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# Effects of Mechanical Deformations on the Structurization and Electric Conductivity of Polymer Composites

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Structural changes proceeding in composites under the effect of various mechanical deformations (stretching, compression, shear, *etc.*) definitely affect the structure of an electrically conducting system. Mechanical stresses, induced by deformation of composite materials during deformation, affect both molecular and supermolecular structure of polymers. As a consequence, they also affect a substructure, bound to it and composed of filler particles. It is evident that in the case of conducting polymer composites mechanical deformations should reflect on electric conductivity of materials.

*Keywords:* Electric conductivity; mechanical deformations; polymer composites

## 1. ELECTRIC CONDUCTIVITY OF CARBON BLACK-FILLED RUBBERS UNDER STRETCHING DEFORMATIONS

Mechanical deformations which initiate intertransformations of macromolecules are able to affect the topology of conducting particles interacting with macromolecules. Until the present time, many works appeared which studied connections between structural features of composites and their electric conductivity at deformation [1–3]. Analysis of the information shows that no systematic study exists yet, which would allow to clear up general regularities explaining wide

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spectrum of the features of connections between structural transformations and conductivity. There is no doubt that such situation is caused by the existence of numerous factors, which affect electric conductivity of electrically conducting polymer composites (ECPC) under the effect of mechanical tensions. Among these factors the following are deterministic: the type and composition of the components; their adhesion and cohesion; the method (conditions of production of composites, the prehistory of composites). Studying the problem is complicated by one more condition that electroconducting properties of materials change inadditively with the deformation rate, exposure duration at measurements, temperature, *etc.*

### 1.1. Electric Conductivity of ECPC at Low Deformations

There is some information in literature about electrically conducting rubbers, sensitive to wide-range deformations [1–6]. At the same time, there are no literary data on electroconductivity of rubbers under low deformations ( $\varepsilon \leq 1\%$ ). Interest to the study of electroconducting properties of ECPCs under low deformations is stimulated by the perspectiveness of electrically conducting rubbers application for creating tensosensitive elements.

The behavior of electric conductivity of organosilicon electrically conducting rubbers, based on SCTV and P357E carbon black, at low deformations was studied in the work [6]. In some cases composites contained lowmolecular elastomer SCTN. The composites were obtained by the additive vulcanization technique. Electrodes were introduced into the samples during vulcanization of rubbers. This provided their reliable connection and minimal resistance of the contact. Geometrical size of the samples fitted the requirements to standard tensosensitive elements.

At determination of tensosensitivity coefficients the sample was set to deformation with the help of a taring bar. In this case, relative change of resistance  $\Delta R/R$  was measured by a recorder of the bridge type. Loading of the bar was conducted gradually up to 0.1% deformation level. On each stage of loading and discharging  $\Delta R/R$  of tensoresistors, induced by deformation, was estimated. Several cycles of loading-discharging were conducted. Figure 1 shows dependences of the sample resistance on deformation during three consecutive

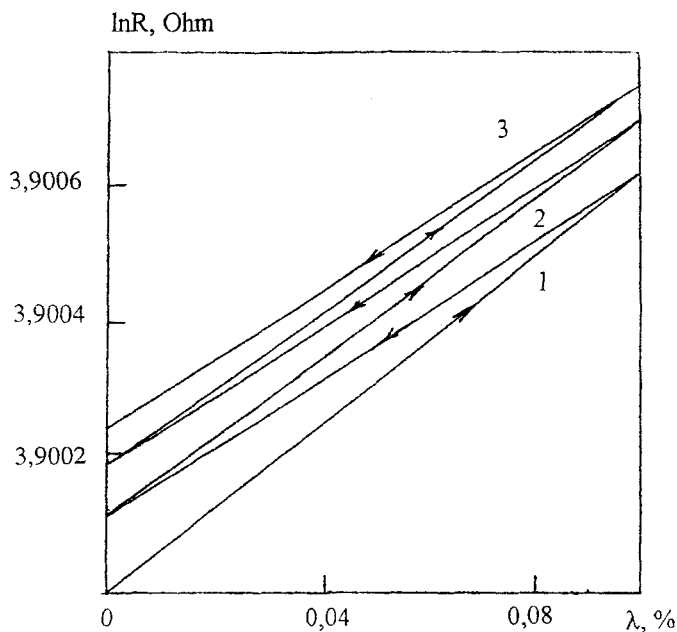


FIGURE 1 The dependence of longitudinal electric resistance of vulcanizates on deformation at stretching in three cycles.

cycles. Exponential growth of curves can be satisfactorily explained by the tunneling mechanism of the charge transfer between filler particles [3], distributed in the polymer. Tunneling is complicated up with the deformation growth because of growing of spaces between filler particles. This leads to the growth of electric resistance. The existence of hysteresis loops on the curve (Fig. 1) is explained by an irreversible degradation of conducting bridges, disposed in gaps between globules of the elastomer. They are also explained by the fact that for rubbers mechanical stress dependence on deformation is characterized by a hysteresis, easily observed at cyclic one-axis stretchings. To decrease hysteresis effects it is necessary to reduce concentration of carbon black associates. In the presence of supermolecular formations (globules) [7] this can be performed by increasing uniformity of distribution of ingredients in the polymer mass by reducing geometrical size of supermolecular conglomerates.

It is known that any polymer can be obtained in the globule state from its diluted solutions. At growth of the solution concentration of polymer with coagulated molecules their aggregation probably begins with the formation of large-sized globules. Varying polymer concentration in the solution, the part of large globules was supposed to be changed. Comparison of dependences  $\Delta R - \lambda$  for samples with different polymer concentration in the solution (Fig. 2) allowed to speak about a possibility of the above described model application for electrically conducting rubbers.

