THE STRUCTURE ASPECTS OF RADIATION MODIFICATION OF ELECTRIC PROPERTIES OF POLYOLEFINES

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The variety of elements of supermolecular structure (SMS) of polyolefines, in particular polyethylene (PE) low and high density (LDPE and HDPE), izotactic polypropylene (PP) create reason for directive and effective modification their structures and electrical properties and the action of γ- and e^-- radiation . It is know that PE is mainly stitching polymer, but PP has inclination to destruction processes. Their electrical and dielectrics properties on the radiation modification essentially depends on the crystallize condition polymer and regime of irradiation [1]. In [1,2] it is shown that the action of definitude doses of γ- irradiation to PE and PP leads to increase of electrical strength E_{st} [1-3], change of dielectric characteristics tg δ, ε charge state and conductivity [4], mechanical strength of PE and PP films. These changes of dielectric properties of polymer is connected, in the main, with processes of stitching, oxidize, destruction turnover and unturnover processes. It should be noted, that to the kinetic and directivity of these processes can influence SMS and the crystallize regime of polymer [5]. So it is important to make more precise of role of crystals phase and separate elements of SMS of crystallites, sferolites and etc. of polymer. For example on data [6] in stitched PE treelike treks is developed along the growth of lamellae structure. However in the literature have not discussed the question about possible influence of intermediate particles - ions and radicals, formation of germinal and connected couples, volume and polarization effects to the electrophysical and exploited properties of PE and PP. It is studied insufficiently the mechanism of radiation oxidative destruction of PP, the role of between-and intermolecular stitching , excited and ion states, forming of radicals to the modification processes of structure and properties of polymers with taking into consideration of the effects of synergism and antogonic. Synergic effects were observed at radiation chemical reactions of modifications taking account of macroradicals at great pressure to PE. The study of these questions in the aspect of "structure - property- technology" has high science - practice interest . In present work it is studied the influence of crystallize regime of PE and PP to the rate of change of E_{st} and to the processes of stabilization of radicals , and correlation this processes under action of γ-irradiation.

The samples of films of LDPE and HDPE and izotactic PP with thickness of 100±3 μm were prepared from grain in the regimes of hardening (regime A) and by means of slowly cooling (regime B) of melt. The temperature of pressing under pressure 10^7 Pa for LDPE was 453 K, HDPE - 473 K, PP - 490 K. The rates of cooling at hardening in the regime B 30-35, (3 - 4) $\cdot 10^{-2}$ degree/s, correspondingly. In order to obtain high crystal samples the part of hardened samples

were thermal treatments in vacuum at temperature below T_{melt} to 10^0 during 5 hours (regime C). The irradiation of Co^{60} of films in range of doses 3-5 Mrad were carried out on RX-γ-30 preliminary pumped out up to10^{-2} atm; amplyas at 273 and 77 K. The value of $E_{st} = U_{st}/h$ were determined at 50 Hz and rate of growth of field voltage 1,5 kV. The structure of samples was investigated by the method of angle scattering of polarized light by help of laser LG-75 with λ= 6328Å, optical microscopy using microscope MIM-7 ; on DRON - 0,5 (Cu K_α γ- radiation λ= 1,54Å, with Ni filter).

In table 1 are shown the main structural parameters of samples of polyolefines with various SMS. It is seen from table, all samples of PE - B , PE-C, PP-B, PP-C have the value of density, crystallite over, and the value of T_e below in comparison with analogous values for hardened samples. Because of the presence large sferolite forming the samples of PP-B have minimum values of E_{np}.

On the fig.1 is shown the dependence of E_{st} on the close of γ- irradiation for hardened (1,4) and slowly cooled (2,5) samples of HDPE (1,2) and thermal treatment (3,6) samples of HDPE (1-3) and PP (4-6) . It's shown , that up to dose 30-50 Mrad E_{st} increases, but then slowly decreases . For the samples of PP-A , of E_{st} is 5 Mrad (curve 4). the films with developed sferolite structure have high rate of decreasing of Est under action of γ-irradiation. This essential difference of strength to action of γ- irradiation of the without sferolits and large sferolits samples of PE and PP can be connected , on the one hand, with difference rates of proceeding of radiation-chemical processes (stitching, destruction, forming of radicals), on the other hand, with

Table 1. Structure parameters of PE and PP samples.

