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Chapter 22

FILLED LOW VISCOSIVE EPOXY COMPOSITION MATERIALS

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ABSTRACT

On the base of accessible epoxy-dian oligomer ED-20, fillers and other ingredients high technology fill up compounds with valuable complex of exploitation properties are obtained.

Keywords: Epoxy oligomer, electric insulation material, viscosity, heat conductivity.

Low heat conductivity of polymer electric insulation materials limits the field of their use, especially for the purpose of pressurization of radio electronic instruments. That's why the development of high heat conductive filling epoxy compounds was done.

For filling compounds producing one of the most accessible epoxy dian oligomers ED-20 was chosen as an initial reagent. It has 20-21% epoxy groups contaminant.

Among the requirements to the base of composition, providing its high effectiveness, are: low viscosity, run out ability through the nozzle of 0,5 mm diameter. At the same time the base has to have the viscosity, which eliminates the filler subsiding. The life time of composition has not to be less than 8 hours and the composition has to be soluble in water.

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Proceeding from above mentioned requirements the optimal formula of composition was matched. Among known epoxy oligomer hardeners the most satisfied to the set problem is the isometiltetrahydroftal anhydride, because of its liquid consistence.

After matching of hardener system, compositions, containing the mixture of above mentioned hardeners with epoxy oligomer, were prepared. Viscometric measurements showed, that despite the fact that the composition is a mobile liquid (η = 493,6 Cst) it still has high viscosity. For viscosity reduction a styrol was matched as a diluent.

On fig. 1 the curve of dependence of composition viscosity upon styrol concentration is shown.

The influence of fillers on the heat conductivity of epoxy compositions was studied. The heat conductivity of pure composition without filler was determined; it ranges from 0,2 to 0,25 Wt/m·K in wide temperature interval.

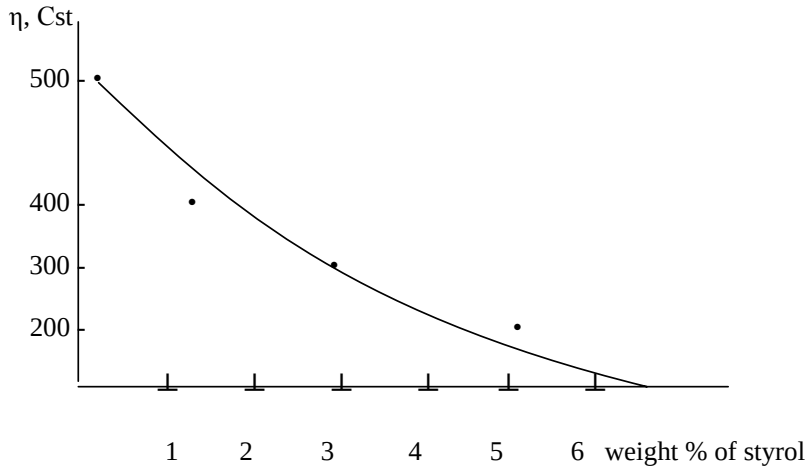

Fig. 1. The dependence of composition viscosity upon styrol concentration

On fig. 2 the dependence of heat conductivity of epoxy compositions on filler content is shown.

The increase of filler content courses the increase of heat conductivity; at the same time the viscosity of composition is also increases, which makes difficult its processing.

During the studies, which were done in wide temperature interval from 0^0C to 200^0C, the maximums on the curves of temperature dependence of heat conductivity were detected. These maximums correspond to the glass-transition temperatures.

