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## **COMPOSITION BUILDING MATERIALS ON THE BASIS OF MODIFIED LIQUID OLIGODIENES**

The results of elaboration of efficient building composites on the basis of modified oligodienes are presented. The basic propositions on design of material formulations for different purposes with consideration for the particularities of their use are given. The ways of improvement of technology of composites preparation subject to proposed operation conditions are suggested.

**Keywords:** modified oligodienes, building composites, cold consolidation.

### **Introduction**

Rapid growth of production of polymers including rubbers is due increasing industrial demands for efficient durable materials with unique properties. These unique properties make a major contribution to the fact polymer composites displace many traditional materials such as metals, ceramics, glass, and wood. Intensive studies and technological developments in the field of polymer production have revealed new opportunities and determined the scopes of their efficient application [1].

Polymers being multipurpose materials are needed in all industrial branches as well as in medicine. However, social and economic reforms in 1990s led to sharp rise in cost and reduction in production of artificial resins with unabated growth of demands for efficient polymers in all industrial branches.

The problem can be solved with the use of new types of polymer binders, such as diene oligomers, which belong to the liquid rubber type and differ in a crucial respect from the known polymers.

The elaboration of materials using rubber properties in full measure is considered one of the most efficient ways. Many studies on efficient composite preparation by cold consolidation were carried out; however, the most extensively used polymers are traditional epoxy, polyester, and carbamide resins. Expanding production of polymers in liquid phase and, therefore, handy for technological process makes it possible to solve the problem of design of efficient compositions for construction demands.

Recommended characteristics of rubber binders are prescribed viscosity, consolidation ability in the wide temperature range, minimum content of a solvent or its total absence, atmospheric and operation conditions resistance, guaranteed reliability under long-term operation. These properties of rubbers depend directly on their structure and composition.

By and large design of efficient compositions on the basis of oligodienes can be represented as the sequence of certain operations involving exposure to the structure and composition of raw materials. Structure formation peculiarities determine rubber composite properties. Formation of one or other structure, in its turn, depends not only on qualitative and quantitative composition of composites, but also on technology of their preparation. Because of this, ascertainment of kinetic dependences of rubber compositions structure formation and their association with operation characteristics of the end product is an important scientific and technological problem.

