

Chapter 13

**THE MECHANISM OF INHIBITION
THERMOOXIDATION DESTRUCTION OF PBT BY
POLYMER AZOMETHINES**

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ABSTRACT

All possible mechanisms of inhibition of thermooxidation destruction of polybutylterephthalate by polyazomethines on basis of triarylmethane line diamines have been examined. The dependence of stabilizing properties of polyazomethines from their chemical structure and molecular mass has been shown.

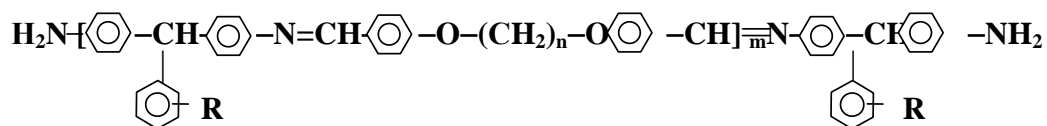
Keywords: polybutylterephthalate, stabilization, mechanism, polymer azomethines.

It has been mentioned before that [1] there are potential reactivity centers at synthesized polyazomethines (PAM). Each of them can take part in radical processes, which are a part of summary thermooxidation destruction of: polybutylterephthalate (PBT), which acts mainly according to chain-radical mechanism.

It is important contribution of azomethines groups of these PAM into inhibition of thermooxidation destruction of PBT deserves attention. Particularly inhibiting ability of such compounds is stipulated by conjugate effect –CH=N- bonds [2]. The mechanism of action –C=N- bonds consists of the following: π -electrons of these systems are clever to turn into higher energetic level when activated, which can effectively accept free radicals. The acceptance of free radicals grow especially at high temperatures with help of –CH=N-bonds.

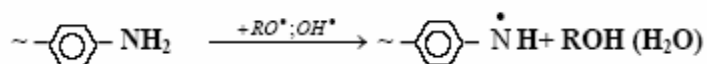
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Next reactivity central of PAM, which is clever to inhibit radicals processes is end amino groups:



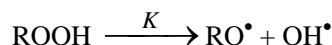
where, R- H; CH₃; NO₂. n=4,6,8,10.

The mechanism of their action is as follows. Firstly, it is possible formation of complex with transfer of charge between aromatic nucleus of inhibitor and peroxide radical, which is responsible for development of oxidative processes [3]. In consequence of destruction of this complex molecular products are formed. Secondly, another mechanism, which is more investigated is a process of inhibition, which accompanied by isolation of hydrogen from aminogroup on scheme[3,4]:



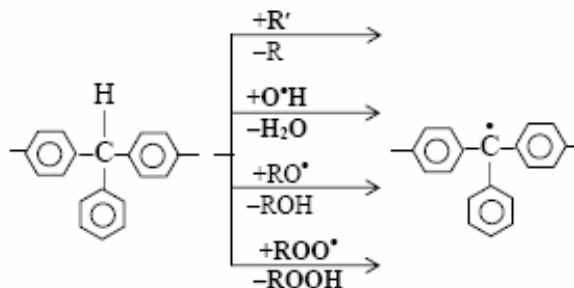
During this process a new radical stabilizes thanks to its conjugation with aromatic nucleus.

Here it is important to note also, that availability of two end aminogroups with macromolecule of PAM allows to deactivate radicals in the same degree on certain mechanism, which are formed with disintegration of hydro peroxides:

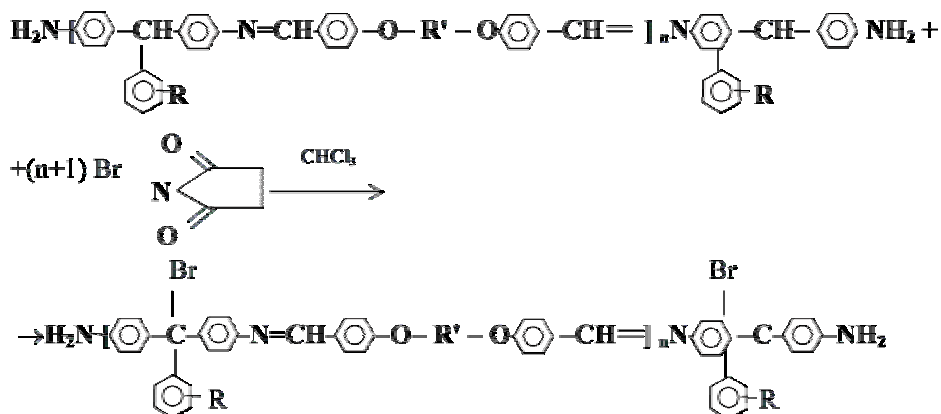


In its turn formed radicals (RO[•] and OH[•]) are deactivated by end aminogroups of PAM macromolecular according to scheme shown above.

And, finely, the third reactivity central in the molecular of PAM is a labile atom of hydrogen of triarylmethane grouping. Availability of this atom allows us to assume about possible inhibition of radical processes because of isolation this hydrogen atom according to the following:



The high reactivity of hydrogen atom of triarylmethane fragment has been proved with its act for brom atom. For this purpose bromsuccinamide, which is used as a rule, for act of mobile hydrogen atoms ore for joining to double bond was used in this work. Reaction takes place according to the following scheme:



where R=H, CH₃; R'=(CH₂)_m; m=4, 6, 8.

The formation of such compound (bromcontent PAM) was acknowledged with help ¹H-NMR(nucleated-magnetic resonance), infrared spectroscopy and element analysis.

It received triarylmethine radical is sufficiently stable[5], that is acknowledged with the help of EPR(electron-para-magnetic) (fig.1) Further life of these radicals depends on different condition. So, in consequence of high-temperature oxidation in the process of diffusion of oxygen in polymeric female triarylmethine radicals can join in reaction with it. The scheme of reaction interaction of triarylmethine radicals with oxygen can be shown like this[6]:

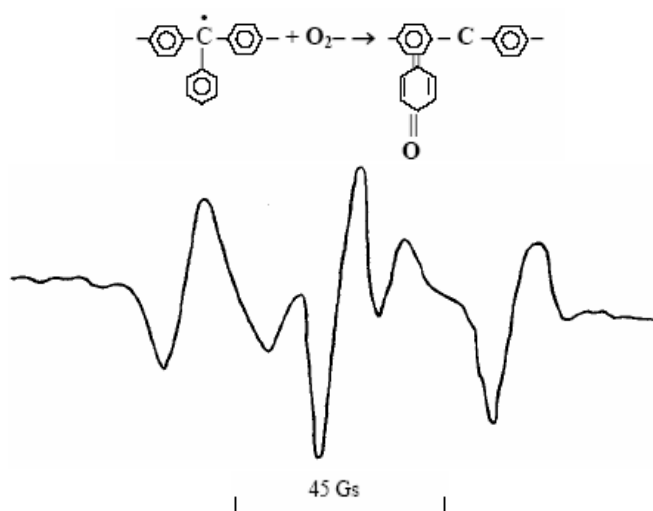
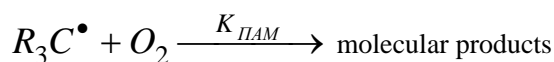
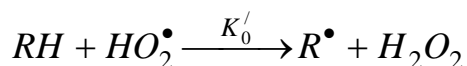
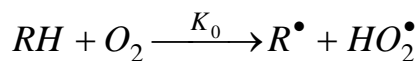


Fig. 1. Spectrums of EPR of PAM with triphnylmethane radicals in basic chain. (Gs- gauss-magnetic induction)

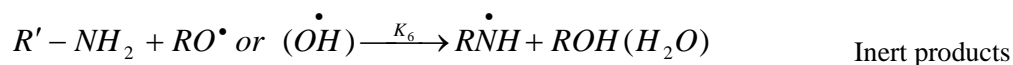
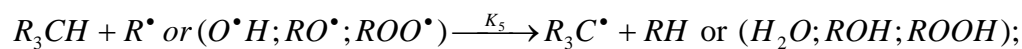
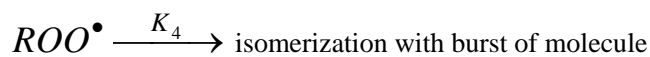
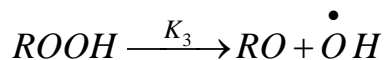
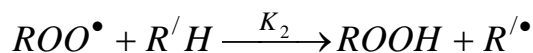
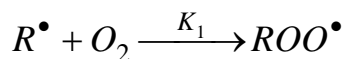
Consequently, PAM with triarylmethine fragments in basic chain can inhibit thermooxidation destruction almost on all stage of oxidation of PBT or on account of interaction with radicals, giving molecular or stable products.