According to the experimental data, sensitivity of electric resistance to deformations grows with polymer concentration in solution. Indeed, growth of globule formation size causes a decrease of their total surface and the square to be covered by filler particles. Thus, probability of carbon black particles aggregation in the intermediate layers is increased. The change of globule formation diameter at constant filler concentration may also cause a corresponding change of

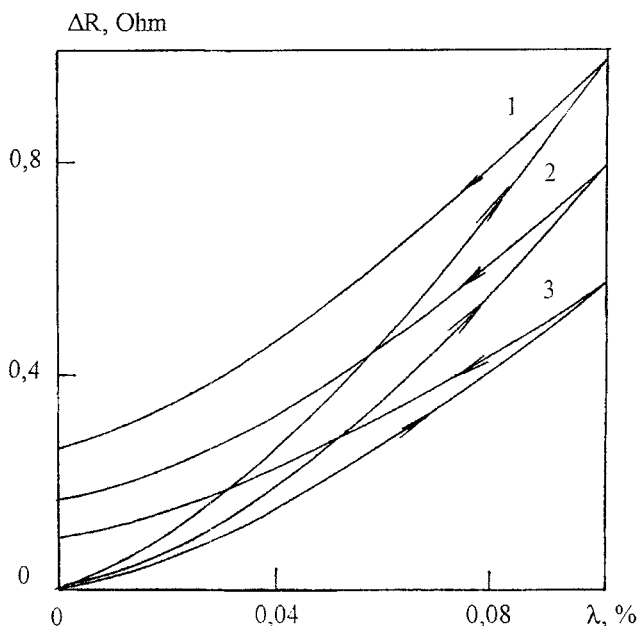


FIGURE 2 The dependence of the resistance change on deformation for vulcanizates obtained from mixtures containing 100 (1), 200 (2), and 300 (3) mass parts of toluene.

the depth of its penetration [8]. Then the sensitivity of conductivity to deformation will increase in consequence of reduction of the total amount of conducting chains. Taking into account the above mentioned facts, it seems advisable to use a lowmolecular elastomer as an additional component of the composite. The results of the composite obtained tests are shown in Table I.

According to the data from Table I, the inclusion of low-molecular elastomer SCTN into the composite promotes the increase of uniformity of the filler distribution in the it. Apparently, application of an elastomer with low viscosity allows a significant increase of the volumetric part of the filler particles, localized near the surface of supermolecular formations and actively interacting with them [9]. The increase of the part of rigid component in the elastomer matrix was displayed by a significant reduction of deviations between  $\Delta R$  and  $\lambda$  values at the beginning and in the end of the "stretching-contraction" cycle. This confirms the above mentioned suggestion about correlation of mechanical and electric properties, and the effect on them of the elastomer phase ratio in filled rubbers. A significant increase of the interaction between macromolecules of the elastomer and filler particles induces a sharp growth of rubber tensosensitivity. This is also supported by the data on a composite, obtained by the polymerization filling technique.

TABLE I Electromechanical characteristics of rubber ECPC

<i>Samples, mass parts</i>	$\rho$ <i>Ohm · m</i>	<i>Homogeneity, %</i>	<i>Relative elongation, %</i>	<i>Tensosensitivity coefficient</i>
SCTV:carbon black:toluene				
100:50:100	0.2	16	170	8.0
100:50:200	0.12	9	280	7.5
100:50:300	0.08	6	210	5.0
SCTV:carbon black:toluene:SCTN				
100:50:150 10	0.07	3	220	9.0
100:50:150 20	0.04	2	200	10.0
SCTV:carbon black* (complete filling)				
150:50	0.009	0.08	150	10.0

\*The samples was obtained by polymerization filled technique.

Thus, the increase of sensitivity of conducting rubbers to deformation is possible at the application of polymers with different viscosity, which possess different thermodynamic affinities to fillers. Growth of the tensometric parameters is also reached by selection of an optimal polymer concentration in the solution.

## 1.2. Electric Conductivity of ECPC at High Deformations

The effect of high deformations of various types was studied in several works [9–13]. The models are known, which explain the character of electric conductivity dependence of stretching and compression deformations of these materials. However, attention is paid in literature low to the effect of the filling degree and the factor of interaction between ECPC components. The concentrational factor affects electric conductivity of the composites both quantitatively and qualitatively [12].

The work [12] studied the effect of stretching deformations (stretching-contraction) in the range of  $0 < \varepsilon < 150\%$ . At deformation of the samples (ECPC based on organosilicon rubbers filled by carbon blacks of different types and contents) the following parameters were recorded continuously and synchronously: electric resistance of the sample,  $R$ ; mechanical tension,  $\sigma$ ; elongation at stretching,  $\varepsilon$ ; time of deformation at three rates of stretching,  $t$ ; the change of the cross-section square of the sample,  $S$ . The device scheme for studying  $\rho$  and  $\sigma$  dependences on deformation of stretching  $\varepsilon$  are shown in Figure 3.

The data from Figures 4–6 show that the character of  $\rho$  change significantly depends on both value of the change of initial lengths of the samples at deformation and type, and concentration of the filler. For example, if  $\rho$  of the rubber with relatively low concentration of P357E carbon black initially grows little at elongation and then decreases, in the case of related composites containing the same filler in higher contents the  $\rho$ – $\varepsilon$  dependence grows monotonously until elongation end (Fig. 4). Significant differences are also observed in the  $\rho$ – $\varepsilon$  dependence at sample contraction. Similar differences are observed in the case of rubbers containing P803 carbon black (Fig. 7).