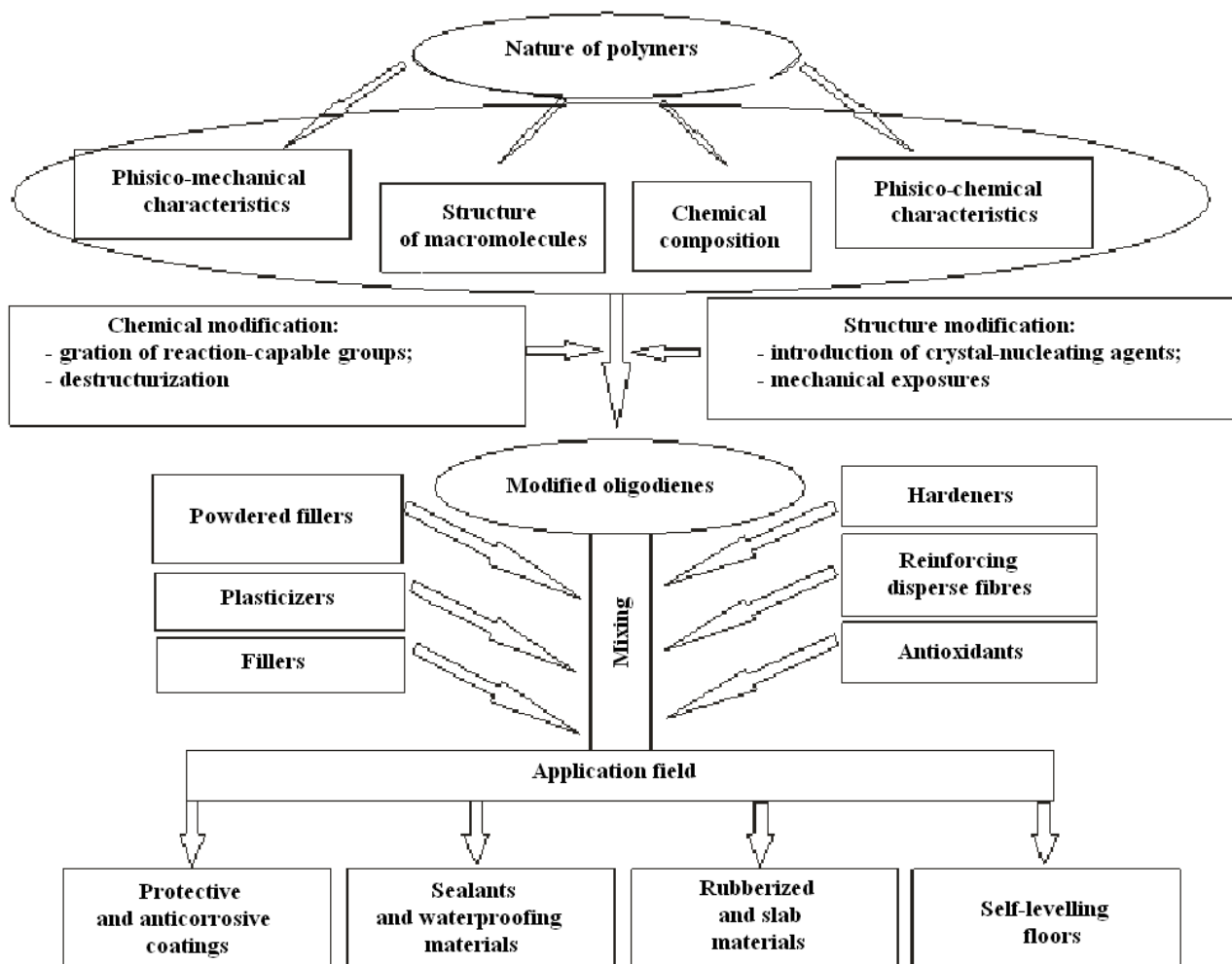
Binder properties depend primarily on physicochemical characteristics of an oligomers, amount and chemical nature of the hardener or hardening group. Furthermore, binder properties are regulated by introduction of different modifying agents which are capable of changing base characteristics of oligodienes. Rubber extenders are crucial in structure formation because extender particles are active centers of new formation growth. The most important characteristics of extenders are dispersion ability, surface quality, pH index, surface energy (Gibbs energy). The number of extenders or ratio "polymer/extender" ( $n/h$ ), and intensity of physicochemical interaction between binder and extender influence the character of product structure. Besides this parameter, the availability of disperse reinforcement as well as operation conditions affect the change in physical-mechanical properties of rubber compositions [2].

When designing compositions based on modified oligodienes it is necessary to pay attention not only to their components but also to preparation technology. To impart special properties to the indicated composites is the topical problem of material science involving both structure studies of rubber raw materials and purposeful regulation of the synthesis, processing, preparation, and operation of the oligodiene-based products. All the processes mentioned above are concerned with structure or chemical modification of the input oligomers. The selection of priority method of modification is based on financial viability.

Theoretical generalization and experimental corroboration resulted in integral system of selection of components and technology of production of all-purpose building ma-

materials based on modified oligodienes. Developed system allows efficient method of composite material design to be determined on the basis of modified oligodienes with consideration for proposed operation conditions.

The circuit diagram of the design of the above materials is shown in Fig. 1.



**Fig. 1.** Design scheme of compositions based on modified oligodienes

The principle of maximum correspondence between nature (genesis) of input oligodienes and required properties of the finished material is used as the basis for the developed system. The chemical modification the binder through grafting the reaction-capable groups is used for purposeful improvement of initial binder properties. The epoxy groups make the binders capable of mixing, provide adhesion to the different substrates, tensile strength, impact elasticity. The hydroxyl groups impact the same properties as well as moisture resistance, flexibility. The carboxyl groups impact, in addition to the stated above, such properties as heat and cold resistance. The choice of the type of grafted groups is determined by anticipated operation conditions of fi-

nished composite. The type and the number of extenders as well as their combination are defined by the field of efficient use of the composite. The technology of composite application is selected with consideration for their composition, prescribed viscosity, and durability.