According to this the scheme of process of inhibited thermooxidation destruction can be shown in the following form:

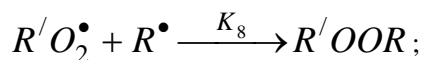
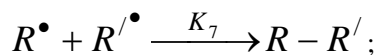
I. Inhibition on stage of chains original:

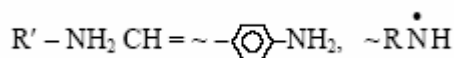
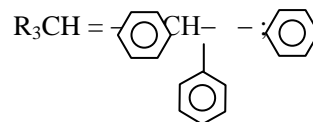
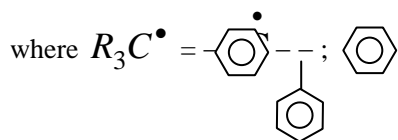
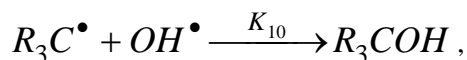
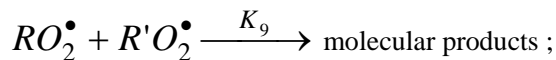


II. Inhibition on stage of chains development:



III. Precipice of chain





its radicals.

It should be noted that PAM used in work had different chemical structure. It was important to investigate influence of these structures on their stabilizing properties. So, using substituted diamines by synthesis of PAM, inhibiting activity of the previous ones lowers. In particular, PBT stabilized by PAM on basis 4,4'-diamino-4''-p-methyltriphenylmethane and 4,4'-diformyl di phenoxyhexane on significance of 2% mass loss is worse than industrial PAM on 10%. It is obviously that such conduct of this compound can be explained by big inclination to oxidation C-H-bond of methyl group. These sonfirmations indirectly confirm comparison of induction of period τ of PBT, stabilized PAM of different chemical structure. In particular, induction period τ can be valued as follows[7]:

$$\tau = f[U_0]/V_i$$

where f- stoichiometric coefficient of inhibition, that is quantity of chains, which one molecule of inhibitor tears off. It successively joins reaction of isolation; $[U_0]$ -concentration of inhibitor; V_i -speed of chains initiation.

With use of PAM with not substituted triarylmethane fragments in basic chain $f=2$ (tear off hydrogen atom, accepted of oxygen). Then, we can substitute meaning f in the initial formula and induction period can be defined as follows:

$$\tau = 2[U_0]/V_i$$

For substitution of triarylmethane fragments in basic chain f will be equal to one, most probably, as reaction with oxygen are improbably. Then:

$$\tau = [U_0]/V_i$$

From these equations we can define that PAM as polymer antioxidant on basic not substituted diaminotriphenylmethane are more effective. It can be shown as follows:

$$\tau / \tau = (2[U_0]/V_i) / ([U_0]/V_i) = 2$$

Consequently, PAM with not substituted triarylmethane fragments in basic chain surpass PAM on basic not substituted diamines two times on itself stabilizing properties.

Important significance have number of methylene groups in elementary link of macromolecule for stabilizing properties of PAM. Investigations of PBT thermofirmness, stabilized PAM with different number of methylene groups showed that with increase of "spacer" length is the result of temperature drop of 2% mass loss (fig. 2). And with change of thermofirmness of PBT+PAM compound are not with the transition from four methylene groups to six methylenes. Apparently, from standpoint of influence of the conformity facts (and as result, the change of agility and flexibility of macromolecule etc.), PAM is in more profitable position with six methylene groups then other. It causes higher stabilizing properties of this polymer.

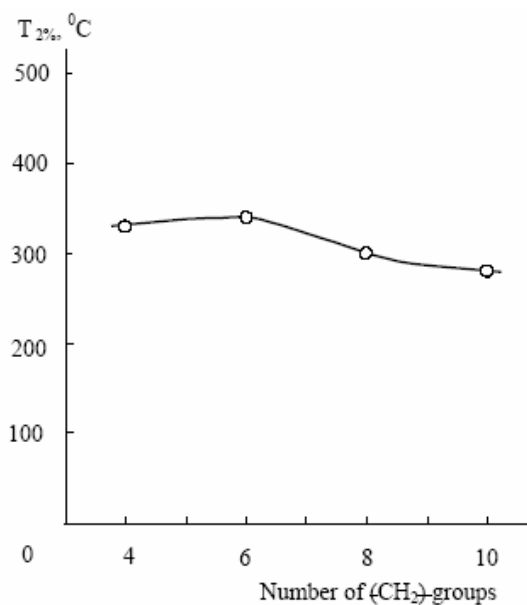


Fig. 2. The dependence T2% mass loss PBT+0,3% PAM compound from number of methylene groups in PAM

Besides, stabilizing properties of PAM are defined of molecular mass some extent. So, on the figure 3 the dependence of temperature of 2% mass loss of PBT+0,3% PAM compounds (PAM- on basic 4,4'-diaminotriphenylmethane and 4,4'-diformyldiphenoxyhexane) from molecular mass of polymer antioxidant is shown.

From figure we can see that temperature significances of 2% mass loss of PBT=PAM compound is increasing visibly with growing of molecular mass of polymer antioxidant. With this temperature drop of 2% mass loss is happening not constantly, and to the definite meaning of molecular mass of antioxidant ($\overline{M}_w=30000$). It shows that stabilizing properties of PAM are constant with arrive at $\overline{M}_w=30000$ in future. Such conduct of stabilizing properties of PAM happens because with increase of molecular mass of PAM extension of conjugated chain does not happen but weakening of delocalization of π -electrons on chain takes place. This circumstance allows PAM to have sufficiently flexible and agility

conjugated system, which together with aliphatic series creates more favorable conform conditions of interaction reaction proceed with free radicals.

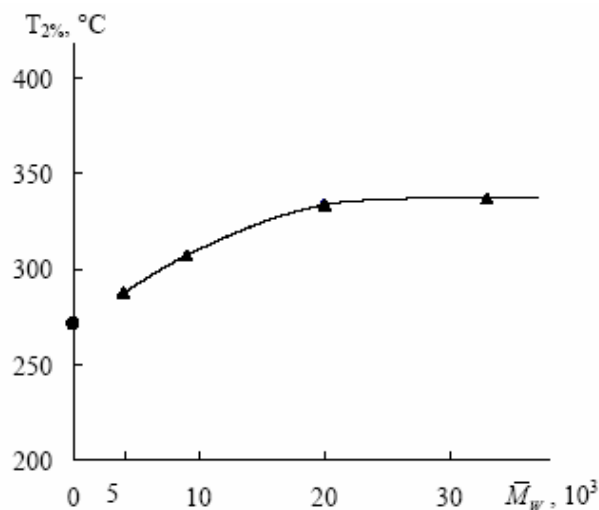


Fig. 3. The dependence $T_{2\%}$ mass loss PBT+0,3% PAM compound from polyazomethines

Thus modifying chemical structure and molecular mass of PAM meaning we can elaborate polymer antioxidant, which can effectively inhibit thermooxidation of polymers and, in particularly, PBT.

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Chapter 14

AROMATIC BLOCK-CO-POLYETHERS AS PROSPECTIVE HEAT RESISTANT CONSTRUCTIVE MATERIALS

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ABSTRACT

Aromatic polyetherketones of various structure and composition, which have good physical and chemical properties and good dissolubility in organic solvents were obtained by the method of acceptive and catalytic polycondensation. The reaction was carried out in two stages. In the first stage oligoketones of different degree of condensation were obtained on the basis of various bisphenols by the method of high temperature polycondensation. In the second stage block structure polyetherketones were synthesized with the use of the obtained oligoketones and dichloral hydrate iso- and terephthal acids by the accept-cathaletic polycondensation method. The connection between the oligoketone structure and polyetherketone properties was studied.

Key words: polyetherketone, oligoketone, heat resistance, polycondensation, viscosity, 1-2-dichloroethane, triethylamin.