Another series of experiments applying the same rubbers, but obtained by the peroxide vulcanization technique, showed that beside the factors mentioned the production technique plays the role of the

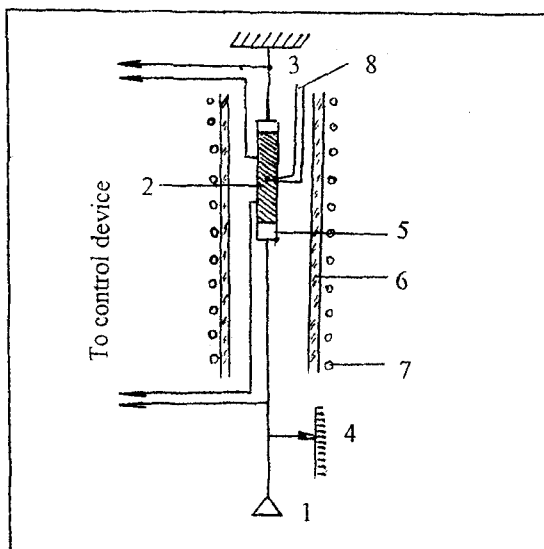


FIGURE 3 The measuring scheme for  $\rho$  dependence of ECPCs on mechanical load under various temperatures. See the text for details.

same important in determining deformation dependence of electrically conducting properties of filled rubbers. The  $\rho$ - $\epsilon$  dependences, recorded for rubbers obtained by the peroxide vulcanization technique (Fig. 8), point out the fact that difference in the processes of structurization, formation of vulcanized network, in particular, leads to quantitative changes of  $\rho$  values at stretching.

The character of dependences shown in Figures 4-8 can be explained, if electrically conducting polymer composite represents a spatial network of filler particles, 'suspended' in the polymer (according to the chain model of conducting composites [14]).

The changes proceeding at deformation of a macromolecular system by mutual translation of supermolecular formations (globules) may play the role of electric switches or reversers of carbon chains, which are in a definite connection with each other. One of the deterministic factors, effectively affecting the electric conductivity at deformation of rubbers, is changing of their microstructure.

On the initial stage of deformation decomposition of the conducting system proceeds as a consequence of polymer chain elongation and growth of the average distance between filler particles interacting with



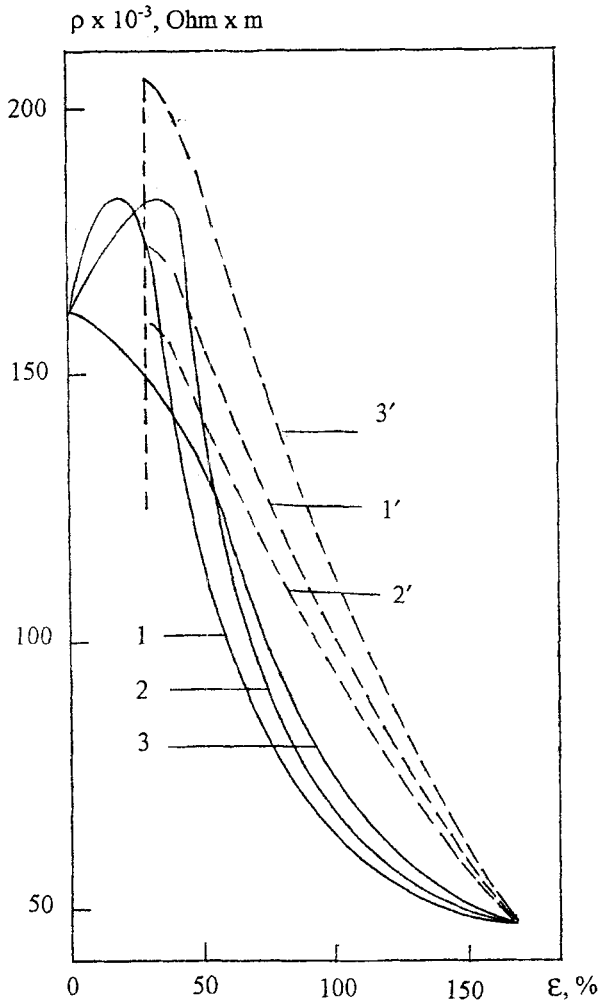


FIGURE 4 The  $\rho$ - $\epsilon$  dependence at stretching (1-3) and contraction (1'-3') of rubbers based on SCTV and P357E carbon black (40 mass parts). The rates of deformation: 0.84 (1, 1'), 2.5 (2, 2') and 5 mm/s (3, 3').

macromolecules. Breaks of some chains of conducting particles leads to weakening of an infinite cluster and results in the increase of  $\rho$ . At further increase of deformation the opposite processes can proceed in the materials. At elongation, the cross-section square of the sample

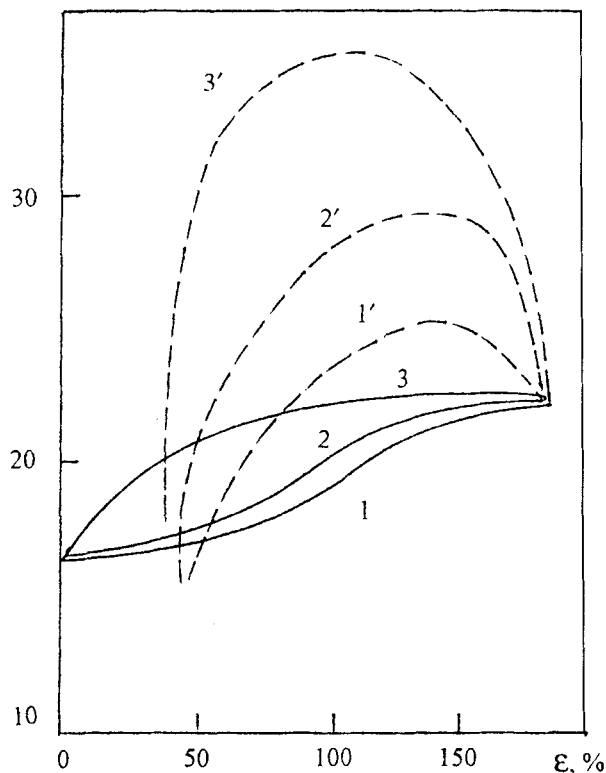
$\rho \times 10^{-3}, \text{ Ohm} \times \text{m}$ 

