

The Mechanism of Electric Discharge Effect on the Modification Process of Linear Low-Density Polyethylene

Abstract. *The article analyses the mechanism of the electric discharge effect on the process of copolymerization of linear low density polyethylene. Under the influence of electric discharges, a change in the electrophysical property occurs, which makes it possible to change the properties of materials in a predetermined direction. The resulting material, due to the absence of a homopolymer of the grafted monomer, has improved mechanical characteristics, increased resistance to aggressive environments, and the traditional initiator is 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 step in solving the problem of achieving the efficiency, economy, and ecological purity 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, co umożliwia zmianę właściwości materiałów w zadanym kierunku. Otrzymany materiał, ze względu na brak homopolimeru szczepionego monomeru, posiada ulepszone właściwości mechaniczne, podwyższoną odporność na agresywne środowiska, a do jego syntezy nie stosuje się tradycyjnego inicjatora. Można stwierdzić, że opracowanie metody elektroerozyjnej syntezy kopolimeru wydaje się być ważnym krokiem w rozwiązaniu problemu osiągnięcia wydajności, ekonomiczności i przyjazności dla środowiska procesów technologicznych. (Mechanizm wpływu wyładowań elektrycznych na proces modyfikacji liniowego polietylenu małej gęstości)*

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 effects of electric fields and discharges are accompanied by changes in the physical and chemical state of the substance and make it possible to change the properties of materials in a given direction [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 nonequilibrium, that is, the difference $T_e - T_i$, 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 also 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].

The course of chemical reactions in a discharge depends not only on the type of discharge but also on a number of conditions. One of them is the pressure (density) of the gas.

Taking the above information on the impact of discharges on chemical processes in gases into account, we can draw the following conclusions:

Free electrons play the role of the most intense gas ionizers:

- In gases, ions tend to form charged complexes that, when combined with neutral molecules, form intermediate compounds of chemical reactions.

- As the degree of gas separation increases, so does the difference in the directional velocities of the separated components' ions.

One of the most difficult issues is determining the best mode and type of discharge to control the mechanisms that occur during polymer modification processes.

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: $U_{sh.inh.} = 11 \text{ kV}$; $U_{w.inh.} = 17 \text{ kV}$.

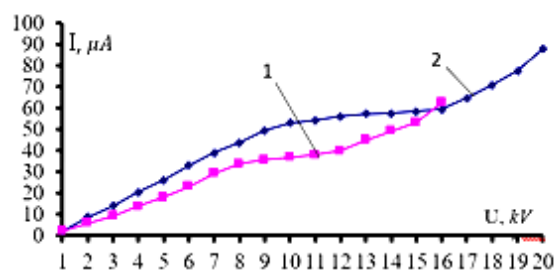


Fig. 1 Current-voltage characteristics of an electric discharge in sharply inhomogeneous (1) and weakly inhomogeneous (2) fields in a viscous liquid

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 $4 \times 10^6 \text{ Pa}$ ($\sim 40 \text{ atm.}$), a temperature of 413 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].

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.

Table 1 compares the electrical characteristics of the graft copolymer, the original linear low-density polyethylene, and polyethylene modified with chlorine (polyvinyl chloride).

Table 1. Electrical characteristics of the original, chlorinated, and graft copolymer of linear low-density polyethylene.

Parameter	linear low-density polyethylene (initial)	polyvinyl chloride	linear low-density polyethylene, grafted by electrical discharges synthesis
ρ , [Ohm×m]	10^{15}	$10^{13} - 10^{15}$	10^{14}
ε	2.3-2.4	3.1-3.4	3.1
tg δ (at 1MHz)	0.0004	0.015	0.003
E_{ess} , [MV/m]- electrical strength (with thickness 1mm)	45-55	35-45	40-45

As can be seen from Table 1, grafted polyethylene in some electrical characteristics (ε and tg δ) is slightly inferior to the initial polyethylene, however, in relation to polyvinyl chloride, grafted linear low-density polyethylene surpasses it in almost all basic electrical characteristics. In addition, as is known, with energy and mechanical effects on polyvinyl chloride during its operation, dehydrochlorination, oxidation, macrochain destruction, and other structural changes take place. It is believed that the main reaction responsible for the loss of operational properties of the polymer is the release of HCl due to dehydrochlorination when heated above 373°K, which also poses an environmental hazard to the environment.

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:

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

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.

Authors

Ahmadov Elbrus Nasi. Associate Professor, Candidate of Physical and Mathematical Sciences. Head of the Department of Electromechanics Azerbaijan State University of Oil and Industry. Baku city, Azadlyg avenue 20, E-mail: elbrusahmed@gmail.com .