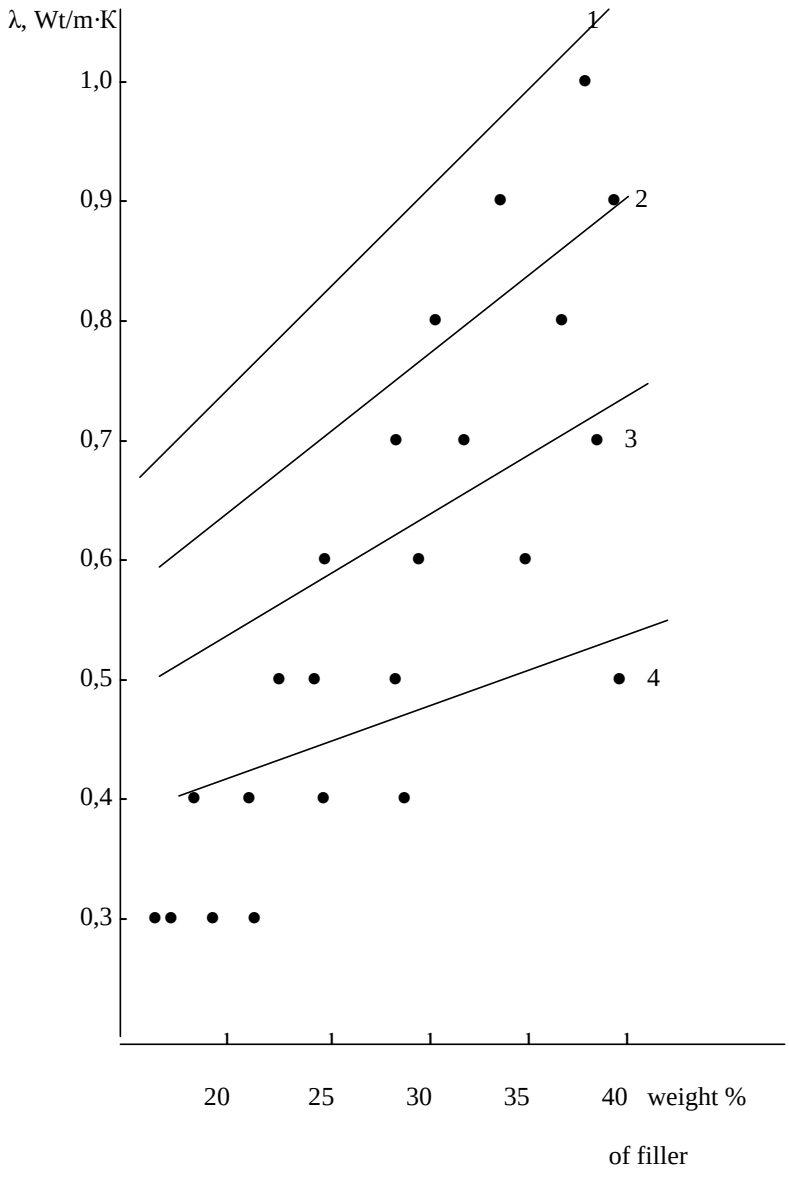

Fig. 2. The dependence of heat conductivity of epoxy compositions on filler content. 1-SiC; 2-33,3 % BN + 66,7 % Al_2O_3; 3-50% SiO_2 + 50 % Al_2O_3; 4-SiO_2

It was established that for obtaining epoxy compositions with maximum heat conductivity it is necessary to keep samples in low vacuum at pressures 50-100 mm.mer. during 15-20 min.

Otherwise the heat conductivity of samples is low and its concentration dependence is extreme. This may be explained by the fact that high loading of filler leads to bubble formation in casting.

The studies of dielectric properties showed, that the developed compositions maintain its properties in the temperature interval from 20^0 C to 150^0 C. Dielectric constant of compositions is 4-5 tangent of angle of dielectric loss - 10^{-2}, specific volume electrical

resistance - 10^{-15} Om·cm. These data corroborate, that heat conductive compositions are useful for pressurization of electronic instruments.