FIGURE 5 The  $\rho$ - $\epsilon$  dependence at stretching (1-3) and contraction (1'-3') of rubbers based on SCTV and P357E carbon black (50 mass parts). The rates of deformation: 0.84 (1, 1'), 2.5 (2, 2') and 5 mm/s (3, 3').

decreases. This results the growth of density of stretched macromolecules along stretching direction on the current part. In this case, orientation of macromolecules will promote the formation of new conducting chains in both directions of stretching and in the cross-section of the material *via* completion of carbon chains, randomly oriented in space, and their convergence according to the scheme shown in Figure 9. Thus, two competing processes proceed at rubber stretching: degradation and formation of conducting chains. The change of  $\rho$  of the material depends on prevailing process.

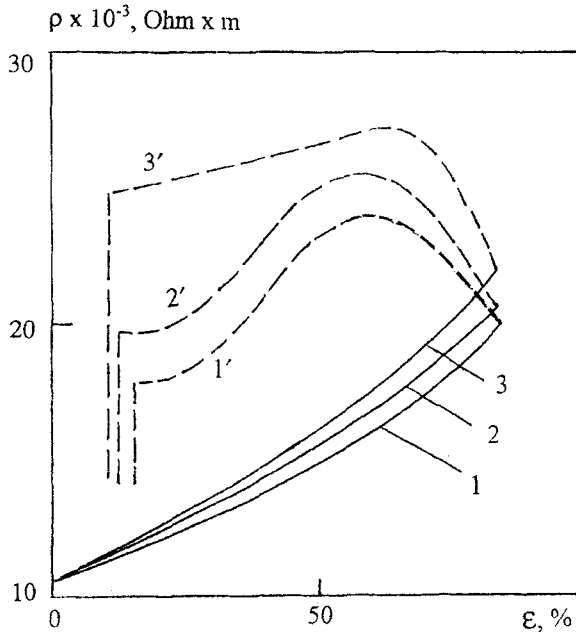


FIGURE 6 The  $\rho$ - $\epsilon$  dependence at stretching (1-3) and contraction (1'-3') of rubbers based on SCTV and P357E carbon black (60 mass parts). The rates of deformation: 0.84 (1, 1'), 2.5 (2, 2') and 5 mm/s (3, 3').

The process of longitudinal conducting chains break ( $\rho$  increases) due to the sample elongation along stretching direction and increase of the average distances between conducting filler particles in this direction predominate at the beginning of the composite stretching with comparatively low filler concentration (40 mass parts) as a result of their entrainment by globule structures of macromolecules. The probability of cross chains formation increases with deformation and gradual convergence in the transverse direction of carbon black particles.

At stretching of rubbers with higher filler concentrations, the probability of formation of new cross chains is low (the initial material already possesses the developed conducting network). In this case, the process of degradation of the conducting system prevails as a result of breaks of longitudinal conducting chains, which limit electric conductivity of the sample. This is the reason of  $\rho$  growth at stretching. The growth of  $\rho$  at stretching of rubbers increases with the filler

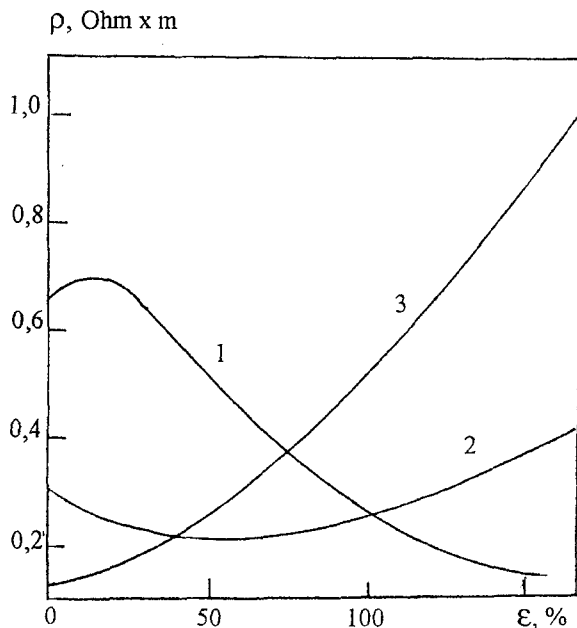


FIGURE 7 The  $\rho$ - $\epsilon$  dependence for the rubber based on SCTV at P803 carbon black concentration of 60 (1), 80 (2) and 100 (3) mass parts. The method of obtaining is additive vulcanization.

content (Fig. 6). Horizontal parts of the curves in Figures 5 and 6 are corresponded, apparently, to the equality of probabilities of degradation proceeding and formation of conducting chains. Therefore, it can be suggested that in a definite range of deformation  $\rho$  does not depend on it. It is evident that setting of the equilibrium between destructive and reductive processes depends on correlation of interaction forces between components of the homogeneous polymer system.

