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OBTAINING ENVIRONMENTALLY FRIENDLY COMPOSITE MATERIALS USING LOCAL RAW MATERIALS

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ANNOTATION

The paper shows the rational use of mineral raw materials and technogenic secondary products by modifying them and obtaining high-quality ingredients with the subsequent development of effective elastomeric composite materials.

The article also shows that heat treatment and chemical modification of fillers leads to significant structural changes due to the course of chemical and thermophysical processes, and also considers their effect on the properties of composite elastomeric materials of various nature.

Keywords

Composition, elastomer, structure, filler, antioxidant, polymer, ingredients

Introduction. At present, with the expansion of the production of rubber-technical products, the role of ingredients is significantly increasing, which can significantly improve the technical properties of elastomeric composite materials.

One of the effective methods for modifying composite polymer materials is filling. The introduction of fillers makes it possible to obtain composites with improved technological and physical-mechanical properties while reducing their cost. For these purposes, the most widely used solid, highly dispersed, fibrous fillers of inorganic and organic origin [1-4].

The current stage in the development of chemistry and technology of composite materials is largely determined by the search for ways to create products with improved technical properties.

To date, a number of measures are already being implemented aimed at solving this general problem, among which a large place belongs to the introduction of structurally-chemical modified fillers into the composition of the composition.

In addition, elastomeric composites are used under conditions of intense exposure to solar radiation, heat and other climatic factors. In this case, destruction

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occurs. Therefore, the problem of stabilization of composite elastomeric materials with high molecular weight antioxidants is very urgent. A serious disadvantage of conventional antioxidants is that they are lost from the composite matrix either by solvent extraction or due to volatility, which leads to an increase in the rate of destruction and an increase in the fragility of the composition.

This disadvantage can be overcome by using high molecular weight antioxidants. In this regard, the behavior of vulcanizates under the influence of solvents was investigated, as well as the constancy of the effect of antioxidants under these conditions.

Experimental part. Modified modified Angren kaolin (MAK), unmodified Angren kaolin (NAK), natural burnt clay (GLEZH) and modified wollastonite (MB), unmodified bentonite (NB), modified bentonite (MB), modified phosphogypsum (MPG) (waste from the production of phosphorus fertilizers) and stranded [5].

We have studied the modification of rubber compounds based on rubbers SKI-3 and SKMS-30 RP with polymeric antioxidant-polythiobenzpolithiazole methacrylate (PTBTM). Polythiobenzthiazole methacrylate was synthesized as described in [6-8]. Vulcanization was carried out at a temperature of 416 K for 0.5 hour, heat aging at a temperature of 372 K for 24 hours.

The discussion of the results. One of the most important tasks in the field of physicochemistry of filled polymers is the study of the processes occurring at the polymer-filler interface, which largely determine the behavior of the compositions under the conditions of their processing [9].

In this regard, the peculiarities of the interaction of elastomer macromolecules with various mineral fillers have been studied by the method of statistical adsorption from dilute polymer solutions. The study of the kinetics of adsorption of elastomer macromolecules on modified Angren kaolin (MAK), unmodified Angren kaolin (NAC), natural burning clay (GLEZH) and modified wollastonite (MB) showed that with increasing time (τ) the value of adsorption (T) noticeably increases to 20 hours.

The increase in adsorption is mainly determined by the dispersion of the filler and their structural features. So, for example, in slus unmodified bentonite (NB), modified bentonite (MB), MAK and GLEZH, when their structure and dispersion change under the influence of temperature, the value of G changes noticeably (Table 1). It was found that the amount of adsorption also depends on the nature of the elastomers. In particular, in the investigated system of aluminosilicate fillers - SKI-3 solution, adsorption equilibrium is reached in about 48 hours, and the equilibrium value of adsorption (Gy) is 0,8-1,4 mg / m^2. At the same time, in the

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case of SKMS-30 PR solutions, the effect on the adsorption parameters is very pronounced.

The maximum adsorption value (Γmax) depends mainly on the structural features and dispersion of the adsorbent. In the case of NB, MB, GLEZH and MAK, the least is the adsorption of elastomer macromolecules on MB and MPG (modified phosphogypsum). However, it should be borne in mind that the value of Γmax is influenced by the chemical nature and segmental duration of elastomer macromolecules.

Table 1. Kinetics of adsorption of elastomer macromolecules on NB, MB, MAK, NAK, GLEZH, MV, MFG and Mel

Γ_{max} (mg / m²) per 1 g of adsorbent								
SKI-3	NB	MB	MAK	NAK	GLEZH	MB	MPG	Mel
	1,98	1,92	1,08	059	1,14	0,45	0,15	0,21
SKMS-P	1,99	1,94	0,92	0,45	1,02	0,33	0,25	0,34

The oil absorption of mineral fillers has been studied and it has been found that NB, MB, MAK and GLEZH, due to the developed specific adsorption surface, have an increased oil absorption. The latter indicator decreases significantly with an increase in the content of aromatic hydrocarbons in the oil (table 2).

Solving the issue in specific areas of their application requires comprehensive research aimed at developing formulations of composite materials, as well as modification methods and finding processing conditions.

When creating composite polymer materials, a significant role is assigned to carbon fillers [10-13]. Among them, carbon black occupies a special place, the structure and properties of which are largely determined by the methods of their synthesis [14-18]. In this aspect, it is worthwhile to clarify the structural and chemical features of modified carbon (MC) -waste formed during the production of acetylene by pyrolysis from natural gas. Table 3 shows the elemental composition of MU and some grades of carbon black.