The basis of design are requirements to the composites based on modified oligodienes in terms of operation conditions. When selecting the liquid oligodienes from among the available ones we were guided by compliance of the base characteristics of the oligodienes with the properties of designed composite; as well as by compromise between price, quality and availability; viscosity required to provide the use of oligodiene as the liquid phase of the composition; minimum toxicity.

However, the situation is possible that physicochemical properties of the basic oligodiene do not suit to the requirements of operation in full measure. Its modification is justified if it is impossible to achieve the required result in any other way. It is naturally enough that modified oligodiene should also suit the requirements stated above and modification costs should not exceed affordability of its use.

To obtain the data on influence of physicochemical properties and structure characteristics of input oligodienes on properties of the finished compositions, we use the group sampling method (see Table 1).

Table 1

## Physicochemical properties of the oligodienes being studied

Type	Molecular mass MM	Viscosity at 25°C, Pa·s	Functionality	Microstructure, %			
				1.2-vinyl	1.4-trans	1.4-cis	Cycle
The first group – malenized oligodienes							
N4-5MA	5500	40	5	-	-	-	-
N4-10MA	8200	75	7.5	-	-	-	-
The second group – oligodienes without functional groups							
AL	1000	4	-	40...55	15...25	10...20	15...20
PH	2600	8	-	35...50	30...40	15...25	-
PM4	1500	0.7	-	15...25	40...50	20...30	-
HFN4*	5000	4	-	10...20	50...60	25...35	-
The third group – butadiene copolymer							
СКДП-Н	3200	до 16.0	1.1	15...20	58...62	18...28	-
СКДН-Н	3000	до 12	1.0	10...20	20...30	50...60	-

**Notation:** \* Contains end hydroxyl groups at a rate of 0.2 meq OH/g.

In addition, divinyl styrene thermoplastic elastomer ДСТ-30P-01 was used for modification in liquid phase. Divinyl styrene thermoplastic elastomer ДСТ-30P-01 is a bulk copolymer (30 % of styrene) produced by standard ТУ 38.40327-90. This rubber is very ductile due to bulk configuration and homogeneous. Potential ability of selected nonmodified oligodienes to cross-linking was assessed by the degree of thickening (gel formation) during reaction active substances introduction and characteristic viscosity change in time.

Hardening action of polyfunctional compounds on rubbers was studied at 25 °C. These compounds are 3 % HCl solution, CaCl<sub>2</sub> in the powdered form, triethylenetetramine (ТЭТА), polyisocyanate (ПИЦ), siccative – cobalt naphthenate. It is established that interaction between rubbers from the first group and chlorine-containing reagents is attended with strong thickening and emission of heat and gaseous products, as well as with large pores formation in material. Binding agents hardened by chlorine-containing elements undergo rapid embrittlement. As molecular mass and functionality of oligomer increase, hardening becomes more intensive.

It was observed that there was no direct relation between reaction ability and molecular mass of the used oligomers. It is evidently that in this case spatial structure of the polymer and ratio of the links of different types played significant role providing selective activity of the polymers. Liquid butadiene copolymers react most actively with polyfunctional hardener ПИЦ, and thickening intensifies with increase in concentration of this hardener. Films of all the binders polymerized in mass after 24-hour exposure. When employing amine hardener we observed formation of single bands in each polymer.

The experimental results shown that oligomers with relatively small molecular mass and, consequently, small viscosity were less reactive toward some reagents. However, film formation in oligomers with approximately equal molecular mass occurred disproportionately, which is due to the differences in oligomer structure and in ratio of links of different types. In addition, small molecular mass involves small length of macromolecule and, therefore, minimum number of structure defects. In the absence of thermal action, there was no thermofluctuation cleavage of macromolecular chain and, consequently, there were no active radicals to provide oligodiene cross-linking. It was polymer chain macrostructure that greatly affects oligomer reaction ability. Increase in oligomer reaction ability during cold hardening is possible due to grafting reactive end groups. The number and types of groups subject to are determined by expected operating conditions of composite on the basis of modified oligomer.