The concentration effect is also displayed at different rate deformations of materials. It can be supposed that at relatively low rate of stretching of the rubbers containing 40 mass parts of carbon black relaxational processes in the material, which promote setting of quazistable structure of the conducting system (stable for the current value of the stretching degree,  $\epsilon$ ), follow the rubber deformation. At high rates of stretching the formation of quazistable conducting system is a little bit delay. Thus, the character of the dependence changes. This means that a maximum occurs on the  $\rho$ - $\epsilon$  dependence

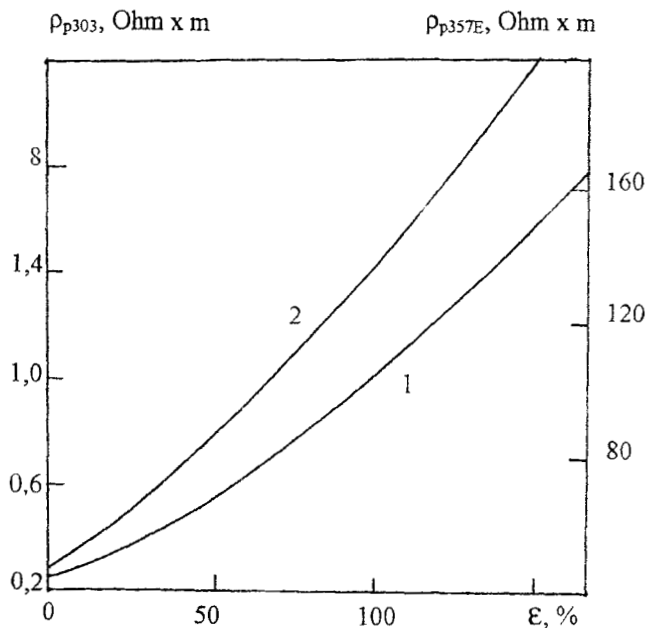


FIGURE 8 The  $\rho$ - $\epsilon$  dependence for the rubbers based on SCTV and P803 carbon black (60 mass parts), and SCTV and P357E (40 mass parts). The method of obtaining is peroxide vulcanization.

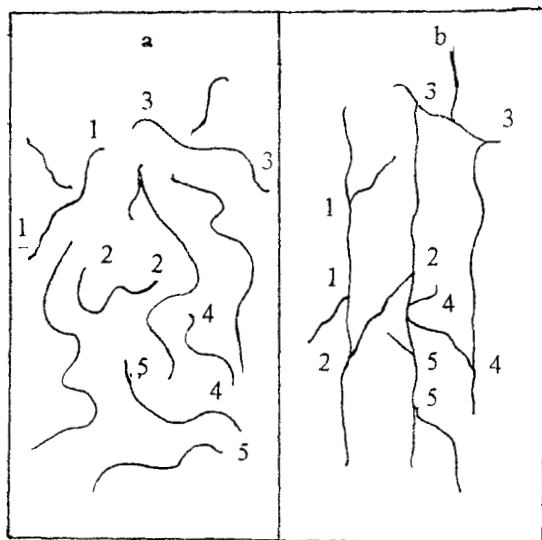


FIGURE 9 The scheme of carbon black channels decomposition before (a) and after (b) elongation.

curve, corresponded to the initial stage of deformation of the sample. In the samples with comparatively high modulus of elasticity, for example, in the rubber containing 60 mass parts of carbon black, the process of setting the equilibrium conducting system proceeds synchronously with the stress relaxation in the current range of deformation temperatures.

During contractions,  $\rho$  of all samples grows first and then decreases to definite values passing the maximum. Similar effect was observed in the work [15] for elastomer-based rubber. Growth of  $\rho$  at the beginning of contraction is explained by destruction of conducting chains as a result of disordering of macromolecule and their globule formations.

Since the length of samples is restored, the process of restoration of broken conducting chains and  $\rho$  reduction is increased. Therefore, at sample contraction a maximum appears on the  $\rho$ - $\varepsilon$  dependence curve. However, rubbers with low filling degree obtain this maximum only before complete discharge of the material at all rates of deformation. Other rubbers obtain this maximum much earlier. This phenomenon is bound to the above mentioned suggestion about formation of transverse conducting channels at stretching of samples. The higher the rate of contraction is, the higher is maximum on the curves. This can be explained by intensification of the conducting system degradation with the increase of the contraction rate.

The difference in values of maxima on  $\rho$ - $\varepsilon$  curves of the samples at contraction is directly connected to the microstructure effect on the processes leading to the equilibrium structure. It is known that relaxational processes in deforming systems are displayed since the very beginning of the deformation (according to Le-Schatelier principle [16]). In this case, it is evident that the relaxation rate and the rate of reduction of the conducting system is directly connected to each other. At high deformations, when internal tensions are able to destruct adhesion forces between a polymer and a filler. Filler particles, splitted from macromolecular formations (globules), can exit from the conducting system and increase total resistance of the material. Moreover, these particles can become the source of destruction of other conducting bridges, survived from degradation as a result of chaotic translations of these particles in the polymer matrix, and contribute into the resistance increase (growth of  $\rho$  at

contraction). These processes from the main reason of occurring hysteresis phenomena at cyclic loads. Based on this fact, the existence of a definite correlation between two hysteresis phenomena would be expected: mechanical tension-deformation, and specific electric resistance-deformation. To clear up such a correlation the  $\sigma$ - $\varepsilon$  dependences were composed for the rubbers containing 40 and 50 mass parts of the filler (Figs. 10 and 11). Comparison of dependences  $\rho$ - $\varepsilon$  and  $\sigma$ - $\varepsilon$  (Figs. 4, 5, 10 and 11) shows that the conclusion is qualitatively supported by the example considered: hysteresis phenomena in the  $\rho$ - $\varepsilon$  dependence are proportional to those in the  $\sigma$ - $\varepsilon$  dependence for every composite.

To check the concept of the deterministic role of the microstructure and polymer-filler interaction forces, special experiments were conducted on rubbers possessing the same compositions, but obtained by the peroxide vulcanization technique. By the way, these rubbers contained SCTN elastomer in some cases.