During last years chemist-synthesists and technologists were interested in aromatic polyetherketones (PEK) and polyetheretherketones (PEEK). The main feature in the composition of aromatic thermoplastic polyethers - polyetherketones and polyetheretherketones is the presence of one ether and one ketone group and two simple and one ketone group in their elementary bonds [1-3]:



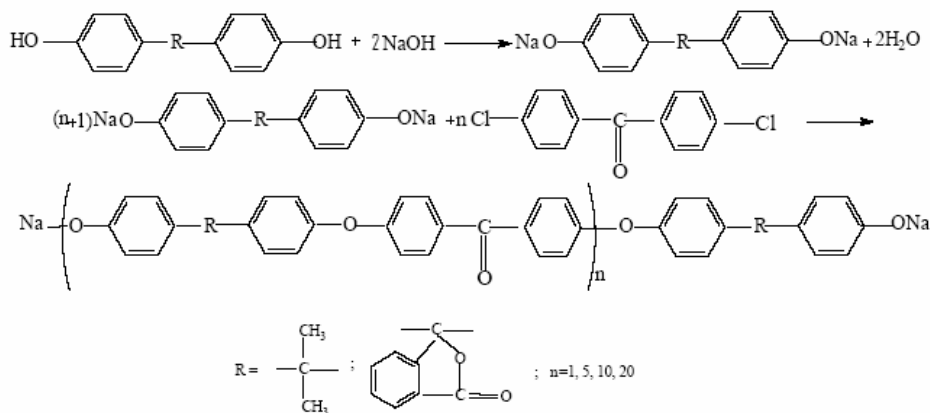
The great interest to this class of polymers is explained by unique physico-mechanical, thermal, electrophysical characteristics of the given polymers conditioned by content phenyl groups in their main chains leading to a high degree of crystallite. According to these indices they exceed considerably many other thermoplasts [4-7]. Polyetherketones are partly crystal polymers their heat resistance depends on the temperature of glass transition (amorphity) and melting (crystallite) and it rises with decrease of molecular mobility. These polymers are insoluble in common dissolvent but they dissolve in concentrated sulphuric acid, they are hardly worn out, they preserve good electric properties in a broad interval of temperature and frequency, they are easily dyed with organic and inorganic pigments and may be glued together with various substratums in conditions of previous abrasive processing of the surface. PEEKs are easily processed by pressing, casting under preassure and extrousion. They are capable of another processing. The working temperature of these polymers with glass transition temperature (t_g) 415-420 K and melting temperature (t_m) 605-610 K is 570-580 K.

Taking into account the valuable properties of these polymers the probleme of perfection of the ways of synthesis and regulation the properties of these polymers becomes actual.

There is much in the literature [8-12] on the synthesis of this class of polyetherketones on the basis of 4,4' – difluorinebenzophenon and well known bisphenols including dioxidephenylpropan and phenolphthalein. The duration of the synthesis (about 30 hours) and a high temperature (~550-570 K and higher) are serious shortcomings of these methods. Besides, even in these rigid conditions of synthesis other benzophenon halogenderivatives do not react actively. Besides, the obtained PEK and PEEK have bad dissolubilty in common organic dissolvents.

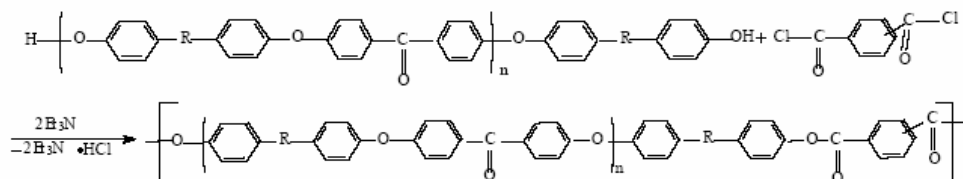
In this connection it was interesting to find the possibility of carrying out of the polycondensational process of polyether obtaining in much milder conditions with the use of 4,4' – dichlorbenzophenon. As 4,4'- dichlorbenzophenon in dimetilsulphoxide medium at 423-433 K with 4,4'- dioxidephenylpropan and phenolphthalein does not give polymers with high molecular mass the obtaining of block structure polyetherketones was used.

With that end in view oligoketones of different composition and structure were obtained for their further use in polycondensational process. Olygoketones are synthesized according to the following scheme:



After precipitation in acidulated water and drying at 373 K oligo ketones with ending hydrostrong groups were used for polymer obtaining. The structure of the obtained oligo ketones is confirmed with elementary analysis and IK-spectroscopy data. The presence of absorption stripes, which correspond to simple ether bonds, isopropiden or lactone groups and also hydroxile and ketone groups witness of poly ketone formation.

By acceptor-catalytic method of polycondensation in 1,2-dichlorethane medium block structure polyetherketones were obtained on the basis of obtained oligo ketones and dichloranhydrides of iso- and terephthal acids mixture according to the scheme:



Optimal conditions of the synthesis of these polymers were defined: 1,2-dichloroethane was a dissolvent, the temperature of the reaction was 295K, the time of carrying out was 60 minutes, concentration was 0,5m/l, triethylamin was used as a catalist. PEEKs were obtained with a quantitative output and high indices of the given viscosity ($n = 1,2-2,5$ d/g).

The composition and the structure of synthesized block structure PEEK are confirmed by the elementary analysis and IK-spectroscopy. The quantitative output and high value of the given PEEKs viscosity show indirectly the structure of the obtained polymers. Stripes of absorption are found on IK- spectra, which correspond to a simple ether bond ($920-940\text{cm}^{-1}$); to a complex ether bond ($1000-1300\text{cm}^{-1}$) to diarilketone group ($1600-1675\text{cm}^{-1}$) and stripes of absorption corresponding to hydroxide group were not found and this confirms the formation of PEEK of the expected structure.

The formation of PEEKs of the supposed structure is showed by the results of turbidimetric titration. The presence of PEEK solutions at one maximum on turbidimetric titration curves confirms co-polymer formation but not homopolymer mixture (fig. 1).

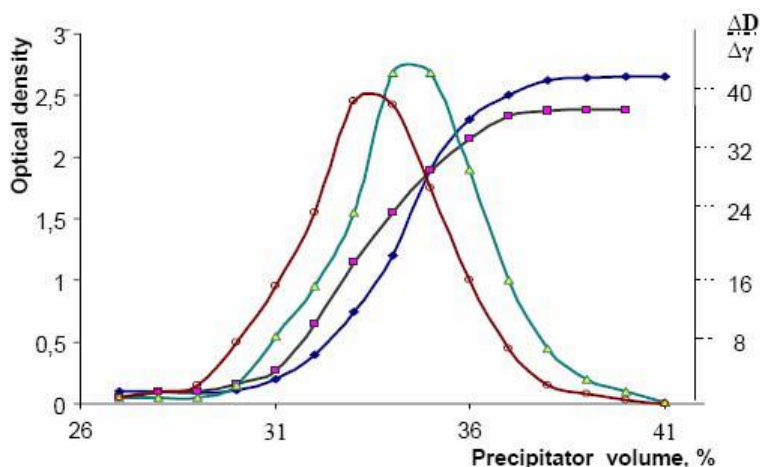


Fig. 1 The turbidimetric titration curves of PEEK obtained from OK-1D (♦, Δ) and PEEK obtained from OK-20D (■, ○); integral curves (♦, ■), differential curves (Δ, ○)

Molecular masses of the synthesized polymers, which were measured with the ultracentrifuge by the method of approximation to equilibrium, are gradient from 40 to 140 thousand.

PEEKs are characterized by a good dissolubility in chlorinated organic dissolvent. The comparison of a series of PEEKs on the basis of dian and phenolphthalein olygoketones shows a better dissolubility of PEEKs on the basis of phenolphthalein olygoketones which is explained by their structure. PEEKs on the basis of phenolphthalein have a more friable structure and this increases dissolubility of polymers.

Some properties of synthesized PEEK are shown in Table 1.

Table 1. Properties of polyetherketones

PEEK obtained from:	Intrinsic viscosity (m ³ /kg)	Glass transition temperature T _g , K	Melt temperature T _m , K	σ _p , MPa	ε _p , %	Mass loss temp., K			Oxygen Index, %
						T _{2%}	T _{10%}	T _{50%}	
OK-1D	0,24	423	513	75,0	15,0	670	733	863	3,22
OK-5D	0,19	425	525	77,2	14,1	678	740	855	3,00
OK-10D	0,16	430	545	80,1	12,5	682	765	873	3,00
OK-20D	0,13	433	563	85,4	8,2	693	813	886	2,97
OK-1F	0,25	448	568	80,1	19,9	678	780	663	3,43
OK-5F	0,18	453	578	82,4	18,0	680	780	863	3,40
OK-10F	0,14	468	590	84,4	16,0	682	785	863	3,25
OK-20F	0,12	473	603	90,0	10,3	690	790	860	3,06

where OK-1D, OK-5D, OK-10D, OK-20D are olygoketones on the basis of 4'-dioxidophenylpropane; OK-1F, OK-10F, OK-20F are olygoketones on the basis of phenolphthalein with condensation degree n=15, 10 and 20 correspondently.

The investigation of PEEK properties showed that a noticeable increase of T_g and T_f with the increase of condensation degree of initial olygoketones is observed in a series of polymers. The comparison of thermo-mechanical characteristics of PEEKs on the basis of dian and phenolphthalein olygoketones shows that an introduction of volumetric card groups as a connecting group into PEEK structure, as it was expected, raises the amorphity and fluidity of the latter.

Low temperature of glass transition and fluidity of PEEK in comparison with PEK may be explained by the presence of a big amount of flexible simple ether bonds in the chain.

The comparison of durable properties of PEEKs shows that some increase of bursting durability with the increase of length of the initial OK is observed in some PEEKs. This may be explained by the density increase in the packing of the chain in PEEK on the basis of longer OK. All the PEEKs on the basis of phenolphthalein OK are characterized by higher results of durability properties in comparison with PEEKs on the basis of dian OK.

