ИЗВЕСТИЯ ВЫСШИХ УЧЕБНЫХ ЗАВЕДЕНИЙ.
Т 61 (6) Серия **«ХИМИЯ И ХИМИЧЕСКАЯ ТЕХНОЛОГИЯ»** 2018

IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY
V 61 (6) **KHIMIYA KHIMICHESKAYA TEKHNOLOGIYA** 2018
RUSSIAN JOURNAL OF CHEMISTRY AND CHEMICAL TECHNOLOGY

DOI: 10.6060/tcct.20186106.5656

УДК: 678.01

СШИТЫЕ И НАПОЛНЕННЫЕ КОМПОЗИТЫ НА ОСНОВЕ ПОЛИОЛЕФИНОВ

У.М. Мамедли

Ульвия Мамедгусейн кызы Мамедли

Лаборатория механохимической модификации и переработки полимеров, Институт полимерных материалов НАН Азербайджана, ул. С. Вургуна, 124, г. Сумгайыт, Азербайджан, AZ5004
E-mail: ulviyyam@mail.ru

В статье приводится обзорный литературный материал ряда авторов по проблеме получения модифицированных полиолефинов в процессе сшивания. Показано, что материалы на основе полиолефинов, отличающихся повышенной теплостойкостью, способствуют улучшению комплекса технических требований по светостойкости, надежности, технологичности применительно к производству и использованию кабельно-проводниковой продукции. В частности, приводятся экспериментальные данные по использованию кремнийорганического карбоксилата олова с целью получения изделий с наилучшими качественными характеристиками. Представлены результаты теоретических и экспериментальных исследований по влиянию состава композиций полиолефинов на кинетику процесса сшивания, а также реологические и теплофизические свойства. Рассмотрена принципиальная возможность изучения влияния дозы облучения на регулирование процесса изменения структуры композитов. Как показали ряд авторов, этот метод позволяет целенаправленно подойти к разработке сшитых композитных материалов с заранее заданными свойствами. Методом радиационно-химического сшивания рассмотрена сравнительная характеристика структуры полимерной основы в присутствии и без различных типов наполнителей в высоконаполненных композитах. Представлены данные по влиянию условий радиационного сшивания на плотность сетки и механические свойства сшитого полиэтилена при высоких температурах. Приводятся данные по химической стойкости сшитого полиэтилена к действию различных химических реагентов, таких как ацетон, бензол, толуол, четыреххлористый углерод, диэтиловый эфир, бензин-76, и смазок. Одним из важных обстоятельств при изучении структуры и свойств полимерных композитов является возможность математического моделирования вязкоупругой податливости густосетчатых полимеров во взаимосвязи с методологией ее теоретической параметрической идентификации с последующим прогнозированием результатов термомеханического эксперимента.

Ключевые слова: пенополиолефин, сшивание, теплостойкость, термостойкость, полиэтилен, каолин, карбонат кальция, наполнитель, сенсибилизатор, экструдер, экструзия

CROSSLINKED AND FILLED COMPOSITES BASED ON POLYOLEFINS

U.M. Mammadli

Ulviyya M. Mammadli
Laboratory of Mechanochemical Modification and Processing of Polymers, Institute of Polymer Materials of Azerbaijan NAS, S. Vurgun st., 124, Sumgait, AZ5004, Azerbaijan
E-mail: ulviyyam@mail.ru

The paper gives an overview of literary material of a number of authors on the problem of the preparation of modified polyolefins during the crosslinking process. It is shown that materials based on polyolefins, characterized by increased heat-resistance favoring improvement of complex of technical requirements for light resistance, reliability, manufacturability in respect to the production and use of cable-conduction products. In particular, experimental data are presented on the use of organosilicon tin carboxylate in order to obtain products with the best quality characteristics. The results of theoretical and experimental investigations of the influence of formulation of polyolefin compositions on the kinetics of the crosslinking process and also on rheological and thermophysical properties are presented. The principal possibility of studying the influence of the irradiation dose on the regulation of the process of changing the structure of composites is considered. As shown by a number of authors, this method makes it possible to purposefully approach the development of crosslinked composite materials with predetermined properties. The method of radiation-chemical cross-linking compares the structure of the polymer base in the presence and without different types of fillers in highly filled composites. The data on the effect of radiation cross-linking conditions on the mesh density and the mechanical properties of cross-linked polyethylene at high temperatures are presented. The data on the chemical stability of cross-linked polyethylene to the action of various chemical reagents such as acetone, benzene, toluene, carbon tetrachloride, diethyl ether, benzene-76 and lubricants are given. One of the important circumstances in the study of the structure and properties of polymer composites is the possibility of mathematical modeling of viscoelastic compliance of thick-cross-linked polymers in correlation with the methodology of its theoretical parametric identification with subsequent prediction of the results of the thermomechanical experiment.

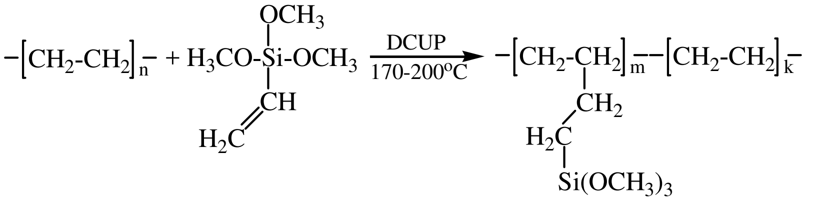
Keywords: polyolefin foams, crosslinking, heat-resistance, thermal stability, polyethylene, kaolin, calcium carbonate, filler, sensibilizator, extruder, extrusion

Для цитирования:
Мамедли У.М. Сшитые и наполненные композиты на основе полиолефинов. *Изв. вузов. Химия и хим. технология.* 2018. Т. 61. Вып. 6. С. 4–16

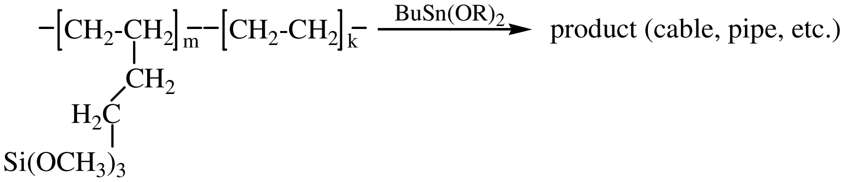
For citation:
Mammadli U.M. Crosslinked and filled composites based on polyolefins. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2018. V. 61. N 6. P. 4–16

For the first time in 1957, the problem of increasing the viscosity of a melt during the foaming of polyethylene was solved by conducting molecular cross-linking of polymer chains by the radiation method [1]. After the discovery in 1963 of the chemical method of cross-linking polyethylene with organic peroxides, great progress was made in the production of high-foamed polyethylene, the industrial production of which was started in 1966 in Japan. Cross-linking of polyethylene extends the range of technological parameters, as the viscosity of the melt of the crosslinked polymer remains at a sufficient level over a wide temperature range, which makes it possible to produce polyethylene foam with a multiplicity of foaming from 5 to 30, with a qualitative cellular structure.

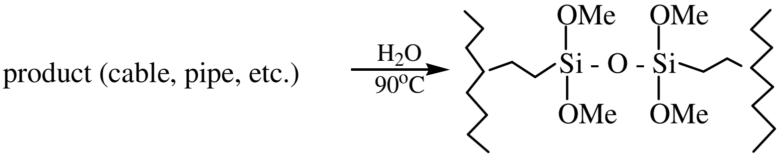
The crosslinked polyethylene is widely used in the manufacture of hot-water pipe, cable insulation and other products [2, 3]. It is shown that the use of organosilicon tin carboxylate makes it possible to obtain products with the best surface quality. The scheme of silanol-crosslinked polyethylene consists of 3 stages: preparation of grafted polyethylene (1), introduction of the catalyst to the grafted polyethylene in the preparation of the final product (2) and crosslinking of polyethylene using hot water or air moisture (3). The correct choice of catalyst plays an important role. The catalyst should not be more active at the stage of manufacturing the product (2), as this may lead to a strong increase of melt viscosity and deterioration of the surface quality of the final product. On the other hand, the catalyst should providesufficient speed and degree of crosslinking during hot water treatment (3).



$$-[CH_2-CH_2]_n- + H_3CO-\underset{CH=CH_2}{\overset{OCH_3}{Si}}-OCH_3 \xrightarrow[170\text{-}200^oC]{DCUP} -[CH_2-\underset{CH_2-CH_2-Si(OCH_3)_3}{CH}]_m-[CH_2-CH_2]_k- \quad (1)$$



$$-[CH_2-\underset{CH_2-CH_2-Si(OCH_3)_3}{CH}]_m-[CH_2-CH_2]_k- \xrightarrow{BuSn(OR)_2} \text{product (cable, pipe, etc.)} \quad (2)$$

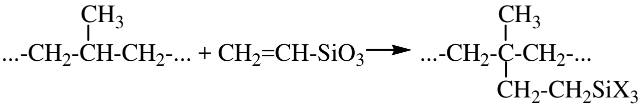


$$\text{product (cable, pipe, etc.)} \xrightarrow[90^oC]{H_2O} \underset{OMe}{\overset{OMe}{Si}}-O-\underset{OMe}{\overset{OMe}{Si}} \quad (3)$$

For the preparation of silanol-crosslinked polyethylene, catalysts based on alkylbenzenesulfonic acid, tin dibutyl diaurate, silicone carboxylate of tin and dibutyldi (trihydrofluoropentanoxy) tin were used, of which tin dibutyl diaurate is well known and is widely used. The effect of catalysts was evaluated by the speed and degree of cross-linking of the grafted polyethylene, as well as by the quality of the surface of the resulting product.