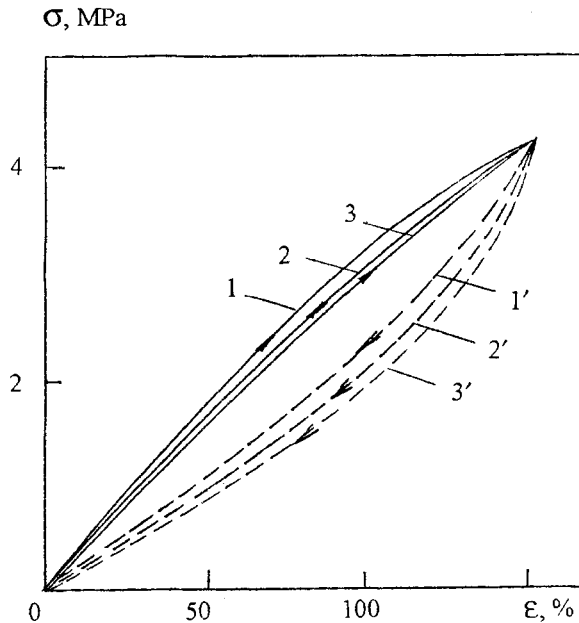


FIGURE 10 The dependence of mechanical tension of stretching deformation (1-3) and contraction (1'-3') of the composite based on SCTV and P357E carbon black (40 mass parts). Deformation rates are: 0.84 (1, 1'), 2.5 (2, 2') and 5 mm/s (3, 3').

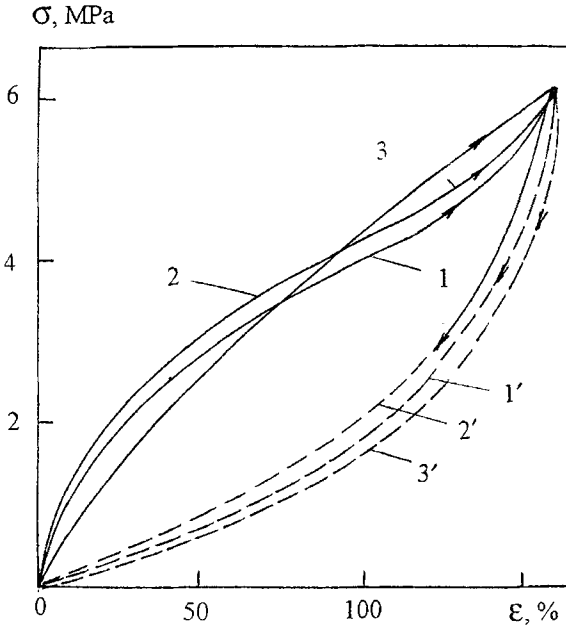


FIGURE 11 The dependence of mechanical tension of stretching deformation (1–3) and contraction (1'–3') of the composite based on SCTV and P357E carbon black (50 mass parts). Deformation rates are: 0.84 (1, 1'), 2.5 (2, 2') and 5 mm/s (3, 3').

It was mentioned above that P803 carbon black belongs to low-structurized carbon blacks with low adhesion (in relation to macromolecules) and cohesion forces. Comparing the character of the curves shown in Figure 7 with those in Figure 10, it can be concluded that the  $\rho-\varepsilon$  dependence starts growing only after the concentration increase of low-structurized carbon black. The experimental data allow to suggest that the increase of total surface of the polymer-filler interphase leads to coming closer the structural effects caused by low- and high-structurized carbon blacks due to an increase of low-structurized carbon black concentration. First of all, this affects the composite density and mobility of macromolecular segments. Resulting the decrease of segmental mobility by formation of intensive cross-links (at peroxide vulcanization), which promote increasing of the equilibrium material modulus, the obstacles for the orientation effect manifestation appear. Change of the microstructure due to cross-link formation in the vulcanizate promotes the opposite change of  $\rho$  at



deformation of rubbers obtained by two different vulcanization method, but possessing equal content of the same filler (P803). According to Figure 8 the composites containing P803 and P357E, obtained by peroxide vulcanization (dense vulcanization network), display growing  $\rho$ - $\varepsilon$  dependence contrary to the same composites obtained by additive vulcanization (weak vulcanization network). Figure 10 shows that  $\rho$  of both rubbers decreases with  $\varepsilon$  growth. In this case density of vulcanization network seemingly compensates relatively low filler concentration.

After the contraction end  $\rho$  of all samples decreases with time until the equilibrium is reached. This process proceeds as a consequence of formation of the conducting system equilibrium structure that results relaxational processes with participation of macromolecules proceeding in the material. The above mentioned suggestion that vulcanization network density affects the character of  $\rho$ - $\varepsilon$  dependence is also confirmed in the case of other electrically conducting rubbers.

The study of the stretching effect by 200% in cyclic regime (stretching-contraction) on natural rubber vulcanizates with 50 mass parts of channel carbon black and vulcanizates of BSC elastomer with 5 mass parts of HAF carbon black [17] showed that on the initial cycle  $\rho$  increases first, until elongation reaches 50–60%. Then it decreases and becomes five-fold lower at the elongation of 200%, than at the initial moment. Contraction of the sample causes sharp increase of  $\rho$ . After discharge it is found 100-fold higher before its initial value. In further cycles  $\rho$  decreases, and then grows up again at contraction. Such character of the dependence is explained by three processes: destruction of carbon black chain structure; orientation of the structure elements; orientation of the structure elements along stretching axis and their reorientation at the sample contraction [17]. Explanation of the effects observed qualitatively correlates with that mentioned above for organosilicon ECPCs. However, the difference is observed in quantitative data, which are deformation ranges, corresponded to degradation or orientation of carbon black bridges, different for in different materials.

