Investigation of Physicochemical Properties and the Efficiency of the Application of Ultrafine Carbonaceous Materials of Different Crystallographic Structure in Elastomer Compositions

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Abstract

The investigation of physicochemical properties of carbonaceous materials of different crystallographic structure is performed; the efficiency of their application as fillers for the elastomer compositions is studied. It is demonstrated that the application of carbonaceous dispersed fillers of mineral and artificial origin in elastomer compositions is the most efficient after their preliminary combination with carbon black in the aqueous phase.

INTRODUCTION

The progress in the synthesis and processing of polymeric materials is closely connected with permanent broadening of the raw material base, mastering the product quality and the efficiency of production. One of the most important processes of latex technology is reinforcement of elastomers with disperse fillers, carbon black being the most important of them. However, even with broad assortment, it cannot meet all the newly appearing requirements to the properties of rubber materials for different purposes.

At present, dispersed organic and inorganic materials of non-oil origin (lignin, graphite, amorphous silica, talc, chalk, kaolin, *etc.*) become increasingly important. However, their application as fillers is limited by the fact that the rubber materials containing them do not exhibit such a set of properties as those filled with carbon black [1–4].

The development of new methods to obtain finely dispersed carbonaceous materials (grinding and mechanical activation of the surface, detonation synthesis, *etc.*) broadens the possibilities to obtain fillers for elastomer compositions with different physicochemical and adsorption properties.

The goal of the present work is to investigate the interconnection between physicochemical properties and the reinforcing activity of different types of carbonaceous fillers.

EXPERIMENTAL

The subjects of investigation were carbon black (CB) of different brands, finely ground dense-crystalline (GS-2) and cryptocrystalline (GLS-3) graphite, products of the detonation synthesis of hydrocarbons: graphite fraction, the so-called technical diamond carbon (TDC) [5], ultrafine products of the biochemical processing of natural coals (BCPO coal) [6] (biochemical processing involves partial biological transformation of the organic mass of coal under the action of a specific association of microorganisms under aerobic conditions).

These materials represent various structural modifications of carbon. Dense-crystalline graphite is characterized by high degree of three-dimensional ordering, while the structure of cryptocrystalline graphite is close to the two-dimensional ordering (amorphous) [7]. Carbon black has a turbostratic (disordered layered) structure. Coals are composed of linear polyconjugated structures which are an intermediate stage of the transformation of glucoside residuals of cellulose into graphite-like layers as a result of the longitudinal or cross polymerization. TDC is condensed carbon of the cluster type; the structure of its particles reminds the layered structure of graphite but particle size is much smaller.

In order to estimate the basic physicochemical and adsorption properties of the materials under investigation, we used modern analytical methods. Total specific adsorption surface was determined using the BET procedure according to the State Standard (GOST) 23401–90, the outer specific surface accessible for caoutchouc macromolecules was determined using the adsorption of OT aerosol (sodium-2-diethylhexylsulphosuccinate) [8]. The iodine number (a measure of the chemical activity of the surface of dispersed materials) was determined according to [9]. Dibutylphthalate (DBP) absorption which characterizes the ability of dispersed materials to structure formation was measured according to the State Standard (GOST) 25699.5–90. The chemical status of the surface was estimated using the pH of the aqueous suspension. The bound oxygen content on the surface was measured according to [10].

To estimate the energy and chemical activity of fillers, electrometric method was used [1]. It involves the measurement of the potential of ferrous-ferric redox system in the presence of the suspension of a filler, which is considered as a model of the filled system.

RESULTS AND DISCUSSION

The adsorption of iron hydroxy complex on the surface of the carbonaceous material depends on the size of dispersed particles, their morphology, and the chemical and energy state of their surface, *i. e.*, on the entire set of properties that determine the adsorption and reinforcing ability of fillers. The surface activity of the fillers is characterized by the yield of the model, the limiting voltage drop (U_{lim}), which is the basis for the calculation of conventional adsorption potential ($\Delta\mu^\circ$) according to the equation

$$\Delta\mu^\circ = 96.5\Delta U + 5.7 \lg \frac{3.6\ 10^3}{S_0 m} - 5.7\Delta\text{pH} \qquad (1)$$

A comparative analysis of physicochemical properties of the materials under investigation (Table 1) allows us to consider the similarity of chemical composition of carbonaceous fillers of separate kinds. At the same time, differences in the nature and formation conditions for the disperse particles of carbon black and of other forms of carbonaceous materials provide a series of substantial differences in their morphology and physicochemical properties of the surface.