Crystallize regime	Size of sfe-rolites, μm	Density kg/m^3	Crystalinity K,%	Tc, K	tgδ at 10^{-4}Hz	ε	Est, kV/mm
LDPE-A	1	917.3	40	230	2.3	2.8	145
LDPE-B	6-9	919.1	55	226	2.4	2.6	140
LDPE-C	1	922.3	60	227	2.4	2.5	156
HDPE-A	3-5	932.2	58	228	2.4	2.4	145
HDPE-B	12-16	958.0	72	222	2.5	2.5	140
HDPE-C	3-5	945.0	65	224	2.5	2.5	155
PP-A	Not Obs.	899.5	48	270	2.2	2.4	145
PP-B	Not Obs.	910.3	70	257	2.3	2.5	50
PP-C	150	905.0	65	266	2.3	2.4	160

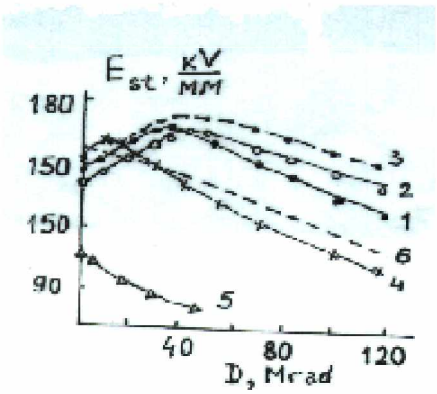

Fig.1. Dependence of electrical strength on dose of γ-irradiation for hardened (1,4), slowly cooled (2,4) and thermal treatment (3,6) HDPE (1-3) and PP (4-6) films.

peculiarities of influences SMS to the rate and direction of this processes. At small doses, as seen, predominant the processes of forming cross-stitching second crystallization and forming of free radicals, which had to increase $E_{st.}$ At the doses over 50 Mrad in PE and PP primary role begin to play the radiation - oxidation processes of destruction of macromolecules with the result that E_{st} begins to decrease. It's important to study temperature dependence's of Est (T) of irradiated PE films with different SMS. Is established that HDPE films irradiated at a doze 40 Mrad in dependence E_{str} (T) consists of two linear sites. These dependence's have two linear part, first - up to temperature 343 - 353 K, where Est decreases insignificant , second - where Est decreases with high rate. It is characteristic, that the irradiation of films of PE leads to growth thermalstability of polymer about 10 -15^0, and more stable are the samples of HDPE - B obtained slowly crystallization. The analogous results were obtained also for LDPE. Besides the B samples obtained by isothermal treatment of hardened samples, which led to increase of crystallites , also were more thermal stable after preliminary irradiation by dose of 40-50 Mrad.

The change of value tg δ and ε after γ-irradiation in vacuum shows, that for PE takes place at first increasing of tgδ which some house later is restored at the irradiation in air it's observed unreversible increasing of tg δ and ε at temperature range 385-395 K. (the begin of α relaxation processes), and higher value of tg δ obtained for hardened PE and PP films. Up to present time it have been suggested the different mechanism of changing of electrophysical, strength properties of polyolefines, including turned and unturned processes at the action of γ-irradiation [5,6] , at the same time , it is known, that in initial step of loss of strength of polymer develop the processes radical formation exiting molecules, ions which lead to unreversible changes in structure of polymer and to its degradation . We studied the processes of formation , stabilization and destruction of "physical" and "chemical" kvazistable radicals in PE and PP at γ-irradiation and their nature and concentration dependence on SMS of polymer, in order to reveal their possible roles in a change of electric strength .

