

## COMPOSITE MATERIAL FOR MEDICAL APPLICATION

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Composite material for medical application on the basis of polydimethylsiloxane rubber (PDMS) and graphite was obtained. The physico-chemical and mechanical properties of the material depending on the quantity, purity of the modifier and its preliminary treatment were studied. The established physico-chemical properties of the material surface allow to make the preliminary prediction of its thromboresistance.

Numerous investigations of interaction of various materials with blood have shown, that there are a few groups of materials, differing in their chemical nature, which possess thromboresistance to some extent or other: the materials with negatively charged surface, modified by physiologically active substances, with non-uniform structures, with an inert surface, carbonic and hydrogels [1]. PDMS, which is made as a material of medical class of purity on industrial scale as products (mobile elements of artificial valves of heart, tubes for the apparatus of artificial circulation and other) [2,3], may be attributed to the group of materials having the inert, hydrophobic surface. PDMS has high chemical, hydrolytic, enzymatic, radiating, thermal stability, and also high bioinertness and non-toxicity [4,5]. Among all the varieties of polysiloxane only PDMS has found wide application in medical practice [3,6,7]. However, insufficient thromboresistance of siloxane rubbers has caused the necessity of improving the latter. The variety of the factors influencing the process of clotting on the surface of a material, contacting with blood, causes various directions in search of improvement of their thromboresistance. One of the ways of such an improvement can be their modification, which allows to form directly composite materials with the given physico-chemical, mechanical and medico-biological properties.

The high biological inertness and good thromboresistance makes carbonic materials promising for the contact with blood [8,9]. It allows to apply them as the modifying agents for the bulk and surface modification of materials for medical application [10-11].

The aim of our research was to work out and study physico-chemical and mechanical properties of the composite material for medical application on the basis of PDMS and graphite depending on the quantity, the purity of the modifier and on its preliminary treatment, and also prediction thromboresistance.

The work on creating the composite on the basis of other kinds of siloxanes and graphite are known [12]. However only the materials for technical use, without hard demands to the quality both initial components, and their final product medico-biological characteristics are considered. The data on the bulk modification by graphite of the PDMS of medical purity are not known to the authors.

### EXPERIMENTAL PART

In the present work PDMS of the medical class of purity (PDMS, M.600000) was mixed up on laboratory rollers at the temperature of 20° C with a bichlorine benzoyl peroxide, silica (mark "AEROSIL"), antistrukture-forming additive and graphite (mark C-1, OST 6-08-431-75). The quantity of the latter varied from 40 to 60 mass parts.

Previously the graphite was purified by 0.1 N solution of the hydrochloric acid for 2 hours at the temperature of 70° C.

The graphite previously purified was treated by an aqueous solution of polyethylene imine (PEI), in order to strengthen the interaction between filler and PDMS in the bulk. PEI has found wide application as a promoter of adhesion in various compositions both in technical [13] and medical application [14].

The samples of the composite material were formed as plates and tubes by the following methods: in glycerol and air vulcanization at the temperature of 130-140° C.

The specific volume electrical resistance of the samples of the composite measured on the four-electrode circuit [15].

For measurement of values of the equilibrium contact angle ( $\theta$ ) on the material surface in relation to water horizontal microscope was used [16].

The infrared spectrums of the initial, and filled PDMS registrated on Spectro fotometer (UR 20).

For the registration of the spectrum of the initial PDMS an element from KRS-5 was chosen. For the record of the spectrum of PDMS filled elements from materials germanium and silicon [17] were chosen, as at filling of PDMS by graphite the parameter of refractivity of system is obviously increased.

On the basis of the data of the physico-mechanical tests (fig.1) the optimum of the graphite percentage in the polymer has been stated (50mass.parts). The values of such mechanical characteristics as relative lengthening ( $\epsilon_p$ ), residual lengthening ( $l_p$ ), the tensile strength ( $f_p$ ) of the filled polymer are changed in comparison with the starting one, but varied in acceptable ranges. The specific volume electrical resistance ( $\rho_v$ ) of obtained composite decreased by 7-8 orders in comparison with the initial PDMS.

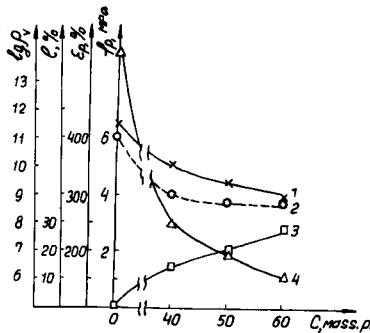


Fig.1 : Dependence of the physico-chemical properties of the composite on content of graphite.

Curves:

1-tensile strengthening  $f_p$ , Mpa;

2-relative lengthening  $\epsilon_p$ , %;

3-residual lengthening  $l_p$ , %;

4-specific volume electroresistance  $\lg \rho_v$ .

It is known [12], that the graphite does not concern a number of strengthening fillers, it has confirmed the results of the research by the method of IR-spectroscopy. The spectra of the initial (fig.2a) and filled by graphite PDMS (fig.2b,c) at 1300-700  $\text{cm}^{-1}$  are indicated.