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Chapter 23

THE ELECTRICAL CONDUCTIVE COMPOSITIONAL MATERIAL WITH LOW INFLAM ON POLIPROPILEN BASIS

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ABSTRACT

Efficiency of application of the method based on receptions of optimum planning of experiment for reception of composite materials on the basis of polypropylene with the set complex of properties is proved. Studying influence carbon наполнителей on properties of electrowire composite materials is lead.

Key words: the method based, polymer compositional materials, electrical conductive, polypropylene, technical carbon, acethylene soot.

Today it is important the problem of electrical conductive polymer compositional materials with low inflame elaboration. The main direction of using these composite materials is to manufacture reining electrodes using in aggressive environment and law temperature heating appliances.

Because it make to provoke these heating and kindling. All over the worlds it is shown the perspectives of receiving electrical conductive inflammable polypropylene materials.

To make electrical conductive polymer material it is necessary to use special types technical carbon. Unlike usual soot it has more specific surface. Industrially producing plumbago has the size 100-1000 times lager then acetylene soot. In fact, to achieve necessary level of electrical conductivity we need use 10-15 % mass of plumbago AG-4 in material 15-20% of soot.

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It was investigated the influence of the given carbon on characteristics of electrical conductive materials with low inflam on base of polypropylene (PP).

This investigations showed us that in these interval it filling concentrations (up to 50% mass) the carbon fillings ensure electrical conductivity like metal powder (diagram 1).

Soot carbonfilled PP has the most electrical conductivity because the soot particles involve a lot of polymer in a state of transitional stratum and increase the concentration plumbago in unsystematic spheres. These regularities are inspected by changing thermophisical properties. Energetic increasing of thermal conductivity PP filled with plumbago 50% mass and more is consequence of contract between the filling particles. The most effect of thermal conductivity is seen by introducing plumbago in material containing 15-20% mass of soot.

Measuring the thermo coefficient of electrical resistance PP showed for these materials it is positive quantity.

Investigation the fotoes which was got by electronic microscope has showed that in case of small capacity of polymer (5-10%) the filling is distributed under the pretext of separate particles or small anglomerates. Here we can see transitional layer of PP. The latter has orientated structure and width of 20-25 mm.

Investigation the mechanism of conductivity of composite material confirm us that on the border of contact between soot and PP the double electric layer is formed which depended upon injection of charge bearer from soot into polymer. In case the diffusion length of injected charge in polymer layer is more than a half distance the soot particles we can see existence of electricity on condition that electric tension. It is necessary to insure steady distribution soot in PP and to decrease quantity at agglomerate of filling to realize injective conductivity in polymer through thin layers of polymer between the particles of filling. Including modifying additions at the beginning and at extrusion leads to good mixing.

Choiceing the modifying addition for electrical conductive unflam composite material it is necessary to take into concideration the effectivity of its influence into PP characteristics (into changing of electrical conductivity. Preliminary trials showed the best results can be achieved in case of introduction of silicon of organic rubber (SKTN-A).

By passing of electrical currents the composite may be heated. To avoied kindling it is necessary to choice the untipierens.

The mechanisms of putting out the flame reactions by galogen supported combinations were investigated.

The bad combination of flame moderates of PP provides their intensive migration on surface. It leads to reduction of effectivity of fire-resistance. It is known that reduction capacity of polymer matrix and creation more firm structure of PP decelerate the process of untipiren migration.

It is known that in silicon organic fillings presence the stability of composites to thermo-oxidise destruction is increased. We have an information that galogen compositions as ingibitors of fireing of PP are quiet effective.

Among them decabromdifeniloxid was chosen. Threeoxid of surema was chosen as a synergist galogenconsisted antipirens.