In this connection the most common quality criteria are revealed for particular types of developed polymer compositions such as sealing materials for airfield and road pavements; repair compositions for these pavements and wearing layer arrangement; moisture proof, anticorrosion and roofing materials; compositions for self-levelling floors. The common characteristics of the compositions are elasticity (within the limits of specified one), water resistance, chemical resistance (for corrosion produc-

tions), and maintenance of operating characteristics during specified time period.

Studies on development and optimization of compositions on the basis of oligodienes were performed at different levels. At first, we investigated the possibility of initial oligodienes modification to provide maximum consistency between physico-mechanical characteristics of developed composites and expected operating conditions. Thereupon we conducted modification with the use of the most efficient method. Secondly, we optimized obtained binder with regard to some most important characteristics.

To obtain binders with high adhesion, we made epoxidation of copolymer СКДП-Н and oligodienes of the first and second groups. Specific characteristic of polymers imparted by end epoxy groups ( $\Theta\Gamma$ ) to the polymers are thermal and light resistance, elasticity at low temperatures, high adhesion to many substrates.  $\Theta\Gamma$  content is affected by reaction temperature  $T$ ; reaction duration  $t$ ; pressure of the air conducted to reactor  $P$ . The ultimate product of this reaction is  $\Theta\Gamma$  content in polymer. Experimental research allowed us to obtain equations reflecting  $\Theta\Gamma$  content dependence  $N$  on reaction parameters:

- for oligomer with MM=5500

$$N = 4.58 + 0.38T + 0.13t + 0.162P - 0.943T^2 - 1.93t^2 + 1.05P^2 + 0.19Tt + 0.16TP + 0.09tP; \quad (1)$$

- for oligomer with MM=1500

$$N = 7.18 + 0.318T + 0.213t + 0.112P - 1.93T^2 - 1.103t^2 + 0.805P^2 + 0.11Tt + 0.36TP + 0.11tP; \quad (2)$$

- for oligomer with MM up to 3200

$$N = 9.49 + 0.88T + 1.03t + 1.32P - 0.88T^2 - 0.73t^2 + 3.5P^2 + 0.19Tt + 0.46TP + 0.39tP. \quad (3)$$

Rubber СКДП-Н gave the largest yield of  $\Theta\Gamma$  – 14.5 % from total mass, with following value of influencing factors:  $P=6$  MPa,  $T=130$  °C,  $t=170$  min.

To conduct the reaction of carboxyl group grafting КГ, we selected rubbers of the lowest viscosity, in so far as grafting the groups stated above is connected with sharp increase in oligomer viscosity. The hardening was conducted with the help of ZnO, and it was accompanied by formation of neutral salts acting as relatively strong cross-links.

It was established that increase in carboxyl group concentration led to decrease in binder elasticity, this tendency maintaining beyond the experimental field. Simultaneously with the decrease in elasticity, we observed the growth of modulus and ten-

sile strength and at 100 % tension. This fact explains the possibility of correction of physico-mechanical characteristics of finished compositions by changing КГ content in the rubber with regard to expected operating conditions of compositions. Initial oligomer structure directly affected the characteristics under investigation. For example, tensile strength of 22.5 MPa was achieved for oligomer PH 2600 with predominance of 1.4-trans links after introduction of 3.5...4.5 % methacrylic acid.

To obtain liquid binder, we conducted destructurezation of initial divinyl styrene thermoplastic elastomer ДСТ-30P-01 resulting in formation of the modified rubber with funnel viscosity less than 9 s at the temperature of 50 °C, with less than 1 mass percent of epoxy groups. Amount of hydroxyl group determined with the use of acetyl number was 0.1 meq OH/g. End hydroxyl groups allowed modified polymer to be hardened with the use of polyfunctional compounds active toward the groups referred above. Examined combinations of modified oligodienes and hardener are presented in Table 2.

