to the synthesis of the copolymer primarily depends on the energy expended by the electric field and the discharge to activate the reaction. It is shown that the activation energy necessary for the implementation of synthesis is provided under the influence of an electric discharge. Chemical processes occurring under the influence of a nonequilibrium electric discharge go through three stages: electrophysical, physicochemical, and chemical.

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