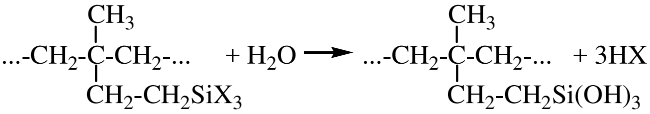
Dependence of deformability on the nature of the force action and on the temperature is established at the stage of production of chemically crosslinked polyethylene foam [4]. The object of the study was the PPE-3M (powder periclase electrotechnical grade PPE-3M) obtained by the press technology using LDPE, as the cross-linking agent was used dicumyl peroxide, the aeration regulator was azodicarbonamide. The preparation of the material consists of such steps as, the preparation of the foaming composition, the forming of the foaming composition, the molding of the molded preforms of the foaming process, the cooling of the foamed block. It is shown that, depending on the conditions of use, PPE-3M turns out to be heat-shrinkable or thermally expanding material. Dilatometric tests of PPE-3M are established the presence of polyethylene foam (below the crystallization temperature of PE) by uniaxial expansion, volumetric shrinkage. From the position of the cellular structure model and the two-phase model of the partially crystalline polymer, possible mechanisms for the appearance of the marked transitions are stated: due to the appearance of orientation stresses in the PPE-3M tensile cords and cell walls in the step of polyethylene foam, appearance orientation stresses in the polyethylene foam due longitudinal-transverse bending cords and the walls of the cells under uniaxial squeezing units in the steps forming, pressing, straightening, and occurrence orientation stresses upon expansion of the surface layer blocks edge zone of differential gas pressure inside and outside of closed cells when the load is removed in the step of straightening and following fixing these stresses in the cooling step the obtained foam blocks. The kinetic parameters of the discussed processes of shrinkage and expansion of polyethylene foam have been determined by investigation of inverse creep.

The results of theoretical and experimental studies of the influence of the composition of crosslinked polyolefin compositions on the kinetics of crosslinking, rheological and thermophysical properties are introduced [5]. Development of materials based on polyolefins with increased heat resistance, providing a set of technical requirements for light fastness, reliability, processability in the manufacture and fabrication of cabling and wiring products is strategic pathway. One of the methods for increasing the heat resistance of polyolefins is chemical cross-linking with the help of bifunctional organosilicon compounds. The method consists in grafting the organosilane to the polyolefin, which can be represented by the following scheme:



$$...-CH_2-\overset{CH_3}{CH}-CH_2-... + CH_2{=}CH-SiO_3 \longrightarrow ...-CH_2-\underset{CH_2-CH_2SiX_3}{\overset{CH_3}{C}}-CH_2-...$$

Spatial structuring of the silane-modified polymer is carried out by the formation of siloxane units in the process of hydrolysis under the action of moisture:



$$\ldots\text{-}CH_2\text{-}\underset{CH_2\text{-}CH_2SiX_3}{\overset{CH_3}{C}}\text{-}CH_2\text{-}\ldots + H_2O \rightarrow \ldots\text{-}CH_2\text{-}\underset{CH_2\text{-}CH_2Si(OH)_3}{\overset{CH_3}{C}}\text{-}CH_2\text{-}\ldots + 3HX$$

which then condense to form -Si-O-Si- bonds and release of water.

The development of industry requires the creation of new polymer materials with a specified combination of properties and low cost [6]. The required combinations of properties are most easily achieved by the creation of filled polymer (composite) materials, the components of which, while working together can exert a synergistic effect. As we move into the "century of composite materials", the need to systematically identify factors that determine the technological and operational properties and cost of polymer composite materials, as well as the potential for their regulation, is becoming increasingly urgent.

The influence of the irradiation dose on the crosslinking efficiency and the structure of ultrathene filled with aluminum trihydrate [7]. The efficiency of radiation-chemical cross-linking of highly filled ultrathene is established in comparison with unfilled, which is confirmed by the results of studying the kinetics of swelling, thermal deformation and analysis of the gel fraction. The presence of fillers in irradiated polyolefins significantly influences the nature of the occurrence of radiation-chemical processes in it, as well as the formation of a supramolecular structure in the polymer during its processing. Data on the study of the structure and properties of filled polyolefins modified by radiation-chemical means, in some cases, are contradictory in nature. Apparently, this is due to the fact that the chemical nature and concentration of the introduced fillers, the dispersity, the size of the surface and the shape of the particles, the presence and nature of the functional groups on the surface of the fillers, the physical and electrophysical nature of the filler particles significantly influence the radiation modification of the polymers. Depending on the parameters of the introduced filler particles, the structure of the polyolefins can undergo various changes.

Aluminum oxide trihydrate (gibbsite) is refined mineral filler used to impart fire resistance to polymers and reduce smoke emissions. The use of aluminum hydroxide is associated with a successful combination of low cost and good properties in it, because it is easily processed, non-toxic, does not contain halogens, and does not produce corrosive products during combustion. The effectiveness of aluminum hydroxide is much lower than halogen and phosphorus-containing compounds, as a result of which its effect becomes noticeable at high degrees of filling of the order of 50-60%wt. The formation of a denser structural grid after irradiation in the filled ultrathene is confirmed by a lesser degree of swelling in acetone and a lower thermal strain when loaded compared to unfilled ultrathene at all doses of irradiation. An increase in the temperature of the onset of oxidative degradation for filled ultrathene at 30 °C was established as compared to uncharged, and the temperature of the onset of oxidation decreased with increasing radiation dose for both filled and uncharged samples.

To increase the efficiency of the radiation modification of the compositions and to reduce the absorbed dose, radiation sensitizers are introdused into composition [8]. Reduction of the dose of irradiation with radiation-chemical modification makes it possible to increase the productivity of irradiation facilities. Reduction of the dose of irradiation provides a reduction in undesirable changes in the irradiated polymer, such as the destruction of macrochains of the polymer, which reduces the physical and mechanical properties; the formation of unsaturated groups that reduce heat resistance; hydrogen evolution at high doses; leading to foaming. In the presence of sensitizers, the required degree of cross-linking is achieved at a lower absorbed dose. The sensitizers used are triallyl cyanurate, allyl methacrylate, unsaturated epoxy oligomers, monomers having a polyfunctional radical, for example methacrylic and cyanuric acid esters, unsaturated acids-acrylic, methacrylic, unsaturated benzene-divinyl, triallylbenzene, etc.

The object of the study was a radiation-cross-linked trekking-resistant composition used for the production of heat shrinkable cable joints of the outdoor installation, which are opposed to such phenomena as tracking, erosion, ultraviolet radiation and other environmental effects. The main task was to impart a high ability to radiation-chemical cross-linking to the test composition by introducing a modifier, an ethylene vinyl acetate copolymer (vinyl acetate content 28%) containing grafting groups of maleic anhydride (1.4%) with a sensitizing effect (SEAB-M). This sensitizer has several advantages over the previously known oligomeric and monomeric sensitizers, since it is a granular polymer that can be easily introduced into the composition while it is being produced along with the rest of the components. The investigated trekking-resistant composition is a highly filled composition, as the polymer base in which is used sevilen (vinyl acetate content 12%), and as filler - aluminum hydroxide (more than 30% wt.).

The effect of the radiation crosslinking conditions on the mesh density and the mechanical properties of crosslinked polyethylene at high temperatures are investigated [9, 10]. The optimum values of the current of the generator of the electronic radiator and the speed of cable pulling, which provide the maximum grid density, are found. It is shown that the gel fraction index does not fully characterize the degree of cross-linking and mechanical properties of cross-linked polyethylene.

The results of an experimental study of the processes of radiation cross-linking of polyolefin cable insulation by ionizing radiation of an electric gas barrier discharge (EGBD) are obtained. Ionizing radiation from the EGBB can be used for radiation crosslinking of polyethylene, polypropylene, polyvinyl chloride and polyimide cable insulation [11-14]. The Kramers-Kulenkampf law holds for the intensity of the X-ray emission of an electric gas barrier discharge. The electret polarizability of cable polyethylene, polypropylene and polyvinyl chloride is recommended to control the degree and uniformity of the radiation cross-linking of cable insulation.