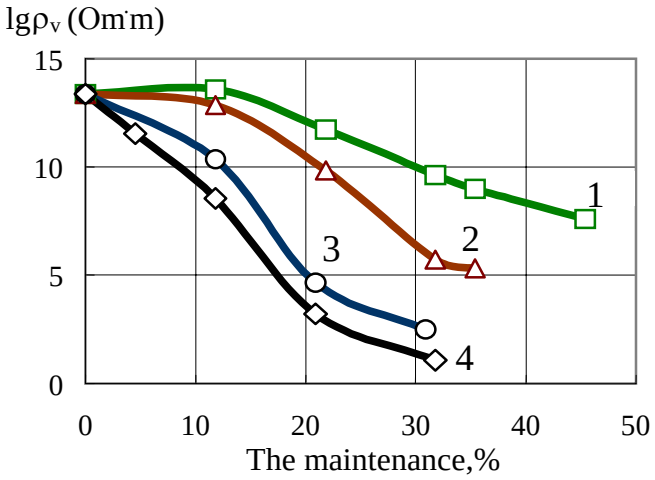

Fig. 1. Dependence of specific volumetric electric resistance of samples of composites on the maintenance: 1 - a powder of copper, 2 – graphite AG-4; 3 - acethylene soot; 4 - acethylene soot +graphite AG-4

It was investigated the opportunity of using disc extrusion for getting things from composite material on modifuing PP bases having electrical conductivity and low inflame.

The choice of process of disc extrusion is depended upon the opportunity of realization of high deformation. The optimisation of composition of multycomponent electrical conductive composite material on modified PP bases with low inflame, getting adequate regressive models were held by methods of optimal planning of experiment.

A lot of factors cause difficulties in carrying experiments for optimization of technological modes and prescription of compositional materials: too expensive raw materials and equipment, etc. That is why it is necessary to elaborate new method of optimization of recipe of composites.

The most actual and perspective task to solve this problem is using methods of mathematic statistics, exactly the planning of optimal experiment. The advantage of thematic models describing the influence the consistence of composite material into its quality in case of simultaneous varying of concentration of several components. These experimental investigations give us opportunity to get identical physical mathematic models "consistence quality" without carrying full set experiments.

These models give us opportunity to have scientific optimization of recipe of multycomponent composite materials and conditions of its conversion into things with specific quality.

Such planning of the concentration of this components of composite materials on PP bases was carried on bases of investigation of influence the parameters of different types of fillings into quality of modified PP.

The presents of acetylene soot- Xi, threoxid surema - Xi, decabrom-feniloxid - - X_3 were the independent variables. The response function is quantity of measureing characteristic in the time of verifying independent variables.

The response function were strength in rapture -Yi, comparative lengthening -¥2, destructive effort during bending -Y_3, specific work of percussion stickiness -Y4, PTR - Ys, specific electric resistance -Ye, oxygen index -Y_7

According to experiment planning the samples of compositional materials were got and their qualities were investigated. It got us an opportunity to determine the meanings of coefficients of regressive equation. The model of linear square equation was created according to intercourse of changeablequantity. This model chows the changer of qualities of compositional material according to its constitution:

$$\begin{cases} Y_1=10{,}05-1{,}73X_1+2{,}36X^2_1+0{,}87X_2-1{,}34X^2_2-0{,}54X_3+0{,}73X_1X_3; \\ Y_2=5{,}97-1{,}22X_1+1{,}35X^2_1-3{,}03X_2-1{,}03X_3; \\ Y_3=13{,}67-1{,}56X_1+6{,}63X^2_1+1{,}99X_2+4{,}23X^2_2+3{,}38X_3-0{,}66X_1X_2-1{,}63X_2X_3; \\ Y_4=6{,}66-1{,}05X_1-0{,}83X^2_1-0{,}32X_2-0{,}54X_3-1{,}33X^2_3+0{,}87X_1X_2; \\ Y_5=10{,}42-0{,}19X_1+0{,}51X^2_1-0{,}26X_2-0{,}24X_3+0{,}71X_2X_3; \\ Y_6=9{,}57+1{,}49X_1+0{,}42X_2+0{,}25X^2_2-0{,}79X_1X_2; \\ Y_7=10{,}67-0{,}53X_1-0{,}01X^2_1-0{,}47X_2-0{,}38X_3+1{,}56X_1X_3. \end{cases}$$

Significance of coefficients of the system was held according to the “Students criterion”. The valuing of identicality of regressive equations was held according to the “Fisher’s criterion” using valuing of probability 0,98.

