The reinforcement of elastomers is so complex that only individual aspects of the problem, mainly concerning interphase interactions, have been studied. The main indicator of reinforcement is considered to be the carbon–rubber gel (refs. 1 and 2). The amount of carbon–rubber gel is influenced, among other factors, by the surface activity of the carbon black (ref. 3), which is determined by a number of chemical factors and by the mobility of \( \pi \)-electrons, governed by the presence on the carbon surface of graphite-like planes (ref. 4) and adsorbed low molecular weight aromatic compounds (ref. 5) capable of forming complexes with charge transfer (refs. 6 and 7). Electron exchange interaction is intensified with increase in the degree of ordering of the carbon surface as a result of the burning off of the less ordered areas with the formation of pores under thermo-oxidative actions (ref. 8) and enlargement of graphite-like planes during heat treatment (refs. 9 and 10).

Earlier (ref. 11), to investigate features of the surface microstructure of carbon black, we used its capacity for electron exchange interaction with nitrogen-containing polar solvents (ref. 12). During the extraction of P245 carbon black with dimethylformamide, about 3.7% of the substances with a sufficiently high molecular weight, i.e. “oligomeric” aromatic compounds, is transferred into the extract, since their quantity does not change as a function of the heat treatment time (Figure 1). Furthermore, on the surface of P245 there is about 3% non-polar low molecular weight hydrocarbons, evidently with fragments of aliphatic structure (ref. 13), that are not transferred into the extract but are removed by devolatilisation, reducing the weight gain of carbon black by several factors. Microporous P267-E carbon black similar in degree of dispersion to standard-production carbon black contains roughly 3 times less low molecular weight hydrocarbons that can be removed by devolatilisation, but they are all transferred into the extract, i.e. they are all aromatic compounds.

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**Figure 1** Dependence (a) of nominal tensile strength (1, 2) and \( r, (1', 2') \) of rubber compounds with 50 parts carbon black per 100 parts SKMS-30ARK rubber and (b) of weight gain of carbon black (1", 2") and relative amount of extract of carbon black in dimethylformamide (1"", 2""") on its heat treatment time: 1 — P267-E; 2 — P245
As an electron donor, dimethylformamide “removes” from old complexes and above all dissolves the strongest electron acceptors — low molecular weight and oligomeric aromatic hydrocarbons. The weight of the carbon black increases on account of the combination of dimethylformamide by “planomeric” aromatic compounds (not extracted with dimethylformamide) and by fine graphite-like planes at which electron acceptors have been “taken away” and gone into the extract. Since the donor properties of polyconjugation systems are enhanced with increase in their size (ref. 6), large graphite-like planes do not interact with dimethylformamide in the presence of “planomeric aromatics” and fine planes. This is confirmed by the results of investigating the properties of graphite-containing rubber mixes (ref. 14). Graphite accepts electrons of a nitrogen-containing vulcanisation accelerator, increasing the scorch resistance of the mix, only in the absence of carbon black. Small additions of a stronger acceptor — carbon black — convert the graphite into an electron donor not interacting with vulcanisation accelerators. Since the initial standard-production carbon black, compared with microporous carbon black, contains a greater quantity of aromatic compounds and fine planes, with a smaller degree of ordering of its surface (ref. 10), it exhibits a greater weight gain of the sample (see Figure 1). With its further heat treatment, as the number of fine planes decreases through their movement and enlargement (ref. 9), the weight gain decreases. Heat treatment of microporous carbon black leads to an increase in its weight gain and in the amount of extract on account of diffusion from within of particles of low molecular weight, oligomeric, and planomeric aromatic compounds. The latter are not transferred into the extract but interact with dimethylformamide, increasing the weight of the sample.