The effect of electron beam irradiation with a dose of 1-8 Mrad on the properties of a number of crystallizable polymers preliminarily subjected to equal-channel multi-angle extrusion is investigated [15-27]. With increasing radiation dose for high-density polyethylene and polyamide-6 increase in microhardness, modulus of elasticity, strength and for polytetrafluoropolyethylene – their decrease has occurred. Irradiation preserves low values of the effective coefficient of linear thermal expansion and increases the thermal stability of extrudates. The achieved effects are associated with the processes of radiation cross-linking, destruction, and chemical crystallization.

In recent years, active interest has been shown in methods of solid-phase polymer processing based on simple shear deformation, in particular, equidirectional angular extrusion. The most promising variant of its realization is equal-channel multi-angle extrusion. With its help, amorphous-crystalline polymers can form a unique combination of deformation-strength characteristics. A slight change in the temperatures of the melting peak maximums of both the initial and deformed polymers upon irradiation can be related both to the preservation of the structure and size of the crystals and to the action of two competing processes: an increase in the free surface energy of the crystal ends, leading to an increase in the melting point and a decrease in the melting entropy, as a result of radiation-chemical cross-linking of chains in disordered regions, which causes a decrease in the melting point [28].

Products made of cross-linked polyethylene are used for the production of pressure pipes, piping fittings, lined pipes, cable insulation and shells, shrink tubing, and other products. Silanol crosslinking is an effective means of increasing the thermal and chemical stability of polyethylene and stabilizing its properties [29-31]. Currently, the main process for the production of silanol crosslinked products is the "Silanoplas" process, which is based on the processing into products of a pre-synthesized graft copolymer of polyethylene and vinylsilane with the addition of a catalyst for silanol crosslinking. The second "Monosil" process consists in processing ordinary grade polyethylene with a batch of crosslinking agents (vinyltrialkoxysilane, peroxidic initiator, as well as silanol crosslinking catalyst) into the working zone of the extruder during molding of the product. In this case the vinyl silane grafting takes place directly in the extruder. This method is used less often, mainly in the cable industry, although it is more flexible from the point of view of choosing the main raw materials, nomenclature and volumes of production. In both methods, silanol crosslinking occurs when the products are processed with steam or hot water. It is here that the activity of the catalyst plays an important role. On the one hand, it should not be very active at the first stage of the process for melt plasticization and molding of the product, as this can lead to an undesirable increase in the molecular weight and MWD of polyethylene, an increase in the viscosity and heterogeneity of its melt, deterioration in the formation and quality of the surface of the extruder (this makes necessary the modification of the equipment). On the other hand, high speed and depth of cross-linking at the stage of processing the product in hot water must be ensured. To assess the thermal stability of the melts of the compositions at the stage of melt extrusion of the crosslinkable compositions, rheological studies were carried out on the IIRT-2A capillary viscosimeter. The crosslinking of polyethylene molecules was judged by the change in the volumetric flow rate of its melt (V, cm^3/10 min) through a standard capillary (8 mm in length and 2 mm in diameter) at a temperature of 190 °C, usually recommended for processing. To compare the effectiveness of tin-containing silanol crosslinking catalysts, the content of the gel fraction in polyethylene samples was measured in the form of rods that emerged from the capillary of the IIRT instrument between 10 and 15 min from the start of the previous experiment. To complete the silanol crosslinking, the samples were treated in boiling water for 6 h, determined as the difference in the masses of the starting material ground to a particle size of less than 0.2 mm and the mass of the residue in the gauze net after extraction of the sol fraction with o-xylene at 140 °C for 8 h and drying, referred to the mass of the original sample.

Silanol crosslinking can significantly improve the complex properties of polymer materials, including oriented heat-shrinkable films [32, 33]. It is known that preliminary cross-linking provides polyethylene films with high and stable values of thermal shrinkage and shrinkage stresses. In this case, it becomes possible to orient and operate the films at temperatures above the polymer temperature.

The manufacture of radiation-cross-linked and peroxidised-cross-linked products requires special technological equipment [34-35]. Silicone cross-linked products can be manufactured on conventional extrusion equipment. However, currently commercially available special grades of silanol crosslinkable graft copolymers of polyethylene and vinyl trialkoxysilanes (the Sioplas method) are intended exclusively for the production of pipes. Greater opportunities are provided by the use of granular concentrates of silanol crosslinking agents and conventional polyethylene (dry "Monosil"), which is used in the manufacture of metal-polymer pipes and cable products. In the latter case, a concentrate containing vinyltrialkoxysilanes, peroxide initiators providing the inoculation of silanes to polyethylene, stabilizers, organotin catalysts for the hydrolysis and condensation of silanes, is mixed with granules of conventional polyethylene and processed into products on conventional extrusion equipment. In the extrusion process, the concentrate is dispersed in the melt of polyethylene, and the reagents contained therein diffuse into the polymer. The conditions of extrusion ensure the inoculation of silane to polyethylene without significant changes in the technological characteristics of the latter.

The influence of silanol crosslinking on thermoelectric properties and heat resistance of polyethylene composites with technical carbon was studied. It has been found that silanol crosslinking increases the heat resistance and eliminates the undesirable effect of the negative temperature coefficient of electrical resistance at elevated temperatures [36-47]. Polymer composites with technical carbon can be used in self-regulating heating elements, thermostatic devices and self-disconnecting electric fuses. This application is based on a sharp increase in electrical resistance in a narrow temperature range for these composites with a certain content of carbon black. This phenomenon is called the effect of an anomalously high positive temperature coefficient of electrical resistance (PTC). Its main reason is considered to be a sharp increase in the volume of the polymer upon its melting, leading to a decrease in the volume fraction of electrically conductive particles and to an increase in the distances between them. However, with further heating, the sharp increase in electrical resistance is replaced by its sharp drop, which is called the negative temperature coefficient of electrical resistance effect (NTC). This phenomenon is associated with an increase in the mobility of carbon black particles in the melt, which facilitates their reagglomeration and the formation of new conductive channels. NTC is undesirable, because can lead to the failure of self-regulating heating devices. The effects of PTC and NTC are due to the predominance of either fracture processes or recovery processes of current conducting channels that are associated with structural changes in electrically conductive polymer composites. At present, the question of the true mechanisms of these phenomena remains open.

Radiation or chemical (peroxide) crosslinking of the polymer is considered to be an effective method of increasing heat resistance, eliminating the effect of NTC and improving the reproducibility of electrical properties. The negative effect of the NTC effect is also reduced or completely eliminated when composites are crosslinked on the basis of mixtures of polymers. PTC at the same time can both increase and decrease. Crosslinking also improves the stability of electrical characteristics during cyclic heating and cooling. In this case, chemically silanol-crosslinked compositions are more stable than radiation-crosslinked compositions. The above effects are explained by the fact that the spatial network of cross-links limits the mobility of carbon black particles at high temperatures, thereby preventing their reagglomeration. There are indications of the prospects for using the method of silanol crosslinking, but there are practically no studies of its effect on the effects of PTC and NTC.

The chemical resistance of cross-linked polyethylene to the action of various chemical reagents such as, acetone, benzene, toluene, carbon tetrachloride, diethyl ether, gasoline-76 and lubricants has been studied. Structured polyethylene with acrylonitrile in the presence of peroxide with the participation of selenium allows to significantly improving the resistance of the polymer to the action of various reagents [48].

Changes in the properties of polyethylene as a result of crosslinking of such characteristics as increasing strength and deformability, reducing the brittleness temperature and increasing the resistance to cracking have a common cause, which is to increase the content of the transmission chains that promote the dissipation of stresses in the amorphous-crystalline polymer by increasing the bond strength between crystalline formations [49].

Polyethylene crosslinked by methods of peroxide (PEX-a), silanol (PEX-b), and radiation (PEX-c) is characterized by a greater grid density for PEX-b, which is approximately 30% higher than for PEX-a and 3-fold higher in comparison with PEX-s, despite the lowest values of the gel fraction. This particularly affects its deformation-strength characteristics, which were determined at 20, 70, 90 and 110 °C on samples of 100×5×2 mm, cut from pipes made from materials of PEH-a, PEX-b and PEX-c leading manufacturers. The durability of the pipes, in addition to strength and other properties, depends on the level of residual stresses in the finished products, which are determined by the rate of relaxation processes. As the test temperature rises, the deformation force, the residual equilibrium strain and the time of its achievement for all cross-linked samples decrease.

The effect of hot chlorinated water on the physico-chemical properties of the peroxide-crosslinked polyethylene REX is investigated [50]. It has been established that even in the harshest conditions of disinfectant treatment (the concentration of sodium hypochlorite was increased 10-20 times compared to the norms adopted for drinking water supply), direct chlorination (interaction of polyethylene with chlorine) of the PEH pipes does not occur. The results of the analysis of pipe samples showed that even after 38 years of operation they maintained a sufficiently high level of physical and mechanical properties, the ability to plastic deformations, high rigidity and the degree of crystallinity, which made it possible to conclude that their operation and the use of these pipes remain within the design life 50 years.