High values of specific surface, determined by different methods allowing one to avoid the difficulties connected with aggregation clotting of particles, point to the fact that the mean particle size of the materials under investigation is likely to be close to the size of disperse particles of carbon black of fine types, such as P324 and P245; in the case of technical diamond carbon, it is even higher.

The value of the total specific surface of fine ground graphite, BCPO coal and TDC, determined by means of low-temperature adsorption of nitrogen, is much lower than the value of the outer specific surface determined by means of the adsorption of SAS. The latter serves as the characteristic of the outer surface of a filler, excluding its microporosity. This indicates that the carbonaceous materials under investigation are non-porous, rather fine materials prone to aggregation. The BCPO coal is obtained in water suspension; its isolation, namely drying, is accompanied by the condensation processes leading to the formation of agglomerates; during the determination of the outer specific surface, peptization is observed under the action of the aqueous solution of SAS; carbon agglomerates pass into the colloid state.

Low values of the oil number, determined from the absorption of dibutylphalate, are the evidence of the absence of the ability of these

TABLE 1

Physicochemical properties of carbonaceous materials

Characteristic	CB			Graphite		TDC	BCPO coal
	P803	P514	P245	dense crystalline	latent crystalline		
Carbon content, %	98.3	98.3	98.3	94.8	80.5	88.0	70.9
Impurities, %	0.35	0.35	0.04	3.95	18.77	6.0	10.0
Interplanar spacing, Å	3.7	3.6	3.5	3.35	3.36	3.2	–
Density, g/cm^3	1.84	1.86	1.86	2.27	2.13	2.70	1.42
Specific adsorption surface (with nitrogen) S_a, m^2/g	16	52	117	92	95	501	14
Specific outer surface S_{out}, m^2/g	–	48	106	86	163	563	156
Iodine number, mg/g	–	37	106	71	107	379	168
pH of aqueous suspension	7.3	7.2	7.3	9.5	8.4	8.6	6.8
DBP absorption, cm^3/100 g	86	101	112	20	22	190	58
Bound oxygen content, %	1.40	1.36	1.00	2.90	3.93	1.00	8.23
Conventional adsorption potential, $\Delta\mu^\circ$, kJ/mol	16.2	19.8	28.6	36.7	41.9	38.3	39.6
Voltage drop per unit surface area, $\Delta U/S$, mV/m^2	7.2	7.5	7.6	6.4	7.2	15.4	3.9

modifications of carbon to form structures in a hydrocarbon medium characteristic of carbon black. Dispersed particles of the latter are formed as a result of thermal decomposition of gaseous or liquid hydrocarbons at the limited air access; as a result of condensation processes, they get complicated shapes, from spherical to grape-like. Particles of close shapes are formed under the conditions of explosive synthesis, one of the products of which is TDC, while the dispersion character of particle formation for the BCPO coal and fine ground graphites leads to obtaining particles of isometric shapes.

The presence of a substantial fraction of mineral admixtures in natural graphites and coals brings complications to their analysis, especially using pH of aqueous suspension, which is considered as an estimate of the surface oxidation degree in the case of carbon black. The investigation shows that in spite of the presence of a substantial fraction of bound oxygen on the surface of fine ground graphite and BCPO coal (see Table 1), pH of their aqueous suspensions is characteristic of neutral or weakly alkaline media. It is most probable that this is due to the dissociation of mineral substances in solution, including the compounds of alkaline metals incorporated into admixtures.

The adsorption of iron ions on various fillers increases with the augmentation of their dispersity, which leads to the increase of the conventional adsorption potential ($\Delta\mu^\circ$) and thus to the increase of the surface activity of a filler. The comparison between the conventional adsorption potential values allows one to consider the activity of fillers only in the row of the substances of identical nature obtained by the same technology (Fig. 1).