From an analysis of the data in Figure 1 it can be seen that two features of the surface microstructure of carbon black of the investigated grades have an adverse effect on reinforcement — the presence on the surface of P245 of low molecular weight hydrocarbons not extracted with dimethylformamide, and a shortage on the surface of P267-E of low molecular weight, oligomeric, and planomeric aromatic compounds, which increases the interaggregate interaction and impedes dispersion of the filler. This shortage is more significant, since at the same time there is a reduction in the conductive and reinforcing properties of microporous carbon black. Therefore, an attempt was made to eliminate the given shortage by increasing the contact time of microporous carbon black with a thermo-oxidative medium (ref. 15) with the aim of depolymerisation of the carbon material within particles and the emergence of the lacking aromatic on the surface as it is produced. Thus, new microporous carbon black of grade P399-E has, by comparison with P267-E with a similar specific external surface (about 160 m\(^2\)/g), a 3 times larger specific surface with respect to nitrogen (about 800 m\(^2\)/g). At the same time, the formulation variant of reducing interaggregate interaction in the carbon black phase by introducing anthracene (white crystalline powder, melting point 216 °C) into the mix was checked. Tests were carried out in the formulation of a standard rubber mix based on Nairit polychloroprene rubber KR-50 with a metal oxide vulcanising group. Standard-production P324 furnace black, similar in degree of dispersion to the new microporous P399-E carbon black, was adopted as the control.

As can be seen from Figure 2, in the absence of anthracene, the lowest tensile strength is possessed by vulcanisates with P267-E, and the highest tensile strength by vulcanisates with P399-E. The electrical conductivity of vulcanisates is an order of magnitude higher in the case of the new microporous carbon black than with P267-E. Anthracene additions in all cases simultaneously increase the electrical conductivity and strength of rubber compounds. Here, the greatest increase in strength occurs in rubber...
compounds with P267-E, and the lowest increase in rubber compounds with P399-E. As a result of the addition of anthracene, there is a reversal of the order of rubber compounds in terms of strength: the highest strength is possessed by vulcanisates with P267-E, and the lowest strength by vulcanisates with relatively less dispersed carbon black P399-E. Control specimens with P324, both in the presence of anthracene and without it, occupy an intermediate position in terms of tensile strength, approaching corresponding rubber compounds with P399-E.

Thus, testing of the surface microstructure of carbon black with dimethylformamide proved to be extremely effective and made it possible not only to establish but also to alter certain interrelations between the structure and the reinforcing properties of the filler. Improved microporous carbon black P399-E with a lower degree of dispersion makes it possible to retain high strength and improves the electrical conductivity of rubber compounds by an order of magnitude. By weakening the intraphase interaction in P267-E carbon black, the addition of anthracene increases the strength and electrical conductivity of rubber compounds filled by them, i.e. has the same effect as that of carbon black P399-E. Control specimens with P324, both in the presence of anthracene and without it, occupy an intermediate position in terms of tensile strength, approaching corresponding rubber compounds with P399-E.

The interaction of anthracene with polyconjugation systems of standard-production carbon black seems to reduce the chemical activity of the hydrogen atoms arranged around their periphery and the quinone and phenol groups, and accordingly the amount of carbon–rubber gel formed during mixing (see Figure 1). Microporous grades of carbon black were obtained with large contact times with a high-temperature medium (ref. 15), which lowers the chemical activity of the carbon surface and increases its capacity for electron exchange interaction (refs. 3 and 8–10). Therefore, their main feature becomes not the chemical but the donor–acceptor nature of surface activity. The first consequence of this is an increased level of intraphase interaggregate interaction and the associated difficulties of dispersion. The addition of anthracene increases the achieved area of contact of the dispersed phase with the elastomeric medium and accordingly the amount of gel. Here, the greatest increase in the amount of gel in a mix with P267-E correlates with the greatest increase in tensile strength and, it seems, in the degree of dispersion of this filler. The second consequence is the predominance of physical mechanisms of gelation — through the occlusion of rubber in microcavities, including cavities within carbon black particles, and the adsorption of electron-active components of the elastomeric medium on the carbon surface. As a result of this there is a sharp reduction in the dependence of the effect of reinforcement on the chemical activity of the rubber (ref. 16), and the gel ceases to be an indicator of reinforcement, correlating better with the index of electrical conductivity than that of strength.