The obtained results on heat-resistance show that PEEKs are characterized by high indices of heat-resistance in the atmosphere.

The destructive process for all the models of polymers begins at 670K and higher. The obtained series of PEEKs do not differ much, but a considerable increase of this characteristic is observed in some PEEKs on the basis of dian OK with the increase of the initial length of olygomers. This phenomenon can be explained as follows. On one hand in this line of PEEKs

a saturation of the polymeric chain with thermo-resistant simple ether bonds is observed; on the other hand, the part of non steady complex ether bonds, which is brought into the structure by the remnants of dichloranhydrates of phtalic acids, falls sharply. Besides, the density of PEEK packing increases considerably with the rise of initial olygoketone length. These three facts in total may promote such a natural increase of heat-resistance of PEEK in this line.

The study of dielectric properties of PEEKs showed that the indices of dielectric penetration (table 1) in the lines fall a little (from 3,22 to 2,97 and from 3,43 to 3,06 correspondingly) with the increase of the initial OK length, and this may be explained by the PEEKs structure and the increase of crystallite degree for PEEKs with longer OK.

The synthesized PEEKs do not differ considerably in fire-resistance and the significance of oxygen index of these polyethers lie in the interval of 30,5-32,5%, which gives an opportunity to affirm that the given PEEKs will not burn in the atmosphere.

The obtained PEEKs are examined in their resistance to aggressive environment (table 2).

Table 2. The dependence of mass change of the models on time exposition

ПЭЭК на основе:	Exposure time $s \cdot 10^5$	Weight variations (%)				
		H ₂ SO ₄ 10%	H ₂ SO ₄ 30%	HCl Conc. acid	NaOH 10%	NaOH 50%
OK-1D	0,864	0,34	0,24	0,67	0,91	0,34
	1,728	0,98	0,90	1,68	2,64	-0,60
	3,456	1,61	1,76	2,71	2,69	-1,97
	13,824	1,69	1,34	2,88	-0,13	-10,13
OK-5D	0,864	0,29	0,27	0,70	0,80	0,30
	1,728	0,64	0,83	1,55	2,33	-0,87
	3,456	1,37	1,55	2,47	2,47	-2,16
	13,824	1,40	1,43	2,60	0,34	-9,91
OK-10D	0,864	0,30	0,17	0,58	0,81	0,24
	1,728	0,55	0,77	1,50	1,94	-0,79
	3,456	1,25	1,31	2,13	2,13	-1,81
	13,824	1,29	1,30	2,21	1,07	-7,64
OK-20D	0,864	0,11	0,15	0,33	0,62	0,12
	1,728	0,38	0,40	1,11	1,55	-0,54
	3,456	0,64	0,98	1,69	1,71	-0,97
	13,824	0,69	1,09	1,71	1,56	-6,33
OK-1F	0,864	0,72	0,87	0,74	0,44	0,57
	1,728	1,34	1,30	1,75	2,00	-0,66
	3,456	2,64	2,88	3,17	-0,09	-2,90
	13,824	2,69	2,60	3,20	-1,34	-17,63
OK-5F	0,864	0,60	0,80	0,91	0,66	0,70
	1,728	1,29	1,14	1,66	2,31	-0,13
	3,456	2,47	2,73	2,98	-0,31	-3,34
	13,824	2,54	2,60	2,95	-1,57	-15,49
OK-10F	0,864	0,43	0,61	0,80	0,50	0,72
	1,728	1,13	1,10	1,55	2,13	-0,17
	3,456	2,00	1,97	2,58	0,11	-0,20
	13,824	2,05	1,99	2,60	-0,94	-10,98
OK-20F	0,864	0,24	0,50	0,71	0,63	0,34
	1,728	0,95	1,01	1,65	1,79	-0,63
	3,456	1,53	1,46	2,00	1,37	-0,28
	13,824	1,58	1,51	2,01	-0,07	-8,88

As the results show, PEEKs on the basis of dian OK demonstrate a good resistance in diluted solutions of sulphuric acid and also in concentrated hydrochloric acid. They dissolve

easily both in concentrated and diluted alkali which is connected with the presence of chemically unstable complex ether bonds in PEEKs chain. PEEKs on the basis of short OK and PEEKs, saturated with these bonds destruct faster than PEEKs on the basis of OK-20D. Besides, a low density of PEEK packing on the basis of short olygoketones promotes such speed of polymer destruction.

In 10%- sulphuric acid stabilisation of mass follows the swelling which witnesses of dissolvency absence and, what is more, the absence of destructive processes. In 30%- sulphuric acid some loss of mass of the model on the basis of OK is observed after swelling. The examining of these models in viscosity showed that this characteristic remains without change which shows PEEK dissolvency but not the destructive process. A big swelling of the models is observed in a concentrated HCl, which is connected to the activity chlorous hydrogen steam.

The above-stated properties of polyetherketones on the basis of different olygoketones and dichloranhydrate of iso- and terephthal acids mixture show that these polymers, both pure and in different compositional materials on their basis may have a wide application as heat- and chemically resistant polymer materials for constructive purpose.

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Chapter 15

POLYMERIC NANOCOMPOSITES, STABILIZED ORGANIC DERIVATIVES OF FIVE-VALENT PHOSPHORUS

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ABSTRACT

On the basis of aromatic polyesters and the block-copolyesters, and also polyethylene of high density compositions c were prepared the contents of organic compounds of five-valent phosphorus with cyclohexyl a radical at atom of phosphorus. The sizes of molecules phosphor organic compounds make $8-10 \text{ \AA}^3$, that allows them to relate to so-called nanoparticles. It is established, that investigated phosphorus organic compounds appeared effective stabilizers thermal and mechanical properties of the investigated polymers, and also good antipyrens.

Key words: aromatic polyesters; polyolefin's; phosphor organic compounds; stabilization; nanoparticles.

The basic directions of researches in the field of increase thermo stability and fire resistance of polymeric materials are replacement of antioxidizers and antipyrens from compounds of bromine (and in general halogens) and threehydrate ammonium on more effective and less carcinogenic substances. Growing cost of compounds of antimony also has resulted in necessity of their replacement on phosphorus containing antioxidizers and antipyrens which in a combination to compounds of bromine, provide synergetic effect, that is obviously expressed in oxygenic polymers.

The general tendency in the given area of a science are questions of compatibility of additives with polymers, their influence on coloring of materials, shock durability and

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adaptability to manufacture, and also development of target additives for concrete types of polymeric materials.

Nanocomposites a new class of the polymeric systems having extraordinary properties. The term "nanocomposites" means biphasic materials in which filled it is allocated in a polymeric matrix on nanolevel (10^{-9} m). Some more years back, before occurrence of the term "nanocomposites", the effects notice in polymeric compositions, additives of the most various origin containing small amounts, explained so-called «effect of small additives».

In the present work results of the researches received at studying of polymeric materials, containing some organic compounds are discussed on the basis of five-valent phosphorus in small concentration.

For an estimation of efficiency of stabilizers of polymeric materials use chemical, physical and chemical and physical-mechanical methods of research, but as most objective of them and important in the practical relation are considered physical-mechanical.

In this compounds, one axis stretching at speed of 40 mm/mines at 20⁰ C us were investigated by a method mechanical properties of film samples of polymeric compositions. They are prepared by a method pour from a solution.

Polymeric compositions on a basis the block-copolyesters contain phosphor organic compounds (PhOC) in quantity of 0,5-30,0 % from weight of polymer, in case of a polycarbonate - in quantity of 0,1-30,0 %, and in PEHD - 0,1-0,5 %.

For an estimation of influence phosphor organic compounds on mechanical characteristics of polymers were used the following parameters: a breaking point (σ_b), the maximal relative lengthening (ε_b), the module of elasticity (E), and also impact strength (A_{st}) which are designed by known techniques. Influence phosphinic acids on mechanical characteristics the block-copolyesters can be looked after on change of values of explosive durability and the maximal relative lengthening depending on concentration phosphinic acids. It is established, that the greatest explosive durability among compositions from block-copolyester on a basis bisphenol A (BCP-7D) the structure containing 1,0 % phosphinic of an acid has. The further increase of concentration PhOC results in gradual decrease of breaking strength.

For block-copolyester on a basis phenolphthalein (BCP-7F) the maximal value of explosive durability falls to a composition with the contents of 10,0 % phosphinic to acids and is equal 139,0 MPa against 116,0 MPa for initial polymer. The greatest value of the maximal relative lengthening for compositions on basis BCP-7D also falls to structure with the contents of 1,0 % phosphinic to acids. For a composition on a basis phenolphthalein the block-copolyester this maximum is observed at the contents of 0,5 % of a researched acid.