Aging is an irreversible change in the useful properties of polymeric materials that occurs over time as a result of chemical and physical transformations that occur during their processing, storage and use [51]. The ability of a polymer material to withstand aging depends on the chemical composition and structure of the macromolecule, the molecular weight, the molecular weight distribution, the composition of impurities (the residue of catalysts, regulators, etc.), i.e. From the conditions for the preparation, isolation and purification of the polymer. Since the storage and operation of the polymer material is carried out under different conditions, characterized by some composition of the atmosphere, a certain temperature, the presence of solar radiation, increased humidity and other features, the change in useful properties observed over time can also be due to their influence.

The change in the operational properties of the polymer material is determined by both internal factors and external factors, depending on the conditions of storage and operation. The role of internal factors in subsequent storage and operation can be minimized if the relevant requirements are met at the stage of processing the polymer material. More significant influence on the aging of polymeric materials is exogenous factors, such as temperature and humidity, light and penetrating radiation, oxygen, aggressive gaseous impurities contained in air (SO_2, NO_2, etc.), mechanical loads from wind, dynamic energy of water drops, hail, sand, dust.

The effect of the chemical modification of a PP/EPDM compound of 80/20% wt. with an organic peroxide system, a polyfunctional vinyl monomer (coagent), on the impact resistance and MFI of compositions of PP/EPDM [52-58]. Specific features of the influence of chemical nature and concentration of coagents on the course and results of modification of PP/EPDM mixtures were determined. Modern technologies of the automotive industry impose a level of requirements on impact-resistant polypropylene compounds, the achievement of which by simple blending of polypropylene with EPDM rubber during extrusion processing becomes a problem. To obtain high physicomechanical characteristics of the rubber-elasticized EPDM PP, various methods for modifying PP/EPDM mixtures in a melt are actively used.

One of the main and well-known techniques of such a modification is to improve the compatibility of the components of this two-phase mixture by using presynthesized compatibility agents – so-called compatibilizers, most often a block or graft copolymer containing structural fragments identical to both of the composition, ingredients. Due to the phenomenon of compatibilization-the stabilization of a disperse system by surface-active copolymer agents-and a thermodynamically caused increase in the degree and homogeneity of the dispersion of EPDM particles in the PP matrix occurs, entailing a significant improvement in the impact resistance of such compositions. A certain drawback of this approach remains the difficulty of controlling the rheological characteristics of PP/EPDM mixtures.

Traditionally directed changes in the structure and properties of polyethylene, like other polyolefins, are carried out in the course of synthesis or by affecting the already prepared polymer by introducing fillers, modifiers and additives [59], among which:

- modifiers in the form of thermoplastic elastomers, rubbers and elastomers, which make it possible to obtain polymer materials intended for the manufacture of products operating under high impact loads, as well as frost and elastic polymeric materials;
- cross-linking agents that have a significant effect on the nature of interchain bonds, the packing

density in amorphous polyethylene zones and, accordingly, the whole complex of physico-mechanical and relaxation properties. Cross-links between linear molecules of peroxide and radiation-cross-linked polyethylene from groups = C-C =, and with silanol crosslinks of = Si-O-Si = bonds. The process of silanol crosslinking of polyethylene (PEX-b) has two stages. In the first stage, an organosilane polyethylene of the general formula RnSiX(4-n) containing radicals R with olefin unsaturated bonds and easily hydrolyzable groups X at the silicon atom (X is hydrogen, halogen or ORm radical, where Rm is alkyl, aryl, cycloalkyl, aralkyl, alkaryl). The second stage, the actual cross-linking, consists in the spatial structuring of the graft copolymer in the presence of water and the hydrolysis catalyst.

The effect of chalk on the mechanical properties of chemically crosslinked polyethylene foam was investigated [60]. The presence of up to 15% filler has little effect on the appearance of the foam. The structure of the filled polymer depends on the characteristics of the filler – chemical and thermophysical properties, particle size and shape, percentage and uniformity of distribution in the polymer mass. The apparent density of the foam increases slightly. The foam characteristics are improved during compression, the strength at break is increased. The preparation of compositions for chemically crosslinked polyethylene foam is associated with the need to ensure an even distribution of components in the volume of the polymer under relatively low temperatures and, as a consequence, high melt viscosities of the polymer. The introduction of chalk increases the melt viscosity of the polyethylene composition, and the activators have a plasticizing effect, partially offsetting the effect of chalk injection. The introduction of chalk in order to save polymeric raw materials is not justified, however, because the structure and calculated apparent density of the foam does not change much, the filling can be considered as a method for regulating the physical and mechanical properties of polyethylene foam. Chalk for polyethylene film forming polyfoam structure is active reinforcing filler and its use as a filler allows expanding the scope of chemically crosslinked polyethylene foam.

In recent years, there has been a clear trend towards increasing working pressure in pipelines by using reinforced pipes [61]. At the same time the main load is taken by the reinforcing system. The inner tube, on which the reinforcing system is attached, in this case can be made with a smaller thickness. Under these conditions, with a rare network of reinforcing elements, there is a danger that the polymer shell can be cut by the reinforcing element in the case of a large internal pressure. In connection with this, a method was developed for determining the resistance to tearing a polymer matrix under the conditions of its cutting by a reinforcing element.

To analyze the economic efficiency of the using materials, it is necessary to determine the purpose for which funds are invested in the reconstruction of heat networks, since it is necessary to take into account the economic components that will allow not only to return the investment of the enterprise funds, but also to make a profit [62]. After the reconstruction, which used energy-save materials, such as pre-insulated pipes, heat losses in the network, while transporting heat energy from the producer to the consumer, significantly are decreased and now they are 247.25 Gcal/year.

The main approaches to optimizing the extraction process is analysed [63]. The extraction methods are traditional methods of sample preparation for subsequent chemical analysis. This applies both to the analysis of low-molecular additives and to gel-sol analysis of polymeric structures capable of branching and cross-linking. In the last 10-15 years, a qualitative breakthrough has taken place in the hardware for these works, not only related to the control of analysis, the collection of information and the processing of results, but also to the introduction of a method of extraction under pressure.

A mathematical model of the viscoelastic compliance of densified polymers is proposed and the methodology of its theoretical parametric identification is shown with the subsequent prediction of the results of the thermomechanical experiment [64]. The developed mathematical formalism and methodology of its theoretical parametric identification open up promising prospects in the field of purposeful synthesis of densely-filled polymeric materials used as binders in polymer composites with the required viscoelastic properties in given temperature and stress fields.

The creation of environmentally friendly technologies for the processing of thermosetting plastics is one of the most important tasks to date [65]. Waste of spatially cross-linked polymeric and polymer-containing materials (fiberglass plastics) do not dissolve, do not melt without degradation, do not biodegrade biologically, polluting the environment. One of the most environmentally friendly ways of processing waste of such materials is the production of highly disperse powder fillers of universal purpose. The most rational approach to the solution of the problem - the effective mechanodestruction of high-strength spatially cross-linked polymeric materials - is the use of the Rebinder effect, namely the finding of adsorption-active medium that reduce the strength of these materials under mechanical action.

In most cases, Rebinder's effect is manifested in the reduction of the free energy of the surface and does not lead, in the absence of the action of force, to the formation of a new surface. Only with a very strong decrease in surface tension, approaching the critical value, spontaneous dispersion without mechanical impact is possible. The possibility of leaking of process of adsorption influence of the medium is determined by a number of factors, such as the chemical nature of the medium and the solid, the defectiveness of its structure, and the deformation conditions, temperature, intensity, quantity and phase state of the adsorption-active medium. The investigations made it possible to determine the conditions and methods for effective mechanical destruction of a high-strength spatially cross-linked polymer material in order to obtain a fine powder filler from its waste.