Orientation of carbon black bridges at stretching of ECPCs is confirmed by the results of simultaneous measuring of longitudinal and transverse resistance changes, which display existence of anisotropy. Figure 12 shows curves composed on the basis of the

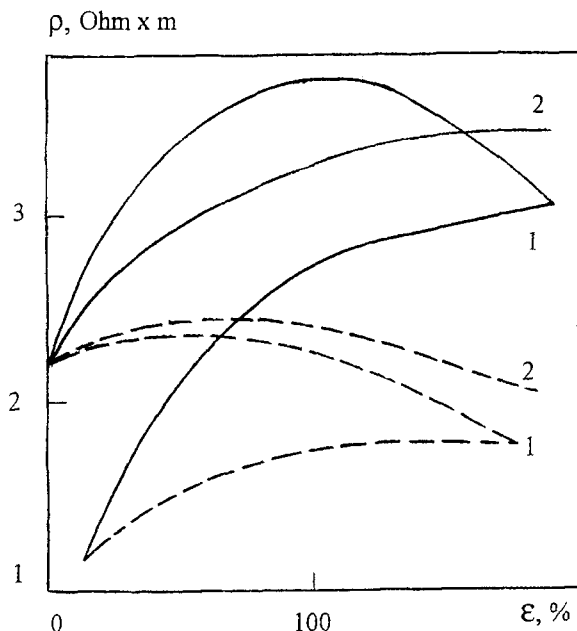


FIGURE 12 Change of longitudinal (dotted lines) and transverse (continuous lines) in two 'stretching-contraction' cycles.

results of measuring longitudinal and transverse resistance of natural rubber vulcanizates with channel carbon black. The measurements were made before deformation, during deformation at elongation by 50, 100 and 200%, and after 'rest' during 15 minutes after each of the deformations mentioned. The difference observed in the change of  $\rho$  testifies the effect of orientation of carbon black particles at high deformations.

Anisotropy of  $\rho$  may occur as a consequence of carbon black chain orientation. In this case, longitudinal resistance can be either lower or higher the transverse one, or their ratio is changed at stretching. Figure 13 shows the dependences of the coefficient of electric conductivity anisotropy, obtained on the basis of vulcanizates of three different elastomers with HAF carbon black. These data show that in the case of BSC elastomer the anisotropy is much higher than for polyisoprene and polychloroprene. These data show also that for HAF carbon black, at least, the longitudinal  $\rho$  on the initial cycle is lower than the transverse one.

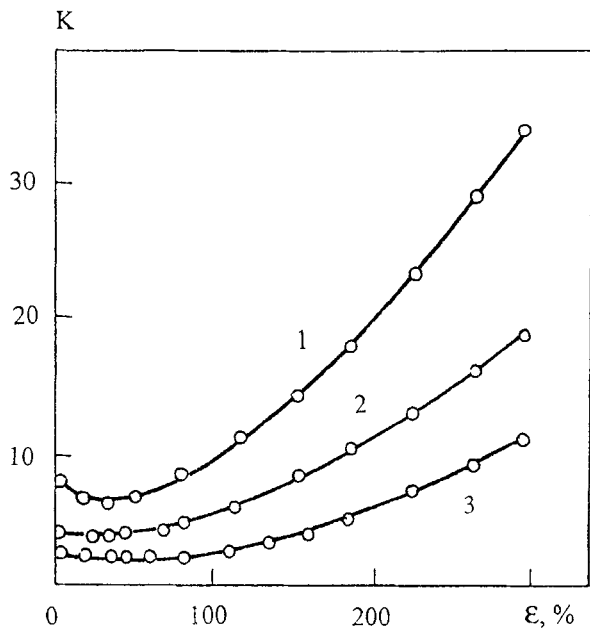


FIGURE 13 The dependence of anisotropy coefficient on elongation of vulcanizates containing 50 mass parts of carbon black: 1-BSC, 2-PCP, 3-polyisoprene.

At high elongations two effects overlap: the orientation of resistant primary structures and decomposition of the polymer-filler bonds. The first effect is clearly expressed in highly structural types of carbon blacks with anisometric primary aggregates and leads to a decrease of  $\rho$ , but is weakly expressed in lowstructural types. The second effect is observed for all types of the filler. The ratio of these two effects is the reason for histeresis occurrence. Low-structural carbon black displaying low interaction with a polymer leads to occurrence of a small histeresis or does not cause any histeresis at all. To confirm the hypothesis about decomposition of the polymer-filler bonds, the adhesion of carbon black particles to the polymer were studied by the replica technique, used in the electron microscopy. It was found that the replica, depicted from the sample preliminary stretched by 350% contains much more technical carbon, than non-stretched one. For BSC vulcanizates, filled by Cetjen EC carbon black, the change of longitudinal  $\rho$  at stretching by up to 150% differs from that for

vulcanizates with Vulcan HS and HAF carbon blacks. The latter carbon blacks are characterized by the existence of a maximum, whereas Cetjen EC displays monotonous and quite small increase of  $\rho$  [18]. Previous deformation, conducted 15 min before the next one, increases  $\rho$  during the repetitive deformation at small elongations. At high elongations the curve of repetitive deformation may be the same as that of the first cycle. As a consequence, previous deformation causes something like the structure softening—the effect similar to the Mallins-Patrikeev effect [19] at mechanical loading of elastomers. Moreover, previous deformation can affect the dispositions of the maximum on stretching- $\rho$  curves. At repetitive deformation  $\rho$  starts its reduction at the elongation lower than in the first cycle. These data point out the preservation of the residual orientation of the conducting system, happened in the first cycle [3].

It was mentioned above that the change of  $\rho$  can depend on the deformation rate. For example, for the BSC–HAF system the structure is highly capable for restoring after slow deformation, than after the fast one [17].