Butadiene–methylstyrene rubber is more reactive in relation to carbon black by comparison with Nairit. Therefore, in rubber compounds based on SKMS-30ARK rubber, there is an increase in the advantage of more chemically active standard-production carbon black over microporous carbon black in terms of tensile strength, and over P267-E carbon black also in terms of the content of carbon–rubber gel (Table 1). Otherwise, the results of tests

![Image of Table 1](image)

Table 1 Influence of addition of anthracene on content of carbon–rubber gel in rubber mixes with 50 parts carbon black per 100 parts SKMS-30ARK rubber and properties of their vulcanisates (vulcanisation conditions: 155°C, 60 min)

<table>
<thead>
<tr>
<th>Grade of carbon black</th>
<th>P267-E</th>
<th>P399-E</th>
<th>P324</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of anthracene, parts</td>
<td>—</td>
<td>1</td>
<td>—</td>
</tr>
<tr>
<td>Content of carbon–rubber gel, %</td>
<td>53.97</td>
<td>55.46</td>
<td>69.82</td>
</tr>
<tr>
<td>Nominal stress under 300% elongation, MPa</td>
<td>10.9</td>
<td>12.8</td>
<td>10.5</td>
</tr>
<tr>
<td>Nominal tensile strength, MPa</td>
<td>16.6</td>
<td>20.4</td>
<td>18.3</td>
</tr>
<tr>
<td>Breaking elongation, %</td>
<td>420</td>
<td>390</td>
<td>450</td>
</tr>
<tr>
<td>Shore hardness, nominal units</td>
<td>68</td>
<td>70</td>
<td>72</td>
</tr>
<tr>
<td>Tear strength, kN/m</td>
<td>57</td>
<td>65</td>
<td>59</td>
</tr>
<tr>
<td>Fatigue strength under repeated elongation (ε = 150%), thousand cycles</td>
<td>100.1</td>
<td>86.1</td>
<td>—</td>
</tr>
<tr>
<td>Volume resistivity ρ, Ω m</td>
<td>0.47</td>
<td>0.25</td>
<td>0.047</td>
</tr>
<tr>
<td>specimens with 20% elongation</td>
<td>1.21</td>
<td>0.88</td>
<td>0.124</td>
</tr>
<tr>
<td>after elongation and relaxation for 2 days</td>
<td>0.96</td>
<td>0.675</td>
<td>0.098</td>
</tr>
</tbody>
</table>
are similar to those obtained for chloroprene rubber. With a similar strength, rubber compounds with P399-E are superior by an order of magnitude to the corresponding rubber compounds with P267-E in terms of electrical conductivity; the addition of anthracene simultaneously increases the electrical conductivity, tensile strength, and tear strength of rubber compounds. The amount of carbon-rubber gel and also the stress under 300% elongation and the hardness increase when anthracene is added for rubber compounds with microporous grades of carbon black, and decrease for rubber compounds with P324. In particular, the considerable increase, from the addition of anthracene, in the fatigue strength under repeated elongation of rubber compounds with standard-production carbon black must be pointed out. Without adjustment of the vulcanising group, rubber compounds with microporous carbon black and anthracene, on account of increased rigidity, are inferior to corresponding rubber compounds without anthracene in terms of fatigue strength, but negligibly. The optimum anthracene content is 0.8–1.2 parts per 100 parts rubber (Figure 3). With a higher anthracene content, the volume resistivity ρv of the rubber compounds begins to increase, and excess anthracene migrates to the surface, forming a white bloom.

![Figure 3](image3)

**Figure 3** Dependence of nominal tensile strength (1) and ρv (2) of rubber compounds with 50 parts P267-E carbon black per 100 parts SKMS-30ARK rubber on anthracene content

It is obvious that the correlation established earlier (ref. 1) between the amount of carbon–rubber gel and the reinforcing effect is valid only for fillers with a similar level of ordering of the carbon surface and intraphase interaction. It breaks down not only with increase in the degree of ordering of the carbon surface on switching from P267-E to P399-E but also with change, by the addition of anthracene, in the level of interaction in the phase of standard-production P324 carbon black, when reduction in the amount of gel leads not only to a reduction but also to an increase in tensile strength of the vulcanisate (see Figure 2 and Table 1). By weakening of intraphase interaction, a high degree of dispersion of carbon black, with a lower level of gelation, and a new unique combination of properties of the rubber compounds, in particular high values of electrical conductivity, strength, tear strength, and dynamic strength, are achieved.

The results obtained give grounds for regarding low molecular weight aromatic hydrocarbons as a new class of dispersing agents for carbon black, increasing the effectiveness of its use. A positive effect from the addition of these hydrocarbons is achieved in rubber compounds both with microporous and with standard-production grades of carbon black. In the latter case, a simultaneous improvement in the strength and dynamic properties of the rubber compounds is achieved. From this it follows that, in standard-production carbon black also, by changing the level of electron exchange interaction, it is possible to have a considerable influence on the reinforcement effect.

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