ЛИТЕРАТУРА

1. **Панкратов А.В., Матюхина Г.Н., Фридман О.А.** Методы получения сшитых пенополиолефинов, свойства и применение. *Пластич. массы*. 2006. № 5. С. 26-28.
2. **Иванов В.В., Криволапова О.В., Белова Л.О., Кирилин А.Д.** Сравнение активности оловоорганических соединений и сульфокислоты при получении сшитого полиэтилена. *Пластич. массы*. 2013. № 2. С. 19-24.
3. **Khonakdar H.A., Morshedian J., Eslami H., Shokrollahi F.** Study of heat shrinkability of crosslinked low-density polyethylene/poly(ethylenevinyl acetate) blends. *J. Appl. Polymer Sci.* 2004. V. 91. P. 1389-1395. DOI: 10.1002/app.13426.
4. **Дементьев А.Г., Матюхина Г.Н., Панкратов А.В.** Деформирование химически сшитого пенополиэтилена. 1. Термическое деформирование пенополиэтилена. *Пластич. массы*. 2013. № 4. С. 8-12.
5. **Чулеева Е.В., Золотарев В.М.** Сшиваемые композиции полиолефинов, не поддерживающие горение. Кинетика сшивания, реологические и теплофизические свойства. *Пластич. массы*. 2015. № 9-10. С. 10-14.
6. **Осипчик В.С., Сухинина А.В., Гуреев Ю.А.** Исследование свойств радиационно-сшиваемых электроизоляционных композиций на основе сэвилена и минеральных наполнителей для производства кабельных термоусаживаемых изделий. *Пластич. массы*. 2008. № 6. С. 31-33.
7. **Сухинина А.В., Осипчик В.С.** Изучение влияния поглощенной дозы излучения на структуру и эффективность радиационно-химического сшивания сэвилена, наполненного тригидратом алюминия. *Пластич. массы*. 2009. № 7. С. 33-36.
8. **Осипчик В.С., Сухинина В.В., Мжачих Е.И.** Исследование свойств атмосферо-трекингостойкости композиции на основе сэвилена, сенсибилизированной к радиационно-химическому сшиванию, для изготовления кабельных термоусаживаемых изделий. *Пластич. массы*. 2009. № 2. С. 53-55.
9. **Лямкин Д.И., Скрозников С.В., Жеремекин А.Н., Кобец А.В., Черкашин Н.А., Черепенников С.В.** Сравнительная оценка возможности использования показателей гель-фракция и плотность сетки для характеристики степени сшивания и эксплуатационных свойств радиационно-сшитого полиэтилена для кабельной изоляции. *Пластич. массы*. 2012. № 3. С. 14-37.
10. **Лямкин Д.И.** Механические свойства полимеров. М.: РХТУ им. Д.И. Менделеева. 2000. 64 с.
11. **Новиков Г.К., Смирнов А.И., Федчишин В.В.** О выполнении закона Крамерса-Куленкампфа при радиационном сшивании полиолефиновой кабельной изоляции излучением электрического газового разряда. *Пластич. массы*. 2010. № 8. С. 35-37.

REFERENCES

1. **Pankratov A.V., Matyukhina G.N., Fridman O.A.** Methods for the preparation of crosslinked polyolefins, properties and applications. *Plasticheskie massy*. 2006. N 5. P. 26-28 (in Russian).
2. **Ivanov V.V., Krivolapova O.V., Belova L.O., Kirilin A.D.** Comparison of the activity of organotin compounds and sulphonic acid in the production of cross-linked polyethylene. *Plasticheskie massy*. 2013. N 2. P. 19-24 (in Russian).
3. **Khonakdar H.A., Morshedian J., Eslami H., Shokrollahi F.** Study of heat shrinkability of crosslinked low-density polyethylene/poly(ethylenevinyl acetate) blends. *J. Appl. Polymer Sci.* 2004. V. 91. P. 1389-1395. DOI: 10.1002/app.13426.
4. **Dementyev A.G., Matyukhina G.N., Pankratov A.V.** Deforming chemically crosslinked polyethylene foam. 1. Thermal deformation of polyethylene foam. *Plasticheskie massy*. 2013. N 4. P. 8-12 (in Russian).
5. **Chuleeva E.V., Zolotarev V.M.** Crosslinkable polyolefin compositions that do not support combustion. Kinetics of crosslinking, rheological and thermophysical properties. *Plasticheskie massy*. 2015. N 9-10. P. 10-14 (in Russian).
6. **Osipchik V.S., Sukhinina A.V., Gureev Yu.A.** Investigation of the properties of radiation-cross-linked insulating compositions based on sevilene and mineral fillers for the production of cable heat-shrink products. *Plasticheskie massy*. 2008. N 6. P. 31-33 (in Russian).
7. **Sukhinina A.V., Osipchik V.S.** Study of the influence of the absorbed radiation dose on the structure and efficiency of the radiation-chemical cross-linking of sevilene filled with aluminum trihydrate. *Plasticheskie massy*. 2009. N 7. P. 33-36 (in Russian).
8. **Osipchik V.S., Suhinina V.V., Mzhachikh E.I.** Investigation of atmospheric-cracking properties of a composition based on sevilene, sensitized to radiation-chemical cross-linking, for the manufacture of cable heat-shrink products. *Plasticheskie massy*. 2009. N 2. P. 53-55 (in Russian).
9. **Lyamkin D.I., Skroznikov S.V., Zheremekin A.N., Kobets A.V., Cherkashin N.A., Cherepennikov S.V.** Comparative evaluation of the possibility of using gel-fraction indicators and grid density to characterize the degree of cross-linking and operational properties of radiation-cross-linked polyethylene for cable insulation. *Plasticheskie massy*. 2012. N 3. P. 14-37 (in Russian).
10. **Lyamkin D.I.** Mechanical properties of polymers. M.: Dmitry Mendeleev University of Chemical Technology of Russia. 2000. 64 p (in Russian).
11. **Novikov G.K., Smirnov A.I., Fedchishin V.V.** On the fulfillment of the Kramers-Kulenkampf law during the course of the cross-linking of polyolefin cable. *Plasticheskie massy*. 2010. N 8. P. 35-37 (in Russian).

12. **Новиков Г.К.** Плазменные электротехнологии модификации и контроля дефектности полиолефиновой кабельной изоляции. Иркутск: Изд-во ИрГТУ. 2008. 100 с.
13. **Новиков Г.К.** Ультрафиолетовое излучение электрического барьерного разряда в технологии сшивания полимерной кабельной изоляции. *Электричество*. 2008. № 7. С. 65-68.
14. **Новиков Г.К., Федчишин В.В.** Электретный эффект в полиолефинах, волновая и корпускулярная модель поляризации короноэлектретов. *Электричество*. 2008. № 12. С. 8-11.
15. **Белошенко В.А., Возняк А.В., Возняк Ю.В., Киселев В.А.** Свойства аморфно-кристаллических полимеров, модифицированных равноканальной многоугловой экструзией и радиационным облучением. *Пластич. массы*. 2013. № 10. С. 13-18.
16. **Сергеева Л.М., Файнлейб А.М., Толстов А.Л., Бардаш Л.В.** Влияние дозы радиации на свойства полиолефинов и их смесей с другими полимерами. *Полимерный журнал*. 2006. Т. 28. № 4. С. 271-283.
17. **Kurtz S.M., Mazzucco D., Rimnac C.M., Schroeder D.** Anisotropy and oxidative resistance of highly crosslinked UHMWPE after deformation processing by solid-state ram extrusion. *Biomaterials*. 2006. V. 27. N 1. P. 24-34. DOI: 10.1016/j.biomaterials.2005.05.102.
18. **Рейнхольдс И., Калькис В., Максимов Р.Д., Зицанс Я., Мерий Мери Р.** Влияние радиационной модификации и постоянного магнитного поля на деформационные свойства смесевого полимерного композита. *Механика композитных материалов*. 2001. Т. 47. № 5. С. 707.
19. **Cybo J., Maszybrocka J., Duda P., Bartczak Z., Barylski A., Kaptacz S.** Properties of ultra-high-molecular-weight polyethylene with a structure modified by plastic deformation and electron-beam irradiation. *J. Appl. Polymer Sci.* 2012. V. 125. P. 4197-4208. DOI: 10.1002/app.36572.
20. **Philips A., Zhu P., Edward G.** Simple Shear Deformation of Polypropylene via the Equal Channel Angular Extrusion Process. *Macromolecules*. 2006. V. 39. N 17. P. 5796-5803. DOI: 10.1021/ma0607618.
21. **Wang T., Tang S., Chen J.** Effects of processing route on morphology and mechanical behavior of polypropylene in equal channel angular extrusion. *J. Appl. Polymer Sci.* 2011. V. 122. N 3. P. 2146-2158. DOI: 10.1002/app.34335.
22. **Qin J., Murata T., Wu X., Kitagawa M., Kudo M.** Plastic deformation mechanism of crystalline polymer materials in the equal channel angular extrusion process. *J. Mat. Proc.Techn.* 2012. V. 212. N 7. P. 1528- 1536. DOI: 10.1016/j.jmatprotec. 2012.02.015.
23. **Beloshenko V.A., Varyukhin V.N., Voznyak A.V., Voznyak Yu.V.** Polyoxymethylene orientation by equal-channel multiple angular extrusion. *J. Appl. Polymer Sci.* 2012. V. 126. N 3. P. 837-844. DOI: 10.1002/app.36971.
24. **Beloshenko V., Spuskanyuk V.** ECAE Methods of Structure Modification of Materials. *Intern. J. Mater. Chem.* 2012. V. 2. P. 145-150. DOI: 10.5923/j.ijmc.20120204.06.
25. **Beloshenko V.A., Voznyak A.V., Voznyak Yu.V.** Control of the mechanical and thermal properties of semicrystalline polymers via a new processing route of the equal channel multiple angular extrusion. *Polymer Eng. Sci.* 2014. V. 54. N 3. P. 531–53953. DOI: 10.1002/pen.23583.
26. **Flores A., Ania F., Balta-Calleja F.J.** From the glassy state to ordered polymer structures: A microhardness study. *Polymer.* 2009. V. 50. P. 729-746. DOI: 10.1016/j.polymer.2008.11.037.