At the end of our investigation it is necessary to solve the task of multy-criterium optimization of material consistence. Harryngton's function of de-sirebility was held as a general criterion.

The control experiment was held to prove calculated facts. This experiment determined the similarity of results and using the elaborated math-ematic model.

As a result the recipe of compositional electrical conductive material with low inflame on modified PP bases was received.

The calculated and received facts differed nomore than 5% from each other. It proves the optimum of calculated recipe and optimisational method. The noticed recipe of compositional material differs from traditional. The level of conductivity we need are ensured by consistens of electrical conductive fillings 35%. Its deformational quality and strength do not change for worse but increased.

The recipes of compositional materials on modified PP bases was alabo-rated with the help of this method: dispersefilled PP with improved technological qualities, electrical conductive materials, electrical conductive materials with increased frost resistance and improved pressing characteristics.

That is why the effectivity of using of this method is proved because it is based upon optimal planning of experiment to get compositional materials on PP bases with the complex of properties we need.

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Chapter 24

RESEARCH OF MIXES ON THE BASIS OF CORN STARCH AND POLYETHYLENE

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ABSTRACT

The aim of the research was to get a number of composition based on corn starch and a synthetic polymer – polyethylene and further study of physical and mechanic properties behaviour under the influence of aggressive mediums and biodecomposition in the soil as well.

Keywords: starch, polyethylene, composition, physical and mechanic properties.

Now, when the rates of growth of plastics manufacturing are extremely high, it is especially important, that development of the plastic industry take into consideration the problem of use of the plastics which are not outdated yet, but have lost their initial properties or consumer value of products, such as the thrown out products, and also technological waste products of their manufactures [1]. The problem under consideration is acute and relevant, it has ecological and economic aspects as it is connected with environmental protection and rational use of natural resources, needs for reduction the price of raw material for manufacture of polymers. At the same time it is the least investigated [2].

The aim of our researches is to get a number of compositions on the basis of corn starch and polythene.

While preparing the compositions on the basis of PEHD (M-273) and corn starch (GOST 12020-72) there were received compositions with the maintenance of starch from 1,5 % up to 15 % [3]. The mixture of polythene and starch, preliminary plasticized with a quantity of

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glycerin, is loaded into the plodder; the temperature in the auger cylinder being 190 o C, the given mixture is fused and then the received melt is divided into grains. It is worth mentioning, that after the extrusion of the polythene and starch composition, the extrudate turns out to have thin foam-like structure. Therefore the received samples were under the same conditions once again.

Then some characteristics were investigated. For this purpose from the extruded composition and the initial polythene using the method of pressing test samples which represent transparent films were made. It is possible to judge the character of the occurred changes by the results represented in tables 1-4 and on figures 1-3.

Researches of the IR-spectra films of the initial polythene and the received compositions reveal that in the process of extruding there take place some changes in the field of 1300-900 sm - 1. In process gelatinization and destroying of starch when extruding compositions there occur changes of dielectric properties. Besides the composition structure, properties of film samples are also influenced by frequency rate of extrusion's. Thus introducing of starch raises polarity and values of a tangent of a corner of dielectric losses.

Introducing of starch and frequency rate of extruding influence the parameter of a melt's fluidity and explosive durability differently (tab. 1).