The minimal value of the module of elasticity for compositions on the basis of both block-copolyesters falls to the contents phosphor organic to compounds in small quantities. It speaks that such structures are more elastic, than initial polymers.

With the purpose of finding - out of the mechanism of strengthening influence phosphinic acids at its use in rather small amounts on mechanical properties the block-copolyesters was carried out roentgen-structural the analysis of compositions on a basis diphenylolpropane polymer with the contents of various quantities phosphinic acids. Diffractogrames were removed on $Cu_{k\alpha}$ radiation ($\lambda=1,5405 \text{ \AA}$) on device DRON-3. It was established, that on diffractogrames both initial polymer, and the compositions containing various quantities phosphinic of an acid, it is not observed crystal areas.

Proceeding from experimental results, it is possible to assume, that small quantities phosphinic acids form the most thin monomolecular layers in interstructural areas macromolecules polymers which carry out a role so-called boundary greasing. In compositions there is "colloids" a system in which PhOC plays a role falling, i.e. phosphinic the acid represents itself as some softener of interstructural action. Besides since in a molecule phosphororganic compounds are available polar P=O and P-OH - groups it, carrying out a role falling, will participate in formation of intermolecular connections with polymeric groupings polymer macromolecules. The this interaction, the is stronger, in view of role PhOC as surface-activity compounds (SAC), probably, mobility over molecules is higher than structures meaning that orientation is facilitated at a stretching, that always promotes hardening of polymer. The further increase of concentration phosphinic acids, apparently, because of stereo the difficulties caused by presence in compositions of a plenty of rather voluminous molecules PhOC, results in easing intermolecular connections in polymers therefore the composite material collapses at smaller loadings. As to compositions on a basis phenolphthalein the block-copolyester and phosphinic acids when the maximal value of a breaking point falls to 10 % the contents phosphororganic to compounds in this case, apparently, for formation of a "continuous" most thin monomolecular layer, i.e. the boundary greasing facilitating mobility over molecules of structures, it is required a lot of surface-active substance (phosphinic acids) because of less dense packing polymer macromolecule on a basis phenolphthalein.

On curve dependences of a pressure on relative lengthening for compositions on a basis diphenylolpropane polymer also at the contents of small quantities phosphinic acids there is a displacement of curves in area of high values σ_b . At transition from phosphinic acids to her potassium salt character of influence phosphororganic compounds on mechanical properties the block-copolyester does not vary. Optimum concentration are small additives potassium phosphinate. But, as against the acid, at her use potassium salts of value of the module of elasticity in all a concentration interval are lower, and the maximal relative lengthening is higher, than in a case phosphinic acids. It is possible to explain greater polarity P-O-K - bond in a molecule phosphinate, in comparison with P-O-H - bond in a molecule of the acid.

With potassium salt in comparison with the structures containing phosphinic an acid it is possible to explain some decrease of durability of compositions larger in volume of an ion potassium, than atom of hydrogen in hydroxyl to group of an acid therefore arise additional stereo difficulties. It also it is possible to explain and some increase of values of the maximal relative lengthening for the compositions containing potassium phosphinate, i.e. because of increase of volume PhOC and, apparently, its polarity, force of intermolecular interaction between molecules potassium phosphinate as SAC and polar groupings macromolecules the block-copolyesters operate on larger distances in comparison with phosphinic an acid.

Use of nickel salt phosphinic acids as the additive to the block-copolyesters brings the contribution, though and not so distinguished from other compounds of five-valent phosphorus. It, first of all, is appreciable by consideration of influence nickel phosphinate on explosive durability of compositions. For diphenylol a block-copolymer of appreciable changes, as against the compositions containing phosphinic an acid or her potassium salt, it is not observed. For phenolphthalein the block-copolyester almost in all a concentration interval value of a breaking point is lower, than at initial polymer. It, most likely, is connected to the greater rigidity macromolecules itself phenolphthalein a block-copolymer in comparison with diphenylolpropane, and also stereo the difficulties brought by phosphinate molecules of

nickel because of increase of number cycloalkyl and butoxyphenyl of groups as against phosphinic of an acid or potassium phosphinate.

As well as in a case potassium phosphinate, nickel salt phosphinic acids in small concentration raises value of the maximal relative lengthening, and the module of elasticity in all a concentration interval is lower, than size E of initial polymers.

Modifying influence nickel phosphinate on aromatic the block-copolyesters, as well as in a case with others PhOC, is more shown in relation to plastic deformation of polymers.

Phosphinate bivalent iron the block-copolyesters practically influences on mechanical properties the same as and nickel phosphinate, except for the module of elasticity - he starts to grow at the big concentration iron (II) phosphinate.

Such identity of character of influence nickel phosphinate and bivalent iron, apparently, is connected to identical assistants at cations both bivalent metals and approximately equal polarity of these molecules.

Character of influence phosphinate trivalent iron on mechanical properties the block-copolyesters practically reflects influence of other salts of bivalent metals: the tendency to reduction of explosive durability of compositions on a basis phenolphthalein a block-copolymer is evidently shown at increase of number phosphinate radicals in phosphor organically salts, that in turn depends on valency of metal. As to compositions on a basis bisphenol A the block-copolyester and iron (III) phosphinate here mechanical parameters remain on enough high level.

Research of influence phosphinic and its salts on mechanical properties of two poly-(arylsulfonoxides) block-copolymers has shown acids, that for all phosphororganic compounds by the optimal concentration their small quantities, basically up to 3,0 % are.

In view of that processing polymers is improved, and at small quantities PhOC also are considerably improved mechanical characteristics of compositions on a basis the block-copolyesters and investigated derivative five-valent phosphorus, it is possible to assume, that offered compositions can find application as high-strength constructional polymeric materials.

After change of character of influence PhOC on mechanical properties the block-copolyesters was considered at transition from phosphinic acids to its salts, changing it the quantity phosphinate groups in a molecule of derivative five-valent phosphorus, was of interest research of influence on mechanical properties of polymers of replacement hydroxyl groups in a molecule phosphine acids on the second butoxyphenyl a grouping. Appeared, that at small concentration phosphinoxyde his action on mechanical properties the block-copolyesters comes nearer to those at use as modifiers phosphinic acids and her salts.

With increase of the contents phosphinoxyde in compositions on the basis of aromatic the block-copolyesters is shown the tendency to decrease of the investigated parameters. As well as others phosphororganic compounds, phosphinoxyde is more effective in relation to BCP-7D.

In a case phenolphthalein polymer, already since 1,0 % additives phosphinoxyde, plastic deformation starts to be reduced, but mechanical characteristics remain a little bit above, than with initial polymer. The further increase of concentration phosphinoxyde in compositions results in fragile destruction of samples.

In conclusion of consideration mechanical properties of compositions on the basis of aromatic block-copolyesters and phosphinic acids and her salts, and also phosphinoxyde, it is possible to notice the block-copolyesters, that all PhOC at their use in small concentration are the effective additives raising mechanical characteristics of investigated polymers. Such

strengthening mechanical properties influence on polymers is shown more poorly in case of compositions on a basis phenolphthalein a block-copolymer. It first of all is connected to distinction in above molecules structures the block-copolyesters, caused by presence of the rests of molecules phenolphthalein in polymer on his basis.

In connection with that the stabilization considered as objects aromatic the block-copolyesters are only laboratory development was of interest to study, as the compounds of five-valent phosphorus received during researches will influence physical and chemical properties of industrial polyesters. As one of such polymers we choose a polycarbonate on a basis bisphenol A marks of the PC-3. It is established, that phosphinic the acid at her introduction in a polycarbonate does not render such appreciable strengthening influence on mechanical the characteristic of polymer as it took place in case of compositions on a basis the block-copolyesters.

On σ_b phosphinic the acid influences explosive durability of a polycarbonate practically a little though at her low concentration in compositions some increase of values of a breaking point is observed. Values of the maximal relative lengthening of compositions raise in comparison with initial polymer at use phosphinic acids up to 0,5 % a little. So, relative lengthening of a composition of the PC-3+0,5 % of phosphinic on 4,8 % is more than acid, than at an initial polycarbonate. The module of elasticity of compositions also is a little bit higher in comparison with the initial PC.

As the polycarbonate concerns to in part crystal polymers was of interest to find out influence PhOC on a degree crystallite a polycarbonate.

With this purpose in the same conditions, as for compositions on basis BCP-7D, was carried out X-ray structural the analysis polycarbonate compositions with the contents of various quantities phosphinic acids.

Compositions prepared as films a method pour from a solution in chloride methylene. It is established, that introduction phosphinic in small quantities results acids in some increase of a degree crystallite a polycarbonate. The increase of the contents phosphor organic up to 10,0 % appreciably reduces compounds crystallite polymer. The further increase of concentration practically does not render appreciable influence on a degree crystallite polymer. It is established, that on diffractograms both a clean polycarbonate, and the compositions containing various quantities phosphinic of an acid, the crystal peak is on 17° , that corresponds to the intermolecular distance equal 5,21 Å.