12. **Novikov G.K.** Plasma electrotechnologies for the modification and control of the defectiveness of polyolefin cable insulation. Irkutsk: ISTU. 2008. 100 p (in Russian).
13. **Novikov G.K.** Ultraviolet radiation of an electrical barrier discharge in the technology of cross-linking of polymer cable insulation. *Elektrichestvo*. 2008. N 7. P. 65-68 (in Russian).
14. **Novikov G.K., Fedchishin V.V.** Electret effect in polyolefins, wave and corpuscular model of coronaelectret polarization. *Elektrichestvo*. 2008. N 12. P. 8-11 (in Russian).
15. **Beloshenko V.A., Voznyak A.V., Voznyak Yu.V., Kiselev V.A.** Properties of amorphous-crystalline polymers modified with equal-channel multi-angle extrusion and radiation irradiation. *Plasticheskie massy*. 2013. N 10. P. 13-18 (in Russian).
16. **Sergeeva L.M., Fainleib A.M., Tolstov A.L., Bardash L.V.** Influence of radiation exposure on the properties of polyolefins and their mixtures with other polymers. *Polimernyj Zhurn.* 2006. V. 28. N 4. P. 271-283 (in Russian).
17. **Kurtz S.M., Mazzucco D., Rimnac C.M., Schroeder D.** Anisotropy and oxidative resistance of highly crosslinked UHMWPE after deformation processing by solid-state ram extrusion. *Biomaterials*. 2006. V. 27. N 1. P. 24-34. DOI: 10.1016/j.biomaterials.2005.05.102.
18. **Reinholds I., Kalkis V., Maksimov R.D., Zitsans J., Meri Mery R.** The effect of radiation modification and of a constant magnetic field on deformation properties of the mixed polymer composite. Mekhanika Kompozitnykh Materialov. 2001. V. 47. N 5. P. 707 (in Russian).
19. **Cybo J., Maszybrocka J., Duda P., Bartczak Z., Barylski A., Kaptacz S.** Properties of ultra-high-molecular-weight polyethylene with a structure modified by plastic deformation and electron-beam irradiation. *J. Appl. Polymer Sci.* 2012. V. 125. P. 4197-4208. DOI: 10.1002/app.36572.
20. **Philips A., Zhu P., Edward G.** Simple Shear Deformation of Polypropylene via the Equal Channel Angular Extrusion Process. *Macromolecules*. 2006. V. 39. N 17. P. 5796-5803. DOI: 10.1021/ma0607618.
21. **Wang T., Tang S., Chen J.** Effects of processing route on morphology and mechanical behavior of polypropylene in equal channel angular extrusion. *J. Appl. Polymer Sci.* 2011. V. 122. N 3. P. 2146-2158. DOI: 10.1002/app.34335.
22. **Qin J., Murata T., Wu X., Kitagawa M., Kudo M.** Plastic deformation mechanism of crystalline polymer materials in the equal channel angular extrusion process. *J. Mat. Proc.Techn.* 2012. V. 212. N 7. P. 1528- 1536. DOI: 10.1016/j.jmatprotec. 2012.02.015.
23. **Beloshenko V.A., Varyukhin V.N., Voznyak A.V., Voznyak Yu.V.** Polyoxymethylene orientation by equal-channel multiple angular extrusion. *J. Appl. Polymer Sci.* 2012. V. 126. N 3. P. 837-844. DOI: 10.1002/app.36971.
24. **Beloshenko V., Spuskanyuk V.** ECAE Methods of Structure Modification of Materials. *Intern. J. Mater. Chem.* 2012. V. 2. P. 145-150. DOI: 10.5923/j.ijmc.20120204.06.
25. **Beloshenko V.A., Voznyak A.V., Voznyak Yu.V.** Control of the mechanical and thermal properties of semicrystalline polymers via a new processing route of the equal channel multiple angular extrusion. *Polymer Eng. Sci.* 2014. V. 54. N 3. P. 531–53953. DOI: 10.1002/pen.23583.
26. **Flores A., Ania F., Balta-Calleja F.J.** From the glassy state to ordered polymer structures: A microhardness study. *Polymer.* 2009. V. 50. P. 729-746. DOI: 10.1016/j.polymer.2008.11.037.
27. **Beloshenko V.A., Voznyak A.V., Voznyak Yu.V., Dudarenko G.V.** Equal-channel multiple angular extrusion of polyethylene. *J. Appl. Polymer Sci.* 2013. V. 127. N 2. P. 1377- 1386. DOI: 10.1002/app.37993.

27. **Beloshenko V.A., Voznyak A.V., Voznyak Yu.V., Dudarenko G.V.** Equal-channel multiple angular extrusion of polyethylene. *J. Appl. Polymer Sci.* 2013. V. 127. N 2. P. 1377- 1386. DOI: 10.1002/app.37993.
28. **Козлов Г.В., Новиков В.У., Белошенко В.А., Заиков Г.Е.** Изменение механизма деформации и структуры в процессе твердофазной экструзии полимеризационно наполненных композиций. *Пластич. массы*. 2001. № 3. С. 21-22.
29. **Марков А.В., Иванов В.В., Копылов В.М., Кулезнев В.Н., Романов А.С., Славин Г.С.** Патент РФ № 2304597. Сухой дисперсный модификатор полиолефинов и их сополимеров. 2007.
30. **Марков А.В., Иванова Е.В., Персиц В.Г., Кулезнев В.И**. Исследование пероксидного сшивания полиэтилена реологическим методом. *Учен. записки МИТХТ им. М.В. Ломоносова*. 2004. № 10. С. 42-45.
31. **Марков А.В., Иванов В.В., Кулезнев В.И., Криволапова О.В., Персиц В.Г.** Исследование термостабильности расплавов силанольно-сшивающихся полиэтиленовых композиций. *Пластич. массы*. 2009. № 5. С. 11-14.
32. **Марков А.В., Кулезнев В.Н., Персиц В.Г.** Ориентационная вытяжка силанольно-сшитых полиэтиленовых пленок. *Пластич. массы*. 2007. № 11. С. 5-7.
33. **Альперн В.Д., Кубанцев К.И.** Силанольно-сшиваемый полиэтилен высокой плотности фирмы PADANAPLAST SOLVAY для труб и фитингов систем отопления и водоснабжения. *Пластич. массы*. 2006. № 9. С. 3-6.
34. **Кулезнев В.Н., Шершнев В.А.** Химия и физика полимеров. М.: Изд. Колос. 2007. 368 с.
35. **Марков А.В., Кулезнев В.Н., Иванов В.В., Персиц В.Г., Марков В.А., Криволапова О.В.** Теплостойкие пленки из силанольно сшитого полиэтилена. *Пластич. массы*. 2010. № 9. С. 18-22.
36. **Dai K., Zhang Y.C., Tang J.H., Ji X., Li Z.M.** Anomalous attenuation and structural origin of positive temperature coefficient (PTC) effect in a carbon black (CB)/poly(ethylene terephthalate) (PET)/polyethylene (PE) electrically conductive microfibrillar polymer composite with a preferential CB distribution. *J. Appl. Polymer Sci.* 2012. V. 125(S1). P. E561-E570. DOI: 10.1002/app.36521.
37. **Huang S.J., Lee J.K., Ha C.S.** Polymeric positive-temperature-coefficient materials: dynamic curing effect. *Colloid Polymer Sci.* 2004. V. 282. P. 575-582. DOI: 10.1007/s00396-003-0980-4.
38. **Zheng Q., Shen L., Li W., Song Y., Yi X.** Nonlinear conductive properties and scaling behavior of conductive particle filled high-density polyethylene composites. *Chinese Sci. Bull.* 2005. V. 50. N 5. P. 385-395. DOI: 10.1360/04wb0095.
39. **Xie H., Dong L., Sun J.** Influence of radiation structures on positive-temperature-coefficient and negative-temperature-coefficient effects of irradiated low-density polyethylene/carbon black composites. *J. Appl. Polymer Sci.* 2005. V. 95. P. 700-704. DOI: 10.1002/app.21220.
40. **Das N.C., Chaki T.K., Khastgir D.** Effect of filler treatment and crosslinking on mechanical and dynamic mechanical properties and electrical conductivity of carbon black filled ethylene vinyl acetate copolymer composites. *J. Appl. Polymer Sci.* 2003. V. 90(8). P. 2073-2082. DOI: 10.1002/app.12811.
41. **Марков В.А., Кандырин Л.Б., Марков А.В., Сорокина Е.А.** Влияние силанольного сшивания на электрические характеристики и теплостойкость полиэтиленовых композитов с техническим углеродом. *Пластич. массы*. 2013. № 10. С. 21-24.
42. **Xie H., Deng P., Dong L., Sun J.** LDPE/Carbon black conductive composites: Influence of radiation crosslinking on