Table 2

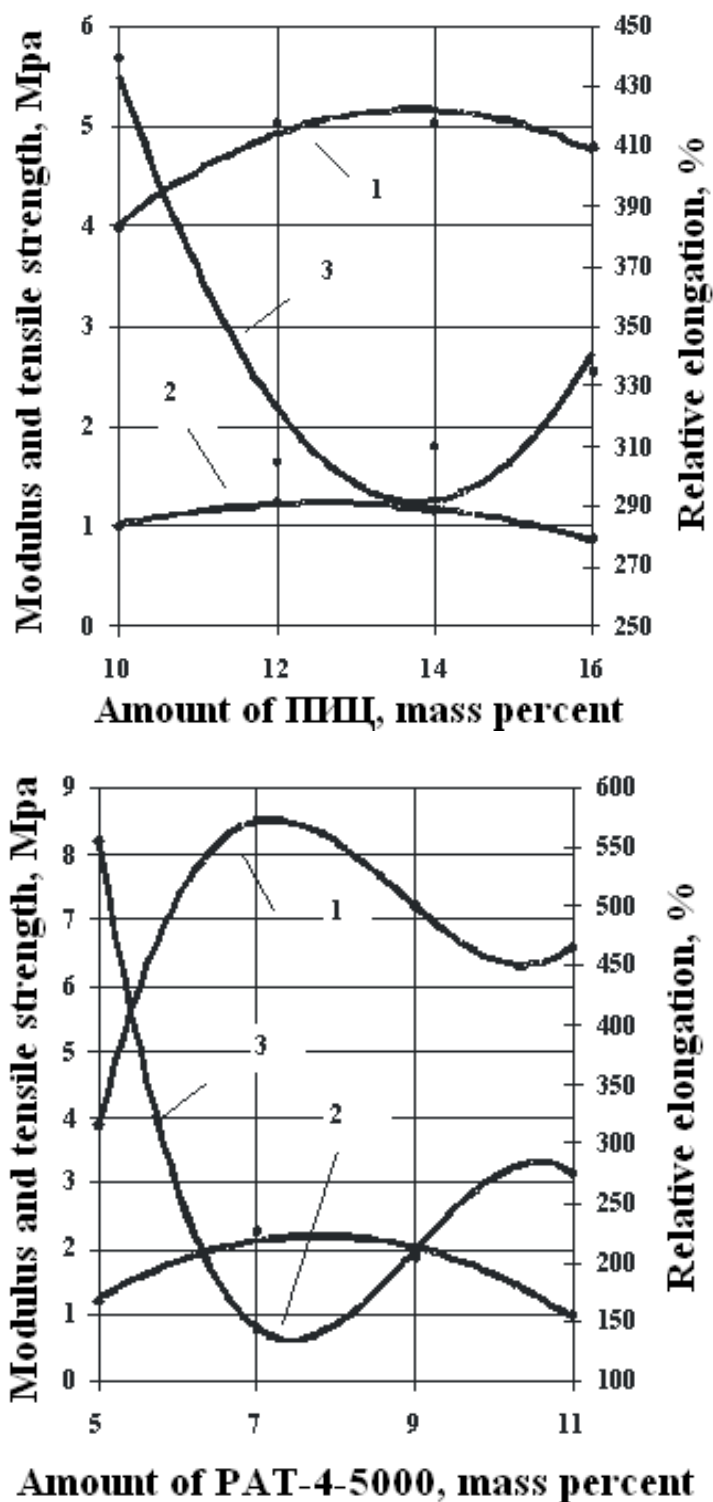
## Examined combinations “rubber — hardener”