Proceeding from the received data it is possible to assume, that rather ineffective influence phosphinic acids on mechanical characteristics of a polycarbonate is connected to some infringement of orderliness of crystal packing macromolecules in a polycarbonate caused stereo by difficulties, voluminous molecules brought in compositions phosphororganic compounds.

It is known, that forces of an intermolecular attraction which bring the certain contribution in mechanical characteristics of polymers, operate on distance 3-4 Å. As in our case the intermolecular distance appeared little bit more than this parameter also the intermolecular attraction will be reduced a little, that, apparently, and results, along with stereo factors, to some downturn of strengthening influence phosphororganic compounds on a polycarbonate, in comparison with compositions on the basis of aromatic the block-copolyesters.

It is revealed, that at small concentration phosphinic acids plastic deformation and explosive durability of a polycarbonate remain on a high level, but the further increase of the contents phosphororganic results compounds in fragile destruction of samples.

Influence potassium phosphinate on mechanical properties of a polycarbonate, as well as in case of compositions on a basis the block-copolyesters, is more sharply expressed in comparison with influence of the acid.

The module of elasticity of compositions at the contents in them up to 3,0 % potassium phosphinate remains to higher in comparison with initial polymer, but further the module of elasticity of compositions is lower, than at a polycarbonate. Apparently, it is connected to increase of polarity phosphororganic compounds at transition from an acid to her potassium salts. Small additives potassium phosphinate raise plastic and mechanical characteristics of a polycarbonate a little.

Character of influence phosphinates bivalent metals (nickel and iron) on mechanical properties of a polycarbonate is practically identical: with increase of concentration of salts value of a breaking point tends to decrease, and the maximal relative lengthening raises at small quantities phosphinates a little; the module of elasticity of both systems gradually raises. Such identity of character of influence of these two salts on mechanical properties of a polycarbonate, probably, is connected to an identical structure of molecules phosphinates.

Phosphinate trivalent iron monotonously reduces explosive durability of a polycarbonate, and value of relative lengthening at break for the contents of salt in quantity of 5,0 % practically does not vary, but further is reduced. The module of elasticity of salt at small concentration varies also a little, and at increase of quantity phosphinate iron (III) this parameter grows.

Introduction phosphinoxyde in a polycarbonate reduces mechanical characteristics of polymer a little. It is possible to explain it to that given phosphororganic compounds less, apparently, as least polar of all investigated compounds of phosphorus, forms (in comparison with phosphinic an acid and her salts) intermolecular bonds with macromolecules a polycarbonate, but at the same time molecules phosphinoxyde have rather big volume and they can represent itself as loosening macromolecules some polymer of the agent therefore the intermolecular distance is a little increased, as results in some decrease of mechanical properties of compositions in comparison with initial polymer.

In connection with that in the industry the stabilized variant of a polycarbonate is issued, and as the stabilizer against destruction of thermo oxidation apply derivative trivalent phosphorus - three(p-nonylphenyl)phosphit (Polygard), was of interest to study, as influences Polygard on mechanical properties of a polycarbonate and to compare him to character of influence investigated by us phosphor organic compounds. With this purpose, and also for revealing an opportunity of display synergetic effect at simultaneous presence at compositions Polygard and synthesized phosphororganic compounds, we investigated mechanical properties of the industrial stabilized polycarbonate with the contents of 1,0 % Polygard, and the compositions containing derivative trivalent phosphorus and investigated compounds of five-valent phosphorus in quantity of 0,1-30,0 %. It is established, that the stabilized variant of a polycarbonate containing Polygard, has the worse parameters mechanical characteristics in comparison with not stabilized and modified offered PhOC (Table. 1).

Table 1. Mechanical properties of compositions on the basis of a polycarbonate and phosphor organic compounds

No	Composition	σ_b , MPa	ε_b , %	E, GPa
1	Polycarbonate (PC)	88	17,6	1,6
2	PC + 1,0 % Polygard	82	14,7	2,3
3	PC + 0,5 % phosphinic acids	108	34,4	2,0
4	PC + 1,0 % potassium phosphinate	101	62,1	1,5
5	PC + 3,0 % nickel phosphinate	104	56,4	1,5
6	PC + 10,0 % phosphinate Fe (II)	103	51,6	1,6
7	PC + 0,1 % phosphinate Fe (III)	155	91,4	1,8
8	PC + 1,0 % phosphinoxyde	94	14,7	2,1

Besides apparently from tab.1, small concentration phosphororganic compounds render appreciable improving effect at their sharing with Polygard. The highest parameter of mechanical properties from all investigated compositions with phosphororganic compounds has trivalent iron phosphinate at his use in quantity of 0,1 %.

Thus, comparison of compositions on the basis of the industrial polycarbonate, containing simultaneously offered by us phosphororganic compounds on the basis of five-valent phosphorus and industrial stabilizer Polygard, allows to approve, that composite materials with improved mechanical properties are received.

In connection with that the stabilization used as objects aromatic the block-copolyesters have high impact strength (in particular for BSP-7D it not less than 117-118 kJ/m²), were of interest to determine character of influence received phosphororganic compounds on impact strength the block-copolyesters. With this purpose compositions on a basis bisphenol A a block-copolymer and phosphororganic compounds in quantity of 1,0 % from weight of polymer were prepared. The choice of such concentration phosphororganic compounds is caused by the optimal contents of these compound by consideration quasi static mechanical properties of compositions. It is established, that investigated phosphororganic acids reduce impact strength of polymer. The highest values of impact strength were received for compositions with the contents) of salts of iron and phosphinic acids. It is interesting to note, that among salts the most effective appeared derivative cyclohexyl phosphonic acids. So, the composition with the contents nickel hydrocyclohexylphosphonate has shown value $A_{st}=107$ kJ/m², with the contents bivalent iron hydrocyclohexylphosphonate - 115 kJ/m², and compositions with trivalent iron cyclohexylphosphonate had $A_{st}=136$ kJ/m².

To one of the major factors determining resistance of polymers to shock loadings, plasticity of polymeric materials and improvement of this characteristic of polymers concerns will promote increase of shock durability of samples. Told practically proves to be true the data received as a result of research of influence PhOC on impact strength the block-copolyester on a basis diphenylolpropane, and also industrial polyarilate DV- salts are more effective modifiers by way of improvement of shock durability and as it was shown above, plasticity of polymers.

The difference in the mechanism of influence phosphororganic compounds on mechanical behavior of polymers, most likely, is connected from them above molecule by structure. Block-copolyester BSP-7F it is worse "diphenylol" than a block-copolymer on mechanical to characteristics for this reason.

It is necessary to allocate the following factors influencing properties of a composition. Except for above molecule structures (AMS) of initial polymer, it is chemical structure PhOC, its volume, a degree of polarity and a way of distribution of the additives- modifiers, changes of defectiveness influencing a degree AMS of polymer. Besides it is necessary to take into account that circumstance, that the mentioned above factors can render various influence on mechanical behavior of a composition at different stages of deformation.

In case BSP-7D (to a lesser degree BSP-7F, meaning) introduction PhOC in small quantities results initial parameters to hardening a block-copolymer, is increased σ_b and ϵ_b . The module of elasticity simultaneously decreases. At an explanation of such character of change of mechanical properties it is necessary to mean, that these characteristics of polymers are determined by the total contribution as inside, and inter chain interaction. Their parity depends and is determined as actually by deformation (size ϵ), and a temperature-time mode mechanical loading. In conditions quasi static the tests used in the present work, speed of deformation is sufficient smaller ($\sim 10^{-2}-10^{-4} \text{ c}^{-1}$) to consider, as inside, and inter chain interaction "have completely time" to realize the influence on mechanical behavior of polymer. The above efficiency of intermolecular interaction, the more its contribution to size of the module of elasticity and rigidity as a whole a composition at all stages of deformation. We shall specify, that the module of elasticity is determined on an initial site of the diagram " σ - ϵ " at very small values of lengthening. For this reason the assumption of role PhOC as SAC and «boundary greasing» is quite allowable. The second mechanism - strengthening of intermolecular interaction as each of considered phosphororganic compounds to some extent is active in this sense in parallel operates.

In view of small contents PhOC and, all the same, reduction of size E, it is logical to assume, that in this concentration interval and in the field of deformations where the module of elasticity is determined, the contribution to its formation of the first mechanism prevails. In process of development of deformation «boundary greasing» facilitates reorganization AMS of a block-copolymer resulting in its steadier to destruction to structure. At the deformations close to ϵ_b , on durability all mentioned above factors have to the full an effect. Influence of polarity PhOC in this case is evidently shown: the maximal values of a breaking point decrease in process of its growth. The same dependence σ_b and from volume of molecules phosphor organic compounds. These experimental facts confirm the assumption that at small contents PhOC the mechanism of interstructural plasticization the block-copolyesters prevails. Comparing BSP-7D and BSP-7F, influence and mechanisms of influence on mechanical behavior BSP-7F of small quantities PhOC more ambiguous is possible to come to a conclusion, that.