28. **Kozlov G.V., Novikov V.U., Beloshenko V.A., Zaikov G.E.** Change in the mechanism of deformation and structure in the process of solid-phase extrusion of polymerisation-filled compositions. *Plasticheskie massy.* 2001. N 3. P. 21-22 (in Russian).
29. **Markov A.V., Ivanov V.V., Kopylov V.M., Kuleznev V.N., Romanov A.S., Slavin G.S.** A dry dispersed modifier of polyolefins and their copolymers. RF Patent N 2304597. 2007 (in Russian).
30. **Markov A.V., Ivanova E.V., Persits V.G., Kuleznev V.I.** Investigation of peroxide cross-linking polyethylene by rheological method. *Uchen. Zapiski MITKhT im. M.V. Lomonosova.* 2004. N 10. P. 42-45 (in Russian).
31. **Markov A.V., Ivanov V.V., Kuleznev V.I., Krivolapova O.V., Persits V.G.** Study of thermal stability of melts of silanol-crosslinkable polyethylene compositions. *Plasticheskie massy.* 2009. N 5. P. 11-14 (in Russian).
32. **Markov A.V., Kuleznev V.N., Persits V.G.** Orientation stretching of silanol-crosslinked polyethylene films. *Plasticheskie massy.* 2007. N 11. P. 5-7 (in Russian).
33. **Alpern V.D., Kubantsev K.I.** Silicone crosslinkable high density polyethylene from PADANAPLAST SOLVAY for pipes and fittings for heating and water supply systems. *Plasticheskie massy.* 2006. N 9. P. 3-6 (in Russian).
34. **Kuleznev V.N., Shershnev V.A.** Chemistry and physics of polymers. M.: Kolos. 2007. 368 p (in Russian).
35. **Markov A.V., Kuleznev V.N., Ivanov V.V., Persits V.G., Markov V.A., Krivolapova O.V.** Heat resistant films of silanol cross-linked polyethylene. *Plasticheskie massy.* 2010. N 9. P. 18-22 (in Russian).
36. **Dai K., Zhang Y.C., Tang J.H., Ji X., Li Z.M.** Anomalous attenuation and structural origin of positive temperature coefficient (PTC) effect in a carbon black (CB)/poly(ethylene terephthalate) (PET)/polyethylene (PE) electrically conductive microfibrillar polymer composite with a preferential CB distribution. *J. Appl. Polymer Sci.* 2012. V. 125(S1). P. E561-E570. DOI: 10.1002/app.36521.
37. **Huang S.J., Lee J.K., Ha C.S.** Polymeric positive-temperature-coefficient materials: dynamic curing effect. *Colloid Polymer Sci.* 2004. V. 282. P. 575-582. DOI: 10.1007/s00396-003-0980-4.
38. **Zheng Q., Shen L., Li W., Song Y., Yi X.** Nonlinear conductive properties and scaling behavior of conductive particle filled high-density polyethylene composites. *Chinese Sci. Bull.* 2005. V. 50. N 5. P. 385-395. DOI: 10.1360/04wb0095.
39. **Xie H., Dong L., Sun J.** Influence of radiation structures on positive-temperature-coefficient and negative-temperature-coefficient effects of irradiated low-density polyethylene/carbon black composites. *J. Appl. Polymer Sci.* 2005. V. 95. P. 700-704. DOI: 10.1002/app.21220.
40. **Das N.C., Chaki T.K., Khastgir D.** Effect of filler treatment and crosslinking on mechanical and dynamic mechanical properties and electrical conductivity of carbon black filled ethylene vinyl acetate copolymer composites. *J. Appl. Polymer Sci.* 2003. V. 90(8). P. 2073-2082. DOI: 10.1002/app.12811.
41. **Markov V.A., Kandyrin L.B., Markov A.V., Sorokina E.A.** Effect of silanol crosslinking on the electrical characteristics and heat resistance of polyethylene composites with technical carbon. *Plasticheskie massy.* 2013. N 10. P. 21-24 (in Russian).
42. **Xie H., Deng P., Dong L., Sun J.** LDPE/Carbon black conductive composites: Influence of radiation crosslinking on PTC and NTC properties. *J. Appl. Polymer Sci.* 2002. V. 85. N 13. P. 2742-2749. DOI: 10.1002/app.10720.
43. **Tsai C.S., Liu C.I., Tsao K.Y., Chen K.N., Yeh J.T., Huang C.Y.** Effect of Initiator on the Over-Voltage Positive

PTC and NTC properties. *J. Appl. Polymer Sci.* 2002. V. 85. N 13. P. 2742-2749. DOI: 10.1002/app.10720.

43. **Tsai C.S., Liu C.I., Tsao K.Y., Chen K.N., Yeh J.T., Huang C.Y.** Effect of Initiator on the Over-Voltage Positive Temperature Coefficient of Linear Low Density Polyethylene/Carbon Black Nano Composites. *Macromol. Symp.* 2009. V. 286. P. 125-134. DOI: 10.1002/masy.200951216.
44. **Lee G.J., Han M.G., Chung S.Ch., Suh K.D., Im S.S.** Effect of crosslinking on the positive temperature coefficient stability of carbon black-filled HDPE/ethylene-ethylacrylate copolymer blend system. *Polym. Eng. Sci.* 2002. V. 42. N 8. P. 1740-1747. DOI: 10.1002/pen.11067.
45. **Yi X.S., Zhang J.F., Zheng Q., Pan Y.** Influence of irradiation conditions on the electrical behavior of polyethylene carbon black conductive composites J. Appl. Polymer Sci. 2000. V. 77. P. 494-499. DOI: 10.1002/(SICI)1097-4628(20000718)77:3<494::AID-APP4>3.0CO;2-K.
46. **Марков В.А., Кандырин Л.Б., Марков А.В., Городницкий М.С.** Влияние кристаллизации полимеров на электричесое сопротивление их композиций с техническим углеродом. *Конструкции из композицион. матер.* 2013. № 3. С. 35-40.
47. **Jong H.K., Hyun-Nam C., Seong H.K., Jun Y.K.** PTC behavior of polymer composites containing ionomers upon electron beam irradiation. *Macromolecular Research.* 2004. V. 12. N 1. P. 53-62. DOI: 10.1007/BF03218995.
48. **Гусейнова З.Н.** Изучение стойкости селенсодержащего сшитого полиэтилена к действию различных химических реагентов и смазок. *Пластич. массы.* 2011. № 12. С. 14-15.
49. **Кикель В.А., Осипчик В.С., Лебедева Е.Д.** Сравнительный анализ структуры и свойств сшитого различными методами полиэтилена. *Пластич. массы.* 2005. № 8. С. 3-6.
50. **Горбунова Т.Л., Гаевой Н.В., Герасимов К.В, Чалых А.Е., Калугина Е.В.** Влияние хлорированной воды на пероксидно-сшитый полиэтилен РЕХ-а. *Пластич. массы.* 2009. № 9. С. 40-46.
51. **Горбунова Т.Л., Иоффе А.А., Евсеева К.А., Калугина Е.В.** Термоокислительное старение пероксидно-сшитого ПЭ РЕХ-а при повышенных температурах и в условиях длительного складского хранения. *Пластич. массы.* 2009. № 10. С. 22-27.
52. **Kim B.C., Hwang S.S., Lim K.Y., Yoon K.J.** Toughening of PP/EPDM blend by compatibilization. *J. Appl. Polymer Sci.* 2000. V. 78(6). P. 1267-1274. DOI: 10.1002/1097-4628(20001107)78:6<1267::AID-APP130>3.0.CO;2-B.
53. **Longxiang Tang, Baojun Qu, Xiaofeng Shen.** Mechanical properties, morphological structure, and thermal behavior of dynamically photocrosslinked PP/EPDM blends. *J. Appl. Polymer Sci.* 2004. V. 92. P. 3371-3380. DOI: 10.1002/app.20340.
54. **Бауман Н.А., Волков А.М., Рыжикова И.Г., Галибеев С.С., Вольфсон С.И.** Совершенствование комплекса свойств смесей полипропилена и этиленпропиленового каучука обработкой перекисью в процессе смешения в расплаве. *Промышл. пр-во и использ. эластомеров.* 2009. № 4/5. С. 20-23.
55. **Бауман Н.А., Волков А.М., Рыжикова И.Г., Галибеев С.С., Вольфсон С.И.** Влияние молекулярной структуры этиленпропиленового каучука на эффективность процессов перекисной модификации бинарных смесей ПП/СКЭПТ. *Каучук и резина.* 2010. № 4. С. 11-14.
56. **Бауман Н.А., Волков А.М., Рыжикова И.Г., Галибеев С.С., Вольфсон С.И.** Изучение влияния процессов перекисной модификации на морфологию ударопрочных смесей ПП и СКЭПТ методом электронной микроскопии. Всеросс. науч. шк. для молодежи. «Проведение научных исследований в области инноваций и высоких технологий нефтехимического комплекса». Казань. 2010. С. 105.

Temperature Coefficient of Linear Low Density Polyethylene/Carbon Black Nano Composites. *Macromol. Symp.* 2009. V. 286. P. 125-134. DOI: 10.1002/masy.200951216.