Rubber	Dynamic viscosity at 25 °C, Pa·s	Hardener*					
		1	2	3	4	5	6
Modified rubbers with hydroxyl groups							
ДСТ-30P-01	9 s (funnel viscosity at 50°C)	+	-	-	-	-	-
Modified rubbers with carboxyl groups							
СКДН-Н	14...16	-	-	-	-	-	+
N4-5000- 10МА	45...48	-	-	-	-	-	+
AL 1000	8...12	-	-	+	+	-	+
PH 2600	12...16	-	-	+	+	-	+
Modified rubbers with epoxy groups							
СКДП-Н	19...22	+	+	-	-	+	+
N4-B-10МА	82...86	+	+	-	-	+	
PM4	1.4...1.6	+	+	-	-	+	+
* 1 – liquid ПИЦ with mass concentration of NCO-groups 30...35 % (types П45-25, ПМ 50-25); 2 – triethylenetetramine (ТЭТА); 3 – ZnO; 4 – Ca (OH) <sub>2</sub> ; 5 – complex BF <sub>3</sub> + monoethylamine; 6 – oligomer with hydroxyl groups HFN4-5000 with viscosity 4...8 Pa·s at 25 °C							

The completeness of reaction was estimated over three indicators such as tensile strength and modulus at 100 % tension, value of relative elongation at rupture.

It was established during ЭГ-containing oligomers hardening that change in their physic-mechanical characteristics directly depends on the amount of grafted ЭГ and

hardener type. The highest adhesion and cohesion values as well as matrix cold resistance were observed at maximum  $\Xi\Gamma$  content in the polymer and 12...14 mass percent of the hardener. The results of researches of kinetics of hardener ЭСКДП-Н with maximum content of  $\Xi\Gamma$  with the use of different hardener are shown in Fig. 2.



**Fig. 2.** Dependence of physico-mechanical characteristics of ЭСКДП-Н on type and amount of hardeners:  
 1 – tensile strength; 2 – modulus at 100 % tension; 3 – relative elongation



Similar researches of KГ-containing oligomers were conducted. Since the number of grafted chains of methacrylic acid was equal for all examined oligomers, we estimated the activity of applied hardener toward oligomers with different structure and molecular mass. We obtained linear dependencies between the values of relative elongation and tensile strength, which made it possible to assess the contribution of different hardener to the formation of composite structure.

The research on degree of cross-linking was combined with research on the rate of reaction capable group consumption by displacement of density of absorption of infrared spectra. Infrared spectra are obtained on spectrophotometer with diffraction grating in the range  $4000...400\text{ cm}^{-1}$ . Change in the number of links of different types for oligodienes was determined from absorption bands: 1.4-cis –  $710\text{ cm}^{-1}$ , 1.4-trans –  $967\text{ cm}^{-1}$ , 1.2-vinyl links –  $910\text{ cm}^{-1}$ , content of  $\text{CH}_2$ -groups –  $1460\text{ cm}^{-1}$ , bonds O-H –  $3600\text{ cm}^{-1}$ , group  $-\text{N}=\text{C}=\text{O}$  –  $2275...2250\text{ cm}^{-1}$ ,  $-\text{COOH}$  –  $3000...2500\text{ cm}^{-1}$  [3].

The data obtained are in good agreement and allow us to make a conclusion about initial consumption of carboxyl, hydroxyl and epoxy reaction capable groups (in order of decreasing rate). Thereupon 1.4-trans links are included in exothermal hardening. Grafting degree of obtained binders was determined by yield of sol-fraction produced by extraction with boiling solvent.

It was established that oligodienes with small molecular mass cross-linked by reaction capable groups, whereas oligodienes with larger molecular mass have chemical bonds over spatial links. In the first case materials with high elasticity, the basis for sealants, are obtained; in the second case leather-like materials, the basis for wearing layers and repair materials.

To obtain objective data on compatibility of examined rubbers and additives, we conducted the experiments on establishment of dependencies of characteristic viscosity on the amount of introduced additives:

- aerosil ( $\text{SiO}_2$ ),
- wollastonite ( $\text{CaSiO}_3$ ),
- hydroxyl ( $\text{Al}(\text{OH})_3$ ),
- powder of glass sodium borosilicate composition, dry-granulation carbon.

The additives were introduced step-by-step, with 2 % volume gradation, with viscosity control on rotary viscosimeter PB-8M.