Decrease with increase of contents PhOC mechanical parameters the block-copolyesters speaks redistribution of the relative contribution of plasticization and strengthening of intermolecular interaction (IMI) both in durability, and in the module of elasticity. Thus it is important to note, that phosphinic an acid and phosphinoxyde at high contents render more effective complex influence on mechanical behavior of compositions: rather high mechanical parameters and growth of the module of elasticity. General, though and in a different degree expressed, result - reduction ϵ_b , and influence on parameters of plasticity of polymer.

Loosen structures of blocks-copolymers can occur at increase of contents PhOC on various mechanisms. However it is obvious, that efficiency of the additive now in the greater degree is determined, except for structural features, volumetric characteristics (steric the

factor), activity phosphor organic compounds in relation to IMI. In this respect higher efficiency of some PhOC can be caused by an optimum parity of parameters of the additive and distribution of free volume in polymer. It is possible to assume, that the sizes appropriate of $\sim 150\text{-}250 \text{ sm}^3/\text{mol}$ – Van der Waals to volume (V_w) phosphinic acids and phosphinoxyde are such. Similar assumptions can be considered and concerning polarity phosphor organic compounds. That strengthening of efficiency IMI ambiguously influences on mechanical properties of compositions that is visible from comparison of some compositions on basis BSP-7D and BSP-7F proves to be true also.

In a polycarbonate the free volume is less, than in the block-copolyesters. On the other hand is in part crystal polymer with rather crystal high degree. In this case again it is necessary to find an optimum parity of properties of additive PhOC (for example, its volume) with distribution of free volume in polymer. Besides the polycarbonate is: more loosen packing and denser packing areas of an amorphous part, crystal and inter crystal areas. Therefore is unequivocal to determine the mechanism of influence PhOC on properties of a polycarbonate more difficulty. For example, the size dense packing areas of the PC is estimated by different authors, different experimental methods in limits $30\div 100 \text{ \AA}$ besides, that its volume fraction of $\sim 50 \%$. On the other hand molecules phosphor organic additives ($V_w \approx 8\text{-}10 \text{ \AA}^3$) borrow, most likely, free volume in more loosen packing parts of amorphous area and, with smaller probability, inter crystal areas.

In view of told above, it was possible to expect less effective strengthening influence of all phosphor organic compounds on a polycarbonate, and laws at his studying can be others, is especial regarding influence of salts of metals phosphinic acids. Here the combination of small concentration and properties PhOC (for example,) has given some salt of trivalent iron the best result.

It is necessary to note, that shock tests differ that in conditions of high-speed deformation the relative contribution to durability and plasticity of effective intermolecular interaction sharply grows. Here it is necessary to take into account that impact strength A_{st} - the integrated power characteristic of durability of polymer or a composition, showing power expenses for destruction, σ_b and E - power.

Results of shock tests (A_{st}) in very big degree depend on plasticity of samples. On the other hand, in plasticity brings the contribution not all free volume, but only his "effective" part. Efficiency of influence of additives PhOC on shock durability depends, thus, on a parity of the sizes of a molecule of the additive with "effective" free volume of polymer and, thus, from as far as concentration PhOC is picked optimum up. In a case block-copolyester BSP-7D in conditions of shock tests are salts of iron and phosphinic acids; for the PC-trivalent iron phosphinate.

One of the basic operational characteristics of polymeric materials is shock durability in this connection structures on the basis of polyethylene of high density (PEHD) are investigated by a technique of shock tests on Sharpy.

Experimental installations with which help polymeric systems are investigated represents pendulum koper UT-1/4, supplied by the piezoelectric gauge of loading, the signal with which moved directly on remembering oscillograph of model from C 8-12. Character of influence PhOC on physical-mechanical properties PEHD in conditions shock loading estimated under such characteristics, as A_{st} , E, ϵ_b , σ_b , σ_{ce} and ϵ_{ce} which values are calculated with use of settlement formulas: $A_{st} = W_{st}/B(D-a)$; $E = (P \times L^3)/4\delta B (D-a)^3$; $\epsilon = [6\delta(D-a)]/L2$; $\sigma_b = 3P_{st}L/2B(D-a)^2$; $\sigma_{ce} = 3P_bL/2B(D-a)^2$, where A_{st} - impact strength; W_{st} - energy of

destruction of a sample; B- width of a sample; D- thickness of a sample; and - size of a cut; P - loading on an initial linear site of the diagram; δ - a deflection of a sample in its middle; L- distance between support of a pendulum; ϵ_b - deformation of destruction; σ_{ce} - a limit of the compelled elasticity; ϵ_{ce} - deformation of the compelled elasticity; σ_b - a breaking point; P_{ce} - loading on diagram P-t (time) appropriate to macroscopically compelled elasticity; P_{st} - loading of destruction.

The received results testify that phosphinic an acid and her salts render plastically influence on polyethylene of high density. To draw such conclusion some increase of impact strength allows at simultaneous decrease of the module of elasticity and increase of relative deformation at destruction of samples.

All phosphor organic compounds appeared practically more effective additives to polyethylene in comparison with the industrial stabilizer polyolefin's Irganox-1010.

At the same time it is necessary to note, that phosphinic acid salts reduce a breaking point whereas the acid practically does not render essential influence on the given parameter a little.

Character of change A_{st} at introduction in polymer PhOC correlates with change of values of a pressure of the compelled elasticity. The given fact can speak about some increase of intermolecular interaction in polymer, that, apparently, is connected by that phosphor organic compounds, occupying "free" volumes in macro chain, the polar groupings strengthen intermolecular interaction a little.

Such behavior of modifiers should result in some improvement of orderliness in macro chain, that practically and occurs, if it to judge on increase of a degree of crystallinity (α_m) (Tables 2, 5). Thus the degree of crystallinity raises with transition from an acid to its salts, i.e. with increase of polarity phosphor organic the modifier.

By consideration of character of influence cyclohexyl phosphonic acids, her potassium salts, and also phosphine oxide on physical-mechanical properties PEHD in conditions shock loading it is noticed (Tables 3, 4), that the behavior of data PhOC practically does not differ from those phosphinic acids and its salts.

The results received at research of character of influence phosphor organic of compounds on physical-mechanical characteristics PEHD in conditions shock loading, allow to assert with the big share of reliability, that irrespective of molecular weight PhOC show plastic property, i.e. the mechanism of influence of modifiers, probably, does not vary. It is necessary to note, that salts phosphinic acids reduce value σ_b polyethylene whereas the acid practically does not render essential influence on the given parameter a little. Character of change of impact strength PEHD at introduction in him PhOC correlates with change of values of a pressure of the compelled elasticity that can speak about some increase of intermolecular interaction in polymer. It, apparently, is connected by that phosphor organic compounds occupying free volumes in macro chain, the polar groups strengthen intermolecular interaction a little. As confirmation of such assumption that circumstance can serve, that at Van der Waals volume (V_w) polyethylene in $20,6 \text{ sm}^3/\text{mol}$, found on a known technique the share of free volume (V_E) makes $7,6 \text{ sm}^3/\text{mol}$ and shares V_w phosphor organic compounds, their falling investigated dosages (0,05-0,5 %), make only $0,005\text{-}0,088 \text{ sm}^3/100 \text{ r}$ polymer. The effect of small additives, probably, is connected by that at such dosages PhOC they in the optimum image "find room" in free volume of polymer, though own Van der Waaloves volumes phosphor organic compounds are greater ($58,1\text{-}423,0 \text{ sm}^3/\text{mol}$), than at polyethylene. For the industrial stabilizer polyolefin's Irganox-1010 value V_w even above also makes $711,1 \text{ sm}^3/100 \text{ r}$ polyethylene.