Table 2. Oil absorption of the studied mineral fillers

The name of indicators	NB	MB	MAK	EK	GLEZH	MPG	Mel
Specific adsorption surface, m² / g	29,1	35,4	24,2	14,5	26,1	2,2	2,8
Oil absorption, ml / 100 g: -linseed oil	32,0	34,1	27,0	21,0	28,0	17,0	18,9

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- Vaseline oil	38,2	44,2	34,0	28,0	33,0	24,6	26,3
- Dibutyl phthalate	36,4	43,0	31,5	25,2	30,4	26,2	27,5

Table 3. Elemental composition of MU and some grades of carbon black

The name of indicators	Content,%				
	MU	T 900	P 701	P 705	P803
Carbon	88-90	96-99	96-98	96-98	97-99
Hydrogen	3-4	0,3-0,5	0,4-0,6	0,6-0,8	0,4-0,6
Oxygen	6-7	0,1-0,2	0,3-0,5	0,3-0,5	0,1-0,2
Sulfur	-	0,1	0,3	0,3	0,2
Ash content	0,8-0,9	0,1-0,2	0,4-0,6	0,4-0,5	0,4-0,5

Table 4 shows the change in the elemental composition of MC after extraction for 72 h.

It can be seen from the table that MU differs from serial technical carbon in the increased content of oxygen and hydrogen. When MC particles are formed, products of incomplete carbonization of raw materials are adsorbed on its surface. The study of the composition of these substances is important because they affect the formation of the structure and the property of the composition.

Thus, the above studies suggest that the structure of MC is, as it were, an intermediate stage in the formation of soot structures, which, upon the formation of its particles, are mycocapsulated into a polymeric-oligomeric functionalized shell with oxygen-containing groups.

Among the new vulcanization methods and curing agents, the use of sulfur, accelerators and thermal activation of the process continues to be of greatest importance. The quality of rubber products is inextricably linked with the conditions for the formation in the process of vulcanization of the optimal structure of the spatial mesh, which makes it possible to maximize the potential properties of elastomeric systems.

Modern sulfur vulcanizing systems minimize the destruction and modification of elastomeric macromolecules, ensuring performance at increased deformations, however, the operating conditions of a number of products put forward specific requirements for specific rubbers [19,20]. Of these properties, one can single out good adhesion of rubber to metal and fibers, a high level of properties during high-

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temperature vulcanization, simultaneously with an increase in the strength of the bond between the layers of the product.

Table 4. Change in the elemental composition of MC after extraction for 72 h.

The name of indicators	Initial MU	Content,% after extraction			
		gasoline	acetone	toluene	alcohol-benzene
carbon	88.37	88,45	91,69	92,69	90,56
hydrogen	3.82	3,74	2,40	1,60	2,10
oxygen	6.95	6,90	4,90	4,59	6,16
ash content	0.86	0,91	1,01	1,12	1,18
light transmission of the extract	does not miss	99,40	51,20	28,3	33,7
Oxygen-containing groups of the extract:					
carboxyl	0,61	0,60	0,36	0,30	0,37
phenolic	0,39	0,39	0,14	0,08	0,06
quinone	3,31	3,34	2,30	1,19	3,13
lactone	2,64	2,60	2,10	1,92	2,60

In solving this scientific and technical problem, which meets the current and future requirements of the industry, the development of new bases for the use of chemically active additives is of great importance. These compounds are generally modifiers of rubber molecular chains, and at the same time have a weak ability to structure elastomers.

The study of the physical and mechanical properties of vulcanizates showed that the introduction of polythiobenzthiazole methacrylate increases the resistance to heat aging (table 5).

Table 5. Physical and mechanical properties of vulcanizates based on rubbers

SKI-3 and SKMS-30 PR modified with polymeric antioxidant

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Indicators	Unextracted		Extracted	
	initial	after aging	initial	after aging
Stabilization with phenyl-β-naphthylamine (neozone D)				
Tensile strength, MPa	13,0	9,3	8,3	too fragile
Relative extension, %	420	354	300	fragile
Residual elongation,%	22	24	24	for testing
Stabilization with polythiobenzthiazole methacrylate				
Tensile strength, MPa	14,0	13,2	12,0	11,8
Relative extension, %	487	476	400	350
Residual elongation,%	20	18	12	12

High molecular weight compounds containing antioxidant compounds in the main chain of the macromolecule are widely used in production to obtain various polymeric materials with high thermal stability, as well as improved physical, mechanical and operational properties.

An azeotropic mixture of methanol-acetone-chloroform (28:35:29 ml, boiling point 330,5 K) was used as an extraction solvent.

The results shown in the table show that the vulcanizate stabilized with polythiobenzthiazole methacrylate and subjected to solvent extraction retains substantially its physical properties after aging at 373 K for 24 hours.

Conclusion. Thus, the studies carried out show relatively high adsorption properties of NB, MB, MAA, which significantly affect the properties of composite elastomeric and polymer materials [21].

The high-molecular antioxidant compares favorably with the low-molecular antioxidant neozone D in rubber compounds. The usual antioxidant used for comparison (neozone D) is removed during the extraction process, as a result of which the sample after aging turns out to be too fragile for testing [22].

The totality of the results obtained on the study of the physicochemical and mechanical properties of the proposed mineral fillers and antioxidant indicate that, in terms of the complex of properties, they meet the requirements for fillers and can be recommended as new ingredients of composite elastomeric materials for the production of general-purpose rubber products.

The use of local raw materials and industrial waste makes it possible to save currency.

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