After mix viscosity had reached  $80\text{ Pa}\cdot\text{sec}$  introduction of additives was stopped. This viscosity provided uniform distribution of polymer composition over the substrates as well as self-alignment under the force of gravity.

Change in viscosity after the introduction of reinforcing fibres (alumina-borosilicate glass, polyamide, basaltic) was determined in a similar way.

After combined introduction of fine-dispersed additives and reinforcing fibres viscosity  $\eta$  changed additively in compliance with dependence

$$\eta = \eta_0 + Ax_1 + Bx_2 + Cx_3, \quad (4)$$

where  $\eta_0$  is the viscosity of the initial rubber, Pa·sec;  $x_1, x_2, x_3$  are the number of components, volume percent;  $A, B, C$  are the coefficients characterizing additives. Combinations of different additives with reinforcing fibres were calculated on the basis of Eq. (4). The variation limits of additive volume content at specified amount of amendment, that is, of component of maximum absorbability. The influence of additives was estimated by cohesion (rupture) strength and by cohesion to the steel substrate. Favourable combination of specified characteristics was exhibited in ЭСКДП-Н with end epoxy groups having maximum initial viscosity and in PH2600 with end epoxy groups having maximum initial viscosity.

For specified oligomers, regression equations are obtained reflecting dependence of optimized parameters on the amount of entered components. For СКДП-Н, when filling, in volume percent:  $x_1$  is the carbon,  $x_2$  is the glass powder,  $x_3$  is the wollastonite:

$$\sigma_t = 3.49 + 0.88x_1 + 1.03x_2 + 1.32x_3 - 0.88x_1^2 - 0.73x_2^2 + 3.5x_3^2 + 0.19x_1x_2 + 0.46x_1x_3 + 0.39x_2x_3; \quad (5)$$

$$A = 63.09 - 11.8x_1 - 8.03x_2 - 1.32x_3 - 4.88x_1^2 - 6.73x_2^2 - 1.45x_3^2 - 5.19x_1x_2 - 7.39x_2x_3. \quad (6)$$

For PH2600, when filling:  $x_1$  is the carbon;  $x_2$  the glass powder;  $x_3$  is the glass fibre:

$$\sigma_t = 4.12 + 1.22x_1 + 0.54x_2 + 1.68x_3 - 0.61x_1^2 - 0.53x_2^2 + 0.5x_3^2 + 0.22x_1x_2 + 0.22x_1x_3 + 0.19x_2x_3; \quad (7)$$

$$A = 72.11 - 8.13x_1 - 3.11x_2 - 1.12x_3 - 2.32x_1^2 - 5.43x_2^2 - 1.55x_3^2 - 3.21x_1x_2 - 4.45x_2x_3, \quad (8)$$

where  $\sigma_t$  is the rupture strength (cohesion), MPa;  $A$  is the value of adhesion to the steel substrate, N/cm.

It is established that increase in the amount of entered additives led to the growth of rupture strength concurrent with decrease in value of adhesion to the steel substrate. Any optimization of composition was impossible. Strengthening of destructured ДСТ-30P-01 can be may be linked to the presence of hydroxyl groups in its main chain. These groups are capable of forming hydrogen links with aerosil. Nevertheless, at specified values of viscosity it is possible to design compositions for various operating conditions.

We obtained equations describing change in cohesion strength at negative temperatures (in particular, at  $-10^{\circ}\text{C}$ ) for different concentrations of hardener and additive  $x$ :

ПИЦ 14 mass parts:

$$\sigma_t = -0.5 \cdot 10^{-4} \cdot x^2 + 0.0152 \cdot x + 0.473;$$

ПИЦ 11 mass parts:

$$\sigma_t = -0.5 \cdot 10^{-4} \cdot x^2 + 0.0153 \cdot x + 0.3254.$$

The optimal degree of filling was established by viscosity index depending upon temperature range of application of developed sealant (in particular, for aerosil): at  $T = +5^{\circ}\text{C}$   $\eta = 62.04 \ln(x)^{-61,521}$ , at  $T = +15^{\circ}\text{C}$   $\eta = 49.04 \ln(x)^{-53,922}$ , where  $x$  is the degree of filling, volume percent. The results of summarized analysis of experimental data showed that favourable field of service properties for the sealant corresponded to the following composition (in mass parts): binder on the base of destructured ДСТ-30Р-01 – 38.5; hardener ПИЦ – 4.6; filler aerosil – 53.9; antioxidant ionol – 3.