Table 2. Influence phosphor organic modifiers on density and degree of crystallinity PEHD

No	Composition	d, g/sm ³	α_m
1	PEHD	0,951	0,701
2	PEHD+0,1 % Irganox-1010	0,958	0,746
3	PEHD+0,05 % phosphine acids	0,952	0,707
4	- « - + 0,1 % - «-	0,957	0,739
5	- « - + 0,3 % - «-	0,951	0,701
6	- « - + 0,5 % - «-	0,957	0,739
7	PEHD+0,1 % - « - + 0,1 % Irganox-1010	0,957	0,739
8	PEHD + 0,05 % nickel phosphinate	0,952	0,707
9	- « - + 0,1 % - «-	0,959	0,752
10	- « - + 0,3 % - «-	0,955	0,727
11	- « - + 0,5 % - «-	0,957	0,739
12	PEHD+0,1 % -«-+ 0,1 % Irganox-1010	0,955	0,727
13	PEHD + 0,05 % iron (II) phosphinate	0,958	0,746
14	- « - + 0,1 % - «-	0,954	0,720
15	- « - + 0,3 % - «-	0,956	0,733
16	PEHD + 0,05 % iron (III) phosphinate	0,957	0,739
17	- « - + 0,1 % - «-	0,960	0,758
18	- « - + 0,3 % - «-	0,952	0,707
19	- « - + 0,5 % - «-	0,958	0,746

Note: the degree of crystallinity α_m is designed proceeding from density

Table 3. Physical-mechanical properties of compositions on a basis PEHD and PhOC in conditions of shock test

No	Composition	A _{st} , kJ/m ²	E, GPa	σ_b , MPa	ε_b , %	σ_{ce} , MPa	ε_{ce} , %
1	PEHD	11,0	1,06	21,1	5,7	27,9	4,8
2	PEHD+0,1 % Irganox-1010	12,8	1,55	18,6	6,4	30,0	3,6
3	PEHD+0,05 % phosphinic acids	22,6	0,81	19,9	7,9	29,1	4,7
4	- « - + 0,1 % - «-	18,5	0,79	17,8	8,3	29,3	4,6
5	- « - + 0,3 % - «-	18,8	0,79	18,1	9,1	29,7	5,1
6	- « - + 0,5 % - «-	11,5	0,94	20,2	6,4	28,9	4,4
7	PEHD+0,05 % nickel phosphinate	14,6	0,85	15,9	9,0	25,5	4,2
8	- « - + 0,1 % - «-	17,9	0,89	14,1	10,6	26,9	4,6
9	- « - + 0,3 % - «-	22,1	0,85	12,8	8,3	26,9	4,7
10	- « - + 0,5 % - «-	17,4	0,72	17,5	7,9	27,1	5,3
11	PEHD+0,05 % iron (II) phosphinate	12,8	0,85	16,0	7,9	28,7	4,3
12	- « - + 0,1 % - «-	11,6	0,85	16,3	7,7	27,1	4,7
13	- « - + 0,3 % - «-	9,8	0,77	12,0	7,5	23,9	4,5
14	PEHD+0,05 % iron (III) phosphinate	13,3	0,77	11,2	8,4	23,9	4,7
15	- « - + 0,1 % - «-	17,6	0,82	15,9	8,1	24,7	4,5
16	- « - + 0,3 % - «-	14,4	0,78	12,5	9,4	21,0	4,7
17	- « - + 0,5 % - «-	6,4	0,62	13,9	8,3	23,0	4,9

It is necessary to note, that polyethylene - more "simple" structure, than the block-copolyesters and a polycarbonate, with the big factor of packing, besides in part - crystal. His studying is complicated that amorphous his phase at room temperatures no glassing, and at shock tests is necessary to bring artificial defect - a cut to have an opportunity supervision of the full diagram of destruction in coordinates "force-deformation".

Table 4. Physical-mechanical properties of compositions on a basis PEHD and PhOC in conditions of shock test

No	Composition	$A_{st}, KJ/m^2$	E, GPa	σ_b , MPa	ε_b , %	σ_{ce} , MPa	ε_{ce} , %
1	PEHD	11,0	1,06	21,1	5,7	27,9	4,8
2	PEHD + 0,1 % Irganox-1010	12,8	1,55	18,6	6,4	30,0	3,6
3	- « - +0,05 % phosphinic acid	19,5	0,82	14,1	9,5	28,1	5,0
4	- « - + 0,1 % - «-	16,3	0,90	18,6	7,6	28,5	4,6
5	- « - + 0,3 % - «-	18,8	0,81	17,1	7,6	28,5	4,7
6	- « - + 0,5 % - «-	20,0	0,87	16,5	8,7	28,5	4,8
7	- « - +0,1 % -«-+ 0,1% Irganox	22,6	0,85	16,2	8,3	28,7	4,8
8	PEHD+0,05 % potassium monophosphonate	20,0	1,05	29,9	5,1	30,6	3,9
9	- « - + 0,1 % - «-	19,3	0,85	16,0	8,1	27,9	4,9
10	- « - + 0,3 % - «-	15,0	0,82	16,0	7,5	27,1	4,8
11	- « - + 0,5 % - «-	12,1	0,57	18,7	6,9	27,3	4,7
12	- « - +0,1 % -«-+ 0,1 % Irganox	23,1	1,03	15,2	9,8	30,4	5,3
13	PEHD+0,05 % potassium phosphonate	20,5	0,92	16,0	8,6	25,4	4,1
14	- « - + 0,1 % - «-	19,0	0,85	18,0	7,6	26,7	4,6
15	- « + 0,3 % - «-	15,5	0,91	17,3	8,4	26,7	4,8
16	- « + 0,5 % - «-	15,4	0,82	18,3	8,5	27,9	4,6
17	- « + 0,1 % -«-+ 0,1 % Irganox	19,5	0,84	15,7	7,9	26,3	4,6
18	PEHD+0,05 % phosphinoxyde	21,8	0,90	12,8	8,8	27,1	4,6
19	- « - + 0,1 % - «-	20,7	0,90	13,3	9,5	28,5	4,7
20	- « + 0,3 % - «-	18,2	0,80	16,0	7,9	26,9	5,2
21	- « + 0,5 % - «-	19,7	0,85	18,3	7,9	27,1	4,4
22	- « + 0,1 % -«-+ 0,1 % Irganox	17,4	0,94	16,5	7,7	27,7	4,4

Therefore it is necessary to take into account not only structure, volume, properties of additives PhOC, but also as far as the put cut (~5 mm) is close or far from structural defect PE. By influence on σ_b , the critical border between PhOC in sense of their influence on defectiveness of a matrix passes between phosphinic an acid and her salts. The integrated estimation of influence PhOC on mechanical properties of polyethylene at impact results in the same conclusions, as earlier, in case of consideration the block-copolyesters and a polycarbonate.

Table 5. Influence cyclohexyl phosphonic acids and her derivatives on density and degree of crystallinity PEHD

No	Composition	d, g/sm ³	α_m
1	PEHD	0,951	0,701
2	PEHD + 0,1 % Irganox-1010	0,958	0,746
3	- « - + 0,05 % phosphonic acid	0,954	0,720
4	- « - + 0,1 % - « -	0,946	0,669
5	- « - + 0,3 % - « -	0,956	0,733
6	- « - + 0,5 % - « -	0,951	0,701
7	- « - + 0,1 % - « - + 0,1 % Irganox-1010	0,954	0,720
8	PEHD + 0,05 % potassium monophosphonate	0,957	0,739
9	- « - + 0,1 % - « -	0,958	0,746
10	- « - + 0,3 % - « -	0,951	0,701
11	- « - + 0,5 % - « -	0,957	0,739
12	- « - + 0,1 % + 0,1 % Irganox-1010	0,954	0,720
13	ПЭБП + 0,05 % potassium phosphonate	0,954	0,720
14	- « - + 0,1 % - « -	0,949	0,688
15	- « - + 0,3 % - « -	0,951	0,701
16	- « - + 0,5 % - « -	0,954	0,720
17	- « - + 0,1 % - « - + 0,1 % Irganox-1010	0,955	0,727
18	PEHD + 0,05 % phosphinoxyde	0,962	0,771
19	- « - + 0,1 % - « -	0,950	0,695
20	- « - + 0,3 % - « -	0,951	0,701
21	- « - + 0,5 % - « -	0,954	0,720
22	- « - + 0,1 % - « - + 0,1 % Irganox-1010	0,946	0,669

In the conclusion it is possible to ascertain, that high efficiency synthesized phosphor organic compounds in quality inhibitors thermo oxidation destruction aromatic the block-copolyesters is established - the appreciable effect is observed at the contents of these compounds in compositions in quantity up to 1,0 %.

On increase of stabilizing effect phosphor organic compounds form a line: p-butoxyphenyl cyclohexyl phosphinic an acid, her potassium salt, di-(p-butoxyphenyl) cyclohexylphosphinoxyde; higher efficiency of the synthesized new compounds of five-valent phosphorus - di-(p-butoxyphenyl) cyclohexylphosphinoxyde - is found out as the stabilizer for a polycarbonate in comparison with the traditional stabilizer for this polymer - Polygard, being derivative of trivalent phosphorus - [tris-(p-nonylphenyl) phosphit], that is shown, in particular, in the best ability to preservation of durability and elasticity after long tests of polymer at 423 K; It is established, that synthesized phosphor organic the compounds containing in molecules atoms of five-valent phosphorus, influence on polyethylene of the low pressure, similar plastifying to effect that is shown in increase of impact strength and relative lengthening at simultaneous decrease of the module of elasticity in conditions of shock tests.

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