Rzayeva Sona Vagif. Head of the Laboratory of the Department of Electromechanics of the Azerbaijan State University of Oil and Industry. Baku city, Azadlyg avenue 20, E-mail: soni_76@mail.ru

Mammadov Nijat Sabahaddin. Laboratory assistant at the Department of Electromechanics of the Azerbaijan State University of Oil and Industry. Baku city, Azadlyg avenue 20, E-mail: nijatms@gmail.com

REFERENCES

- [1] Natalya Ivanivna Kuskova, Olha Mykolaivna Syzonenko, and Andrii Serhiyovuch Torpakov. Electric discharge method of synthesis of carbon and metal-carbon nanomaterials. *High Temperature Materials and Processes* 2020; 39: 357–367
- [2] [101] J. Simao, H. G. Lee, D. K. Aspinwall, R. C. Dewes, and E. M. Aspinwall, "Workpiece surface modification using electrical discharge machining," *Int. J. Mach. Tools Manuf.*, vol. 43, no. 2, pp. 121–128, 2003, doi: 10.1016/S0890-6955(02)00187-6.
- [3] Ramdatti J.L., Gohil A.V. and Dave K.G. Experimental investigation on electro-discharge surface modification phenomenon of P20+Ni die steel using green P/M composite electrode. *JOURNAL OF MECHANICAL ENGINEERING AND SCIENCES (JMES)* ISSN: 2289-4659 e-ISSN: 2231-8380 VOL. 15, ISSUE 3, 8390 – 8404 DOI: <https://doi.org/10.15282/jmes.15.3.2021.16.0660>
- [4] [102] J. L. Ramdatti and A. V. Gohil, "Optimization of surface modification phenomenon for P20+Ni die steel using EDM with P/M composite electrode," pp. 689-697, 2020, doi: 10.1007/978-981-13-8196-6_60.
- [5] Wan Akmal Izzati, Yanuar Z. Arief, Zuraimy Adzis, and Mohd Shafanizam. Partial discharge characteristics of polymer nanocomposite materials in electrical insulation: A review of sample preparation techniques, analysis methods, potential applications, and future trends. *The Scientific World Journal*. Volume 2014, Article ID 735070, 14 pages. <http://dx.doi.org/10.1155/2014/735070>.
- [6] [103] Zhanhai Yao, Jinghua Yin, Guowei Jiang, Yuchun Song, Preparation and Properties of Polyether Pentaerythritol Mono-maleate grafted Linear Low Density Polyethylene by Reactive Extrusion, *Journal of Macromolecular Science, Part A*, 45, 4, (295-301), (2008) doi: 10.1080/10601320701863759
- [7] Necip B. Uner, Elijah Thimsen. Superlocal chemical reaction equilibrium in low temperature plasma. *AICHE Journal*. 13 February 2020. Volume 66, Issue 6, <https://doi.org/10.1002/aic.16948>
- [8] Khagaleev A.N., Ayurova O.Zh., Chuckreev D.A. The properties of polytetrafluoroethylene modified by electrical of alternating current. *Materials Science Forum*. ISSN: 1662-9752, Vol. 945, pp 438-442. doi:10.4028/www.scientific.net/MSF.945.438. © 2019 Trans Tech Publications, Switzerland
- [9] Словецкий Д.И. Механизмы химических реакций в неравновесной плазме, М., Наука, 1980, 310 с.
- [10] 7. Бунят-заде А.А., Салахов Абдель Азиз Ахмед Турк, Садыхов З.А. Исследование некоторых молекулярно-массовых и структурных характеристик сополимеров этилена с октенем-1. Доклады АН Азерб. ССР, 1981, т. 37, № 2, с. 51-55.
- [11] Kissin YV, Brandolini AJ. Kinetics of ethylene polymerization reactions with chromium oxide catalysts - *Journal of Polymer Science*, 2008, Volume 46, Issue 16, Pages 5315-5329
- [12] Sabnis RW, Cazeca M, DiMenna WL... Organic polymeric coatings deposited by plasma enhanced chemical vapor deposition. November 2001. *Journal of Vacuum Science & Technology B Microelectronics and Nanometer Structures.*, Volume 19, Issue 6, November 2001, pp.2184-2189(6):2184-2189, DOI:10.1116/1.1418402
- [13] Мехтизаде Р.Н., Ахмедов Э.Н., Рзаева С.В. Особенности и перспективы применения неравновесных электрических разрядов в химических реакциях. *Проблемы Энергетики*, Баку, Элм, 2007, №3, с.53-57
- [14] ND Morgulis, "И. Доссе и Г. Мирдель. Электрический ток в вакууме и в газах", *UFN*, 33:1 (1947), 147–148 *Uspekhi Fizicheskikh Nauk RUS ENG JOURNALS PEOPLE ORGANISATIONS*.
- [15] João Freire de Medeiros Neto, Ivan Alves de Souza, Michelle Cequeira Feitor, Talita Galvão Targino, Gutemberg Ferreira Diniz, Maxwell Santana Libório, Rômulo Ribeiro Magalhães Sousa and Thercio Henrique de Carvalho Costa. Study of high-density polyethylene (hdpe) kinetics modification treated by dielectric barrier discharge (dbd) plasma. *Polymers* 2020, 12, 2422; doi:10.3390/polym12102422
- [16] Мехтизаде Р.Н., Ахмедов Э.Н. Физико-химические механизмы получения привитого сополимера применением электроразрядных воздействий. *Проблемы Энергетики*, Баку, Элм, 2001, № 4, с. 93-96
- [17] 14. Ахмедов Э.Н. Электроразрядная модификация полиэтилена. *Электронная обработка материалов*, Кишинев, Елан Полиграф, 2003, №4 с. 60-63.
- [18] Болога М.К., Максимук Е.П., Гордеев Ю.Н. Массообмен при коронном и барьерном разрядах. *Электронная обработка материалов*, 1989, № 4, с. 31-32.
- [19] Техника высоких напряжений, (под. ред. М.В.Костенко), для вузов, М., Высшая школа, 1973, 528 с.
- [20] Кучинский Г.С. Частичные разряды в высоковольтных конструкциях, Л., Ленинградское отделение., 1979, 224 с.