To compare the activities of the surface of the substances of different nature, it is proposed to apply the ratio of voltage drop for the oxidative-reductive system (ΔU) to the surface area (S) per unit mass of the filler. This parameter indirectly allows us to estimate the number of active centers on the surface of the filler. In the row of the investigated materials, the least surface activity is exhibited by the BCPO coal, the most likely reason being the overlap of the surface active centers by bituminous substances. Fine ground graphites have adsorption potential higher than the carbon black has, but in the number of surface

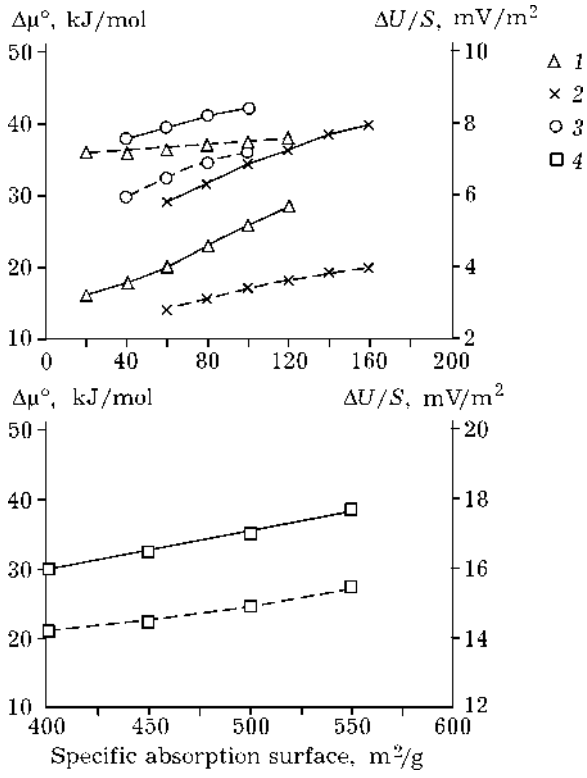

Fig. 1. The effect of specific surface on the characteristics of the surface activity of carbon fillers: *1* – carbon black, *2* – BCPO coal, *3* – graphite, *4* – TDC; *continuous line* – conventional adsorption potential, *dashed line* – voltage drop per unit surface area.

active centers the carbon black exceeds graphite only insignificantly; this may be seen if one compares the $\Delta U/S$ characteristics. In turn, ultrafine (cluster) TDC characterized by the excess surface energy, exceeds the active brands of technical carbon about two times with respect to the $\Delta U/S$ and $\Delta\mu^\circ$ characteristics.

The reinforcing activity of the investigated materials was estimated in the elastomer compositions of standard composition based on methylstyrene-butadiene rubber SRMS-30ARK. Physicomechanical properties of the rubbers are shown in Table 2.

Comparative analysis of the obtained data shows that the natural and synthetic ultrafine carbonaceous materials have lower reinforcing activity than the basic grades of carbon black, but approximately equal to its low-activity grades. It is difficult to add 50 mass parts of TDC into the rubber mixture, because the existing technology of mixing does not allow to achieve the necessary extent of dispersion of the fillers with the specific surface more than 150 m^2/g in the elastomer matrix. Fine TDC causes a sharp increase of the viscosity of the rubber mixture and renders

TABLE 2

Physicomechanical properties of rubber mixtures and vulcanizates with different fillers (50 mass parts of filler per 100 mass parts of rubber)

Characteristic	CB			Graphite		TDC	BCPO coal
	P803	P514	P245	crypto-crystalline	dense-crystalline		
Rubber mixtures							
Minimal torque strength, N	0.40	0.48	0.68	0.20	0.20	2.40	0.13
Maxumal torque strength, N	1.8	1.97	2.0	0.64	0.68	3.90	0.24
Vulcanizates							
Conditional voltage at 300 % lengthening, MPa	9.4	15.8	15.0	2.2	3.3	–	1.5
Conditional tensile strength, MPa	16.3	22.4	27.0	8.5	15.5	14.4	5.6
Relative lengthening at rupture, %	420	430	450	580	790	200	1175
Residual deformation, %	10	8	12	12	27	8	64
Hardness, rel. units	42	51	63	46	48	90	34
Elasticity, %	38	35	28	33	33	12	39