Table 1. Physic-mechanical properties of the pressed samples of compositions on the basis of polythene and starch

	Structure of composition, %		MFR $^{190}_{21,6}$	σ_{pi}, МПа	ε_{sp}, %at tearing up
	polyethylene	starch			
1	100	0	6,36	36,3	>500
2	98,5	1,5	17,57	17,7	35
3	97	3	34,87	17,7	53
4	95	5	45,93	17,7	27
5	93	7	37,94	15,1	15
6	90	10	31,5	10,8	9
7	85	15	17,06	16,7	12

The researches made in the sphere of creating and manufacturing biodecomposed polymers, are not only of theoretical, but also of applied character. So, within the framework of the given work, there was used the corn starch made at the open joint-stock company " KSF " (KBR Maiskiy region, village Aleksandrovskaya). Researches of the electric properties of the samples received by pressing are reflected on fig. 1-3.

It is seen on the diagram that values of tgδ are constant up to 120 ^{o}C, values of tgδ taking into account this frequency 104Гц (10-3-10-2) correspond with those given in literature. This correspondence is important from that point of view that then the observations and conclusions concerning the composition PE+S are possible to be applied to a great extent to other polyolefins.

At temperature higher than 120 degrees a rise of dependence of tgδ on T with a possible peak at 190 ^{o}C is observed. The specified temperature dependence essentially changes when introducing starch (fig. 2). For example, at its maintenance in 1,5 % background values raise a little. The background area extends. The planned peak at temperature of 190 ^{o}C disappears, but the precise maximum is found out at 85-90^{o}C. As this peak didn't take place for the initial

PE, it can be related either to starch, or to the properties of the composition PE+S proper. This assumption is proved at considering of the diagram tgδ on T composition PE+3 %S. There are already 2 low-temperature peaks: approximately at 45 ^{o}C and 100 oC. These observations allow to assume the intensification of the influence of the additives on properties of the composition at these concentration already.

This intensification of the contribution of starch to the properties of the composition is seen in some way when studying structures with higher maintenance of starch.

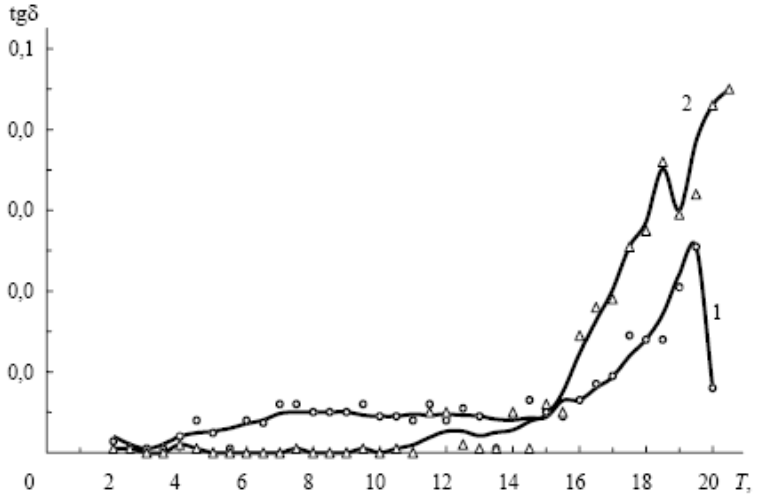

Fig. 1. Dependence of a tangent of an angle of dielectric losses tgδ on temperature *T* for granulated samples of initial not stabilized PEHD (M-273). Modes of preliminary heat treatment: $T = 100^{0}$C vacuum, 5 hours (1) and $T = 100^{0}$C without vacuum, 1 hour. (2). Frequency - 10 кГц