In table 2 are lead the values of doses D_{30} concentration of kvazistable radicals [R] at which Est decreases to 30% of initial value.

From table 2 follows, that the thermal treatment of PE and PP hardened films leads to growth of radicals kvuzistable at 293K. At the same time, it is observed higher values of D_{30}, i.e. it's observed the correlation between increasing of E_{st} and quantity kvazistable at 293 K radicals. In case of PP-B, in spite of remain at 300 K stable radicals (table 2) of high concentration the values of E_{st} are minimum . This fact is connected with presence of large sferolites in this samples. From table 2 also seen, that thermal decrease of coefficient (β/α) i.e. the process of stitching takes place mainly in amorph phase or in near-surface layer of crystallites and lamellas of PE and PP. The stitching and destruction processes in initial time of γ-irradiation begin with oxidation of first macroradicals with forming of oxygen containing groups. In PE containing allil radicals at oxidation is formed 12 carbonyl and 5 hydroxyl groups for one macroradical [7]. At great doses ($\geq$ 30-50 Mrad) with oxidation destructive process on [7,8] can take place also the oxidize macroradicals captured electrons that leads to destruction radicals traps and liberation electrons on scheme [9]

Table 2. The values of doses D_{30} (Mrad), $[R]10^{18}$ spin/g at 293K, relation of probability of destruction β and stitching α (β/α)

Crystallize regime	LDPE			HDPE			PP		
	D_{30}	[R]	β/α	D_{30}	[R]	β/α	D_{30}	[R]	β/α
A	130	9.0	0.3	140	9.2	0.3	85	8.1	0.75
B	150	12.2	0.28	165	10.4	0.25	10	8.0	0.62
C	135	11.4	0.26	150	12	0.27	85	10.3	0.6

$$R^- + O_2 \rightarrow ROO^{\bullet} + e^- \qquad (1).$$

The liberated electrons , as seen , are one of causes decreasing Est at great doses. If the rate of reaction (1) exceeds the rate of capture reaction of stabilized electrons by free radicals on scheme

$$R^0 + e^- \rightarrow R^- \qquad (2),$$

Then it is observed the growth of E_{st}.

On atom-molecular level, the growth of E_{st} of polyolefines under γirradiation at small doses (for PE this dose is 40-50 Mrad, with for PP-up to 5 Mrad), is explained with the processes of between molecular stitching and the capture process of liberated electrons by macroradicals on the reaction (2). So, the reaction (2) leads to an additional decrease of quantity of charges, delay avalanche growth of charges, which proceeds to break-down of samples.

To the use of assumed mechanism in the process of electrical strength on the reaction (2) shows the data of work [10], where was shown for HDPE films (Marlex-6050) with increasing of concentration of radicals gradually decrease the concentration of stabilized electrons. The maximum concentration of electrons ($N=4.2\cdot10^{16}$ electron/g) is obtained at dose of irradiation $3\cdot10^{19}$ eV/g (40 Mrad), the same values of dose of irradiation corresponds to high values of Est of HDPE films (fig.1.). For PP films this dose is up to 5 Mrad.

It should be noted, that it's exist other processes leading to a change Est tg δ and ε of polymer both in the field of radiation and after p-irradiation. These processes are formation of different groups oxygen containing, plastification of polymer because of liberating gas products of radioliz, intermolecular stitching It is important to note, that offered by us the interpretation about participant of kvazistable at a 293K radicals at a change of E_{st} on reaction (1) and (2) has peculiarity, to which essentially influence SMS and condition of crystallize of PE and PP.

The change of values of tg δ and ε of PE under the action of γ-irradiation connected together oxidation with formation of peroxide radicals [6] The role SMS and conditions of thermal treatment of polymer at radiation modification PE and PP consists in that, the samples hardened more underwent to a change of structure and properties at p-irradiation. With a growth of part of crystallite phase at a thermal treatment increases the concentration of kvazistable at 293K radicals and on the mechanism of reaction (2) E_{st} of PE and PP films increases.

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