44. **Lee G.J., Han M.G., Chung S.Ch., Suh K.D., Im S.S.** Effect of crosslinking on the positive temperature coefficient stability of carbon black-filled HDPE/ethylene-ethylacrylate copolymer blend system. *Polym. Eng. Sci.* 2002. V. 42. N 8. P. 1740-1747. DOI: 10.1002/pen.11067.
45. **Yi X.S., Zhang J.F., Zheng Q., Pan Y.** Influence of irradiation conditions on the electrical behavior of polyethylene carbon black conductive composites J. Appl. Polymer Sci. 2000. V. 77. P. 494-499. DOI: 10.1002/(SICI)1097-4628(20000718)77:3<494::AID-APP4>3.0CO;2-K.
46. **Markov V.A., Kandyrin L.B., Markov A.V., Gorodnitsky M.S.** Influence of crystallization of polymers on the electrical resistance of their compositions with technical carbon. *Konstruktsii iz kompozitsionnykh materialov.* 2013. N 3. P. 35-40 (in Russian).
47. **Jong H.K., Hyun-Nam C., Seong H.K., Jun Y.K.** PTC behavior of polymer composites containing ionomers upon electron beam irradiation. *Macromolecular Research.* 2004. V. 12. N 1. P. 53-62. DOI: 10.1007/BF03218995.
48. **Guseinova Z.N.** Study of the resistance of selenium-containing cross-linked polyethylene to the action of various chemical reagents and lubricants. *Plasticheskie massy.* 2011. N 12. P. 14-15 (in Russian).
49. **Kikel V.A., Osipchik V.S., Lebedeva E.D.** Comparative analysis of the structure and properties of cross-linked polyethylene. *Plasticheskie massy.* 2005. N 8. P. 3-6 (in Russian).
50. **Gorbunova T.L., Gaevoiy N.V., Gerasimov K.V., Chalykh A.E., Kalugina E.V.** The effect of chlorinated water on peroxided-cross-linked PEH-a. *Plasticheskie massy.* 2009. N 9. P. 40-46 (in Russian).
51. **Gorbunova T.L., Ioffe A.A., Evseeva K.A., Kalugina E.V.** Thermooxidizing aging of peroxidised cross-linked PE-REX at elevated temperatures and under conditions of long-term storage. *Plasticheskie massy.* 2009. N 10. P. 22-27 (in Russian).
52. **Kim B.C., Hwang S.S., Lim K.Y., Yoon K.J.** Toughening of PP/EPDM blend by compatibilization. *J. Appl. Polymer Sci.* 2000. V. 78(6). P. 1267-1274. DOI: 10.1002/1097-4628(20001107)78:6<1267::AID-APP130>3.0.CO;2-B.
53. **Longxiang Tang, Baojun Qu, Xiaofeng Shen.** Mechanical properties, morphological structure, and thermal behavior of dynamically photocrosslinked PP/EPDM blends. *J. Appl. Polymer Sci.* 2004. V. 92. P. 3371-3380. DOI: 10.1002/app.20340.
54. **Bauman N.A., Volkov A.M., Ryzhikova I.G., Galibeev S.S., Volfson S.I.** Improvement of a complex of properties of mixtures of polypropylene and ethylene-propylene rubber by treatment with peroxide during melt mixing. *Promyshlennoe proizvodstvo i ispol'zovanie elastomerov.* 2009. N 4/5. P. 20-23 (in Russian).
55. **Bauman N.A., Volkov A.M., Ryzhikova I.G., Galibeev S.S., Volfson S.I.** Influence of the molecular structure of ethylene-propylene rubber on the efficiency of the processes of peroxide modification of PP / EPDM binary mixtures. *Kauchuk i Rezina.* 2010. N 4. P. 11-14 (in Russian).
56. **Bauman N.A., Volkov A.M., Ryzhikova I.G., Galibeev S.S., Volfson S.I.** A study of the effect of peroxide modification processes on the morphology of impact-resistant PP and EPDM mixtures by electron microscopy. All-Russian Scientific School for Youth. "Carrying out scientific research in the field of innovations and high technologies of the petrochemical complex". Kazan. 2010. P. 105 (in Russian).
57. **Gilimyanov F.G.** RF Patent N 2241009. 2004 (in Russian).

57. **Гилимьянов Ф.Г.** Патент РФ № 2241009: МПК7 C08L23/12. Ударопрочная композиция. Дата опубл. 2004.11.27.
58. **Рыжикова И.Г., Волков А.М., Бауман Н.А., Казаков Ю.М., Вольфсон С.И.** Особенности модификации бинарных смесей ПП/СКЭПТ системой органический пероксид-полифункциональный виниловый мономер в процессе реакционной экструзии. Часть 1. Влияние молекулярно-массовых характеристик СКЭПТ, химической природы полярного винилового мономера – соагента пероксидной экструзионной модификации полимерной смеси ПП/СКЭПТ на ударную вязкость и значения ПТР конечных продуктов. *Пластич. массы*. 2013. № 8. С. 40-45.
59. **Казанчян А.Э., Осипчик В.С., Чалая Н.М., Кикель В.А.** Модифицирование свойств химически сшитого полиэтилена термоэластопластами. *Пластич. массы*. 2012. № 1. С. 3-7.
60. **Панкратов А.В., Матюхина Г.Н., Панов Ю.Т., Фридман О.А.** Влияние минеральных наполнителей на свойства химически сшитого пенополиэтилена. *Пластич. массы*. 2010. № 7. С. 32-34.
61. **Коврига В.В., Пятин И.Н., Самойлов С.В., Пендик С.С., Сергеев В.И.** Исследование температурных зависимостей сопротивления раздиру армирующим элементом матриц из сшитого полиэтилена. *Пластич. массы*. 2011. № 9. С. 44-46.
62. **Гжибовский Н.В., Волков Р.А.** Анализ экономической эффективности тепловых сетей из сшитого полиэтилена. *Пластич. массы*. 2011. № 9. С. 46-51.
63. **Евсеева К.А., Иванов А.И., Калугина Е.В.** Новое в способе оценки степени сшивки полиэтиленов. *Пластич. массы*. 2010. № 3. С. 42-45.
64. **Улитин Н.В., Дебердеев Т.Р., Дебердеев Р.Я.** Некоторые вязкоупругие свойства плотносшитых сетчатых полимеров. Теоретический расчет. *Пластич. массы*. 2012. № 2. С. 34-39.
65. **Золина Л.И., Кутянина Л.Г., Суторшина Л.М., Собко Т.Е.** Механо-диспергирование отходов пространственносшитых полимеров. *Пластич. массы*. 2005. № 11. С. 44-46.

58. **Ryzhikova I.G., Volkov A.M., Bauman N.A., Kazakov Yu.M., Volfson S.I.** Features of modification of binary PP / DPPTT mixtures with an organic peroxide-polyfunctional vinyl monomer system during the process of extrusion. Part 1. Influence of the molecular mass characteristics of EPDM, the chemical nature of the polar vinyl monomer coagent of the peroxide extrusion modification of the PP / EPDM resin mixture on the impact strength and the MFR values of the final products. *Plasticheskie massy*. 2013. N 8. P. 40-45 (in Russian).
59. **Kazanchyan A.E., Osipchik V.S., Chalaya N.M., Kikel V.A.** Modification of the properties of chemically crosslinked polyethylene with thermoplastic elastomers. *Plasticheskie massy*. 2012. N 1. P. 3-7 (in Russian).
60. **Pankratov A.V., Matyukhina G.N., Panov Yu.T., Fridman O.A.** Effect of mineral fillers on the properties of chemically crosslinked polyethylene foam. *Plasticheskie massy*. 2010. N 7. P. 32-34 (in Russian).
61. **Kovriga V.V., Pyatin I.N., Samoiylov S.V., Pendik S.S., Sergeev V.I.** Investigation of the temperature dependences of the tear resistance of a crosslinked polyethylene matrix reinforcing element. *Plasticheskie massy*. 2011. N 9. P. 44-46 (in Russian).
62. **Gzhibovskiy N.V., Volkov R.A.** Analysis of the economic efficiency of heat networks made of cross-linked polyethylene. *Plasticheskie massy*. 2011. N 9. P. 46-51 (in Russian).
63. **Evseeva K.A., Ivanov A.I., Kalugina E.V.** New in the method for assessing the degree of crosslinking of polyethylenes. *Plasticheskie massy*. 2010. N 3. P. 42-45 (in Russian
64. **Ulitin N.V., Deberdeev T.R., Deberdeev R.Ya.** Some of the viscoelastic properties of the crosslinked network polymers. Theoretical calculation. *Plasticheskie massy*. 2012. N 2. P. 34-39. (in Russian).
65. **Zolina L.I., Kutyanina L.G., Sutorshina L.M., Sobko T.E.** Mechanodispersion of wastes of spatially cross-linked polymers. *Plasticheskie massy*. 2005. N 11. P. 44-46 (in Russian).

Поступила в редакцию 11.01.2018
Принята к опубликованию 23.04.2018

Received 11.01.2018
Accepted 23.04.2018