We developed the material for expeditious repair of airfield pavements based on ЭСКДП-Н. The following correlation equation quantitatively describing dependence of material properties on material composition are obtained:

$$\sigma_c = 25.1\Pi - 0.069C - 0.87\Pi^2 - 0.035C^2 + 0.05A^2 + 0.557A + 0.028\Pi C - 0.089CA - 160.9; \quad (9)$$

$$\sigma_t = 8.63\Pi - 0.75C - 0.3\Pi^2 + 0.08C^2 - 0.55A^2 + 3.39A + 0.03\Pi^2 A - 0.07A^2\Pi - 61.34; \quad (10)$$

$$\varepsilon_r = 0.079C^2 - 0.388A^2 + 0.104\Pi C + 2\Pi - 1.79C - 0.12\Pi^2 - 0.758, \quad (11)$$

where  $\sigma_c$ ,  $\sigma_t$ ,  $\varepsilon_r$  are the rupture and the compression strength, МПа, relative rupture elongation, %, respectively;  $\Pi$ ,  $C$ ,  $A$  are the amounts of the hardener (ПИЦ), siccative and antioxidant, mass parts, respectively.

Prolonged testing in conditions of negative temperature was conducted with consideration for the specificity of the work of a sealing material in the airfield pavement joints. The type of change in plastoelastic properties of the sealant on the basis of destructured ДСТ-30Р-01 after multi-cycle tests, for each temperature of test operation dependences of the form  $\varepsilon = f(t, T)$  are obtained where  $\varepsilon$  is the value of relative elongation, %;  $t$  is the time of load application, hour;  $T$  is the temperature,  $^{\circ}\text{C}$ . The data obtained allowed us to develop the technique of forecast of durability of developed sealants operated in severe conditions. The results of determination of physical-mechanical characteristics of the developed sealant with the use of State Standard (ГОСТ) 30740–2000 are presented in Table 3.

Table 3

## Physical-mechanical characteristics of the developed sealing material

Factor	Value of factor	
	by State Standard (ГОСТ) 30740–2000	for developed sealant
Flexibility on the standard rod, °C	Up to -30	-55
Spreadable life, hours	2	2
Application temperature, °C	Not lower than +5	0...+60
Temperature of beginning of adhesion to pneumatic tyres of aircraft chassis, °C	+150	+154
Relative rupture elongation, %	80	180
Cold resistance, loss of relative elongation after 150 cycles, %	Up to 25	Less than 3
Aging under ultraviolet radiation, loss of flexibility and mass, %	Not standardized	Less than 1
Endurance of the sealant, cycles <sub>B</sub>	Not standardized	42000
Resistance to the action of the gas jets of rocket motor, sec	150	161

### Summary

Specific power inputs  $E_{y\partial}$  of optimal mixing regimes were established. Developed compositions were applied in various climate areas; defects in repaired zones were not revealed during long operating period. The economic efficiency of the developed composite materials was determined.

This efficiency was caused by the use of available raw materials, guaranteed maintenance of the high values of physical-mechanical characteristics, increase in interrepair life of structures.

### References

1. Hozin, V. G. Polymers in construction: borders of real usage, ways of improvement. *Building materials*. 2005. № 11. P. 12—14.
2. Bartenev, G. M., S. Ya., Frenkel. *Physics of polymers*. Leningrad, 1990. 432 pp.
3. Nakanisi, K. *Infrared spectra and structure of organic compounds*. Moscow, 1965. 212 pp.
4. Barabash, D. E., S. A., Goshev. Thermal stability of oligodiene rubber concretes. *Building materials*. 2007. № 11. P. 2—4.