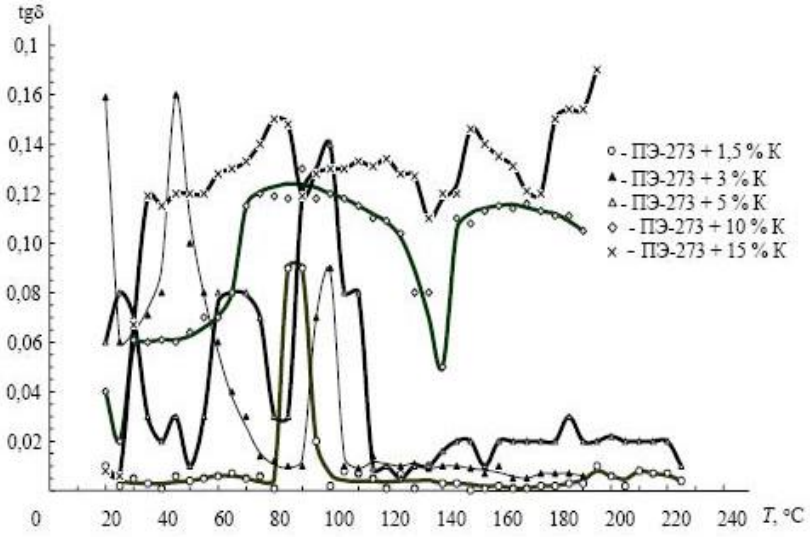

Fig. 2. Dependence of a an angle of dielectric losses tgδ on temperature *T* for compositions PEHD (M-273) + starch. Frequency - 10 кГц

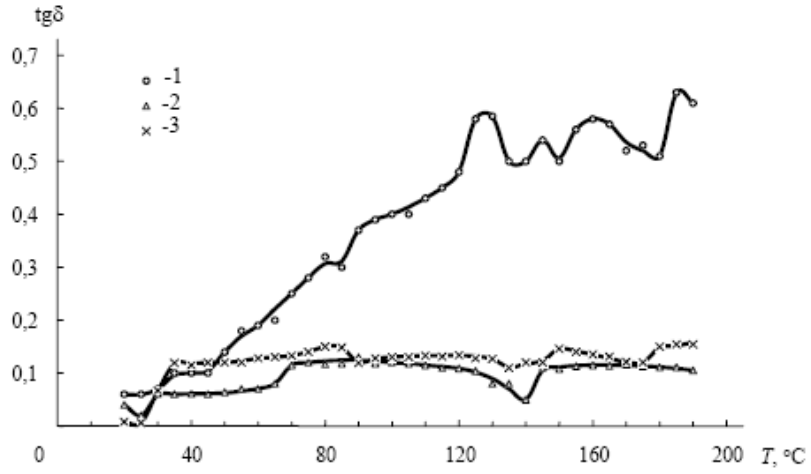

Fig. 3. Dependence of a tangent of an angle of dielectric losses tgδ on temperature *T* for compositions PEHD (M-273) + starch. The maintenance of starch - 7 % (1); 10 % (2); 15 % (3). Frequency - 10 кГц

Thus, at its 5 % maintenance several (3-4) low-temperature peaks already reveal, besides that the general background of tgδ values increases and on all the temperature interval tgδ is not less, than 10-2 (fig. 2).

At 10 % the maintenance of starch the background of tgδ values suddenly increases (5-50 times in comparison with 5 %). Low-temperature peaks merge into one wide (25-130 ^{o}C) peak. It is obvious, that this structure, and in the even greater degree the structure with 15 % maintenance of starch on dependence tgδ on T reveals properties of friable structure, possibly polar to the maximum and easily destroyed in the long term.

It is worth considering separately the compositions with high maintenance of starch in comparison. On fig. 3 the dependence of tgδ on T for compositions with the maintenance of starch 7, 10, 15 % is resulted. It was revealed rather unexpectedly, that referring the structure with 7 % of starch even on the background of tgδ values from 0,05 up to 0,15 (10-15 %K) dielectric losses of composition PE+S are very high in all the temperature interval, beginning from 35 oC and is higher.

Obviously, it is the most "bad" composition, remembering the destructive effect of starch on the initial PE. The question which is now put before us as researchers, consists in the following. It is necessary for us to create a composition which would be easily biodecomposable to the maximum, but at the same time the same composition should keep its properties during the necessary term. Thus, it is necessary to pick up an optimum structure of such composition, but for this purpose researches of the maximal set of physical and chemical properties of the composition PE+S are required.