ТАБЛИЦА 3

Effect of the content of secondary carbon material on physicochemical properties of the binary filler based on carbon black P245 and physicomechanical properties of the rubbers based on rubber: SRMS-30 ARK (numerator) and SKI-3 (denominator)

Characteristic	CB P245	Content of the secondary component in the binary filler based on CB P245, % mass								
		Graphite			TDC			BCPO coal		
		5	10	15	1	3	5	2.5	5	10
Engineering strength at 300 % lengthening, MPa	15.0 13.0	13.0 12.0	11.6 11.3	10.6 11.6	15.3 14.4	15.8 15.2	16.1 15.5	11.8 9.7	10.5 9.1	10.3 8.0
Conventional tensile strength, MPa	27.0 28.0	25.2 28.2	27.9 29.0	25.7 28.5	29.1 28.9	28.4 30.8	28.2 29.0	29.0 27.5	27.8 26.9	27.0 25.2
Relative lengthening at rupture, %	450 510	475 525	510 550	510 555	430 460	420 445	400 440	480 540	490 560	510 600
Resistance to multiple stretching (E = 150 %), thousand cycles	6.5 87.0	18.0 90.0	22.0 91.0	25.0 92.0	7.2 14.8	7.0 14.5	6.8 14.0	11.8 87.0	18.5 88.5	24.0 89.0
Resistance to abrasion, TJ/m^3	0.044 0.030	0.047 0.032	0.048 0.035	0.047 0.036	0.046 0.031	0.049 0.033	0.059 0.039	0.037 0.030	0.035 0.029	0.031 0.028
Bonding strength of the rubber based on rubber SRI-3 with cord 23KNTS (H method), N:										
at 20 °C	130	130	134	135	132	136	141	139	145	145
at 120 °C	110	111	119	113	114	134	116	119	120	121

increased hardness along with low elastic propety to the vulcanizates. It follows from the above that these materials as individual ones can find only limited application in preparing polymeric compositions with low hardness for not very responsible duties. However, high surface activity of the materials under investigation allows assuming the possibility of their combination with carbon black in the synthesis of elastomer compositions in order to improve the set of properties of the combines fillers.

The most efficient method to make combined fillers is their preliminary combination with the dusty carbon black in granulating mixer using the so-called wet method [12]. When combining the carbon black with aqueous dispersion of the natural (synthetic) filler, the particles of the latter are distributed in the mass of carbon black more uniformly than during dry mixing. As a result of blocking the particles of the second component by the disperse units of carbon black, their tendency to agglomeration or condensation decreases substantially, which allows conserving the increased dispersity of natural fillers, realized during peptization in water. In turn, discrete distributed particles of the natural fillers prevent agglomeration of carbon black in the elastomer matrix, help dispersing it and forming a better developed polymer – filler interface. As a result, the rubber mixtures and rubbers with binary fillers obtained in the aqueous phase are characterized by the improved set of technological and technical properties. The dependence of physicomechanical characteristics of the rubbers, based on general-purpose rubber, on the ratio of the constituents of filler is shown in Table 3.

A definite contribution in the formation of the structure and properties of polymeric compositions is made also by specific properties of the natural and synthetic materials incorporated into the binary fillers. For example, the scaly shape of particles and low friction coefficient of graphite provide lower generation of heat in the rubbers under dynamic deformations, increase their impermeability to water and gas, raise their electric conductivity, help increasing the efficiency of the protective action of chemical stabilizers [13, 14]. The BCPO coal, due to the presence of different oxygen-containing functional groups on its surface, augments adhesion of the rubbers to textile materials and the resistance to thermal oxidative aging. Fine TDC, possessing higher specific surface, helps increasing the resistance of rubbers to abrasion.

CONCLUSIONS

Thus, the use of carbon dispersed fillers of mineral and artificial origin in elastomer compositions is the most efficient when they are preliminarily combined with the carbon black in the aqueous phase, which is one of the efficient methods of the directed synthesis of elastomer compositions with the required set of technological and technical properties.

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