The peak 1258  $\text{cm}^{-1}$  is stipulated by symmetric scissoring vibrations of methyl groups [18,19], being at atom Si. It is chosen as the internal standard, as its intensity is not changed during the filling of PDMS by graphite, and  $\text{CH}_3$ -groups don't participate either in formation of new covalent bond, or in donor- acceptor interaction. The intensive peaks at 1000-1100  $\text{cm}^{-1}$  are stipulated by valent fluctuations -Si-O-Si- [18]. The peak at 800  $\text{cm}^{-1}$  belongs to the vibrations of methyl group at the atom Si [19,20]. The reduction of the intensity of the peaks at 1020  $\text{cm}^{-1}$  and 800  $\text{cm}^{-1}$  to the reference peak 1258  $\text{cm}^{-1}$  with increase of the contents of graphite in the bulk of PDMS testifies the decrease of the mobility of rubber's molecules in the presence of the latter.

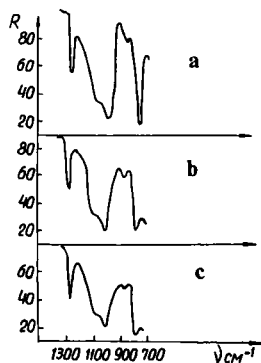


Fig.2: IR-spectroscopy of the initial (a) and filled PDMS with content of graphite 30mass.p. (b) and 40mass. p. (c).

As it is visible from the submitted IR-spectra of the initial and filled PDMS the occurrence of the new peaks, on which it would be possible to say about changes in chemical structure of initial components, is not observed. Thus, the heterogeneous interaction in the filled PDMS has a physical nature.

The treatment of graphite by PEI appreciable influences the interaction between graphite and PDMS, according to the physico-mechanical properties of the composite, Tab.1. The samples of the composite with graphite processed by PEI have higher values of residual lengthening. However, the value of the specific volume electrical resistance of the composite with PEI increases in about 1-2 orders in comparison with the samples without it. It is apparently, connected with the isolation of the particles of graphite from each other by a layer of polysiloxane, and it is possible, with the formation of the conglomerates of graphite's particles in the presence of PEI and their non-uniform distribution in the bulk of the composite.

Table 1

Comparative data on physico-mechanical properties of the composite material and initial components

Material PDMS	Specific volum electro resistance $\rho_v, \text{om}^*\text{m}$	Conditional tension $f_p, \text{MPa}$	Relative lengthening $\varepsilon_p, \%$	Residual lengthening $l_p, \%$
Initial	$10^{14}$	6,5	400	0
Filled by graphite, 50m.p.	$10^7-10^6$	4,5	280	20
Filled by graphite with PEI, 50m.p.	$1-5 \cdot 10^8$	4,6	280	13
Graphite (initial)	$10^{(*)}$	-	-	-

(\*)-Ubbelode A.R., Luice F.A. "Graphite and its crystal compounds", M., 1965.

The chemical, energy and structural heterogeneity of material's surface are known [21] to influence its medico-biological properties. For example there is a opinion [21], that the free surface energy of various substances well correlates with their thromboresistant properties. In the present work the surface free energy ( $\gamma$ ) was calculated from the contact angle data [21] and was stated, that the values of  $\gamma$  of the composite range from 20 to 50 mJg/m<sup>2</sup>, which is typical for the materials, possessing favorable thromboresistance [21,22], Tab.2.

$$\gamma = \frac{\gamma_1 \cdot (1 + \cos \gamma)}{4}$$

where  $\gamma_1 = 72,5$  - the surface tension of water, [mJg/m<sup>2</sup>].

Table 2

Some physico-chemical characteristics  
of the composite material's surface

Material PDMS	Equilibrium contact angle $\theta$ , degree	Free surface energy $\gamma$ , mJg/m <sup>2</sup>
Initial	90	18,2
Filled by graphite, 40m.p.	90-107(*)	
50 m.p.	76	28,2
60 m.p.	72	31,2
	72	31,2
Filled by graphite with PEI, 50 m.p.	70	32,7
Graphite (initial)	60-70	40,1-32,7
	50-80(**)	48,1-24,9

(\*) Ogarev V.A., Ivanova T.K. Influence of temperature on equilibrium contact angle and rate of the spilling of polydimethylsiloxane's drops on surfaces of solid substance. // Kolloidny zurnal. 1974, v.36, issue 3, P.462.

(\*\*) Schrader M.E. Ultrahigh vacuum techniques in the measurement of contact angles water on graphite. // J. Phys. Chem. 1975, v.79, 23, pp.2508-2512.

The developed material was tested in experiment on dogs as temporary shunts (internal diameter 7mm, length 400mm) of the abdominal aorta. The coagulation of blood hasn't been observed for three hours and more.

#### CONCLUSIONS

Thus, the results of physico-chemical, mechanical and preliminary medical tests allowed to come to the conclusion, that the composite material on the basis of medical purity PDMS and graphite (both treated by PEI and not) possess the necessary complex of the physico-mechanical and also favorable thromboresistance, allowing to use it as temporary medical products.

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