The effect of aggressive mediums on the received samples in accordance with GOST 12020 were investigated as well. As aggressive mediums were used:

HCl - 10 % solution
NaOH-10 % solution
H2O - distilled water

It is known, that polythene is inert at action of many chemical reagents, namely, does not react with alkalis of any concentration, with solutions of neutral, sour and basic salts, organic acids (for example, with ant or acetic), with solutions of salts - oxidizers (for example, potassium permanganate) and even with the concentrated hydrochloric and fluoric acids [5].

Hence, the increase in weight of samples when keeping in solutions of 10 % hydrochloric acid and 10 % sodium hydrate solutions is caused by hydrolysis of starch in the beginning up to dextrins, and at full hydrolysis - up to D-glucose [4]. When keeping the samples in water grains of starch, contained in the composition, collapse with formation of paste, then swell, attaching small amounts of water (it is a convertible stage) [5]. It is proved by gradual increase of samples in weight at immersing into water for 3-18 days.

BIODECOMPOSITION IN GROUND

Biodecomposition in ground was defined at keeping the received pressed samples in ground (pH=6,88, the maintenance of humus - 0,16 %, exchange acidity =25,87 mg.экв./ in 100 gr. of ground) during 48 day. Then the study of their rheological and deformation - strengthening characteristics was carried out. The results are given in tab. 2-4.

Table 2. Change of explosive pressure of the pressed samples of compositions on the basis of polythene and starch at biodecomposition

№	Structure of composition, %		σ_p, МПа, исх.	σ_p, МПа, in 14 day.	σ_p, МПа, in 28 day.	σ_p, МПа in 42 day.
	polyethylene	starch				
1	100	0	36,3	35,8	36,2	35,9
2	98,5	1,5	17,7	18,1	19,4	19,7
3	97	3	17,7	17,9	19,3	20,1
4	95	5	17,7	18,0	14,8	19,3
5	93	7	15,1	16,3	15,0	19,3
6	90	10	10,8	13,7	15,8	17,8
7	85	15	16,7	17,5	19,2	20,3

Table 3. Change of relative lengthening at breaking of the pressed samples of compositions of polythene and starch at biodecomposition

№	Structure of composition, %		ε_{sp}.,% исх.	ε_{sp}.,% in 14 day.	ε_{sp}.,% in 28 day.	ε_{sp}.,% in 42 day.
	polyethylene	starch				
1	100	0	500	500	500	500
2	98,5	1,5	35	30	25	22
3	97	3	53	44	25	21
4	95	5	27	23	11	10
5	93	7	15	12	10	10
6	90	10	9	12	10	7
7	85	15	12	18	23	23

Table 4. Change MFR of the pressed samples of compositions on the basis of polythene and starch at biodecomposition

№	Structure of composition, %		MFR, г/10 mines,	MFR, г/10 mines, in 14 day	MFR, г/10 mines, in 28 day.	MFR, г/10 mines, in 42 day.
	polyethylene	starch				
1	100	0	7,26	7,1	7,24	7,18
2	98,5	1,5	50,57	60,3	77,6	89,5
3	97	3	33,3	40,6	77,2	95,7
4	95	5	65,5	78,2	134,5	193
5	93	7	100,6	135	150	193
6	90	10	120	114	158	254
7	85	15	139	97,2	83,4	88,2

The analysis of the received results showed, that at biodecomposition in ground the explosive pressure varies insignificantly whereas the relative lengthening at breaking of samples decreases. It indicates that compositions at burying in ground become more rigid as there are structural changes in the polymer's matrix, as a result of which compositions are exposed to a greater destruction, than initial polythene.

Thus, introduction of starch as an additive to a synthetic polymer allows to quicken up the process of decomposition of the polymer under the influence of microorganisms and at the same time does not have significant influence on the initial physical and chemical properties.

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