While the filling degree increases, preferable growth of the longitudinal resistance at stretching, characteristic for low-filled mixtures, is first substituted by a low change, and then preferable decrease of  $\rho$ . Figure 14 shows the curves of stretching- $\rho$  dependences of natural rubber vulcanizates with different filling degrees by acetylene carbon black, obtained at high rate of deformation [19]. At growth of the filling degree the curves become of the S-like type, and at filling by 100 mass parts even a small reduction of resistance in the range of elongation from 50 to 100% is observed. The same vulcanizates with 60 mass parts of carbon black were studied for the effect of the stretching rate. At the rates from 0.5 to 30% the curves are qualitatively similar until the elongation reaches 150–200%. At higher elongation they are raised up sharper at lower deformation rates. These results are in contradiction with the above mentioned data [20]. An explanation of this difference should be searched in both application of different types of carbon blacks and in a significant (by 2–4 degrees) difference in the deformation rates.

It is also interesting to study the effect of the cross-linking degree of vulcanizates on the character of deformation curves, calculated for the real size of the sample. In the works [19–21] the thickness of

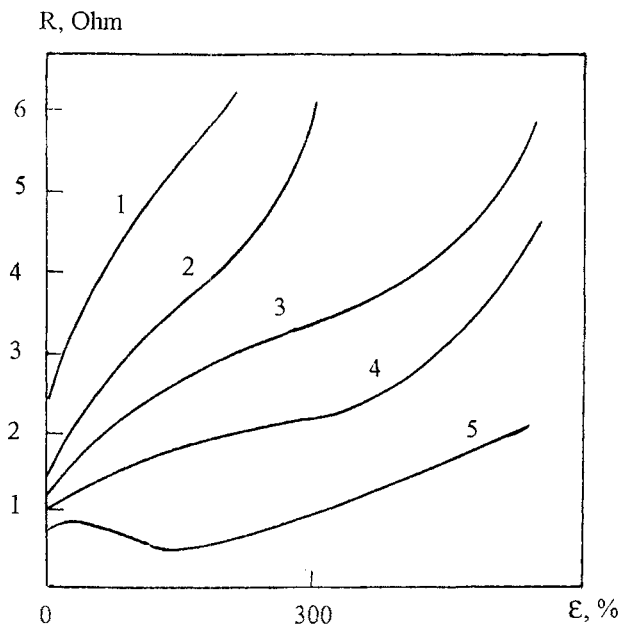


FIGURE 14 The dependence of longitudinal electric resistance of ECPCs based on natural rubber at stretching up to degradation. The degree of filling by acetylene carbon black is 30 (1), 40 (2), 50 (3), 60 (4) and 100 (5) mass parts, respectively.

vulcanization network was characterized by a relative equilibrium modulus  $E_{\infty}$ . The thickness was regulated by the vulcanization duration change. Most of the curves shown in Figure 15 have the maximum on the initial stage of deformation and another minimum at high deformation. Existence of the maximum and its value depend on  $E_{\infty}$ .

There are no maxima and minima at low density of vulcanization network ( $E_{\infty} = 1.3$  MPa). The higher the values of  $E_{\infty}$  are, the lower is the elongation at which the repetitive growth of the longitudinal specific electric resistance begins. Thus, at low density of the network its modulus grows up, obstacles for performance of the orientation effect occur, distances between particles increase, and contact electric resistance between them grows.

Figure 16 shows the curves of changes of  $\rho$  and mechanical tension  $\sigma$ . They show that at any moment of deformation growth of mechanical tension is followed by reduction of  $\rho$  and opposite, excluding only the

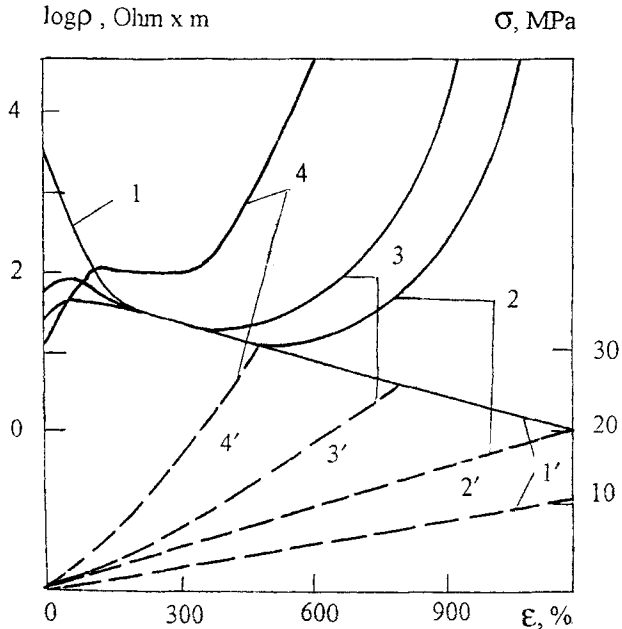


FIGURE 15 The dependence of resistance at break  $\sigma$  (curves 1', 2', 3', 4') and  $\rho$  (curves 1, 2, 3, 4) on the stretching degree up to degradation of SCN-26 vulcanizates with acetylene carbon black (60 mass parts) and the values of  $E_{\infty} = 3.29$  (1); 3.18 (2); 5.09 (3); 8.95 (4) Mpa, respectively.

first cycle of stretching. This hysteresis of the material electric conductivity coincides with the hysteresis of mechanical tensions.

The curves of  $\rho$  dependence on mechanical tension during stretching of four samples of BSC-based vulcanizates with 60 mass parts of acetylene carbon black, which differ by the value of  $E_{\infty}$ , show that under the same mechanical tension the samples with more dense vulcanization network possess higher electric resistance  $\rho$  (see Fig. 17) [21].

The square of the hysteresis loop is stabilized at increasing the number of 'stretching-contraction' cycles. In this case, the square of hysteresis loop decreases. Reduction happens so abruptly, the higher is the cross-linking degree of vulcanizates. For example, NC with 60 mass parts of acetylene carbon black ATG-70 possesses reduction of the hysteresis loop square by 4–5 times at any increase of  $E_{\infty}$  from 1 to 2.5 MPa. The decrease of the hysteresis loop square also happens at growth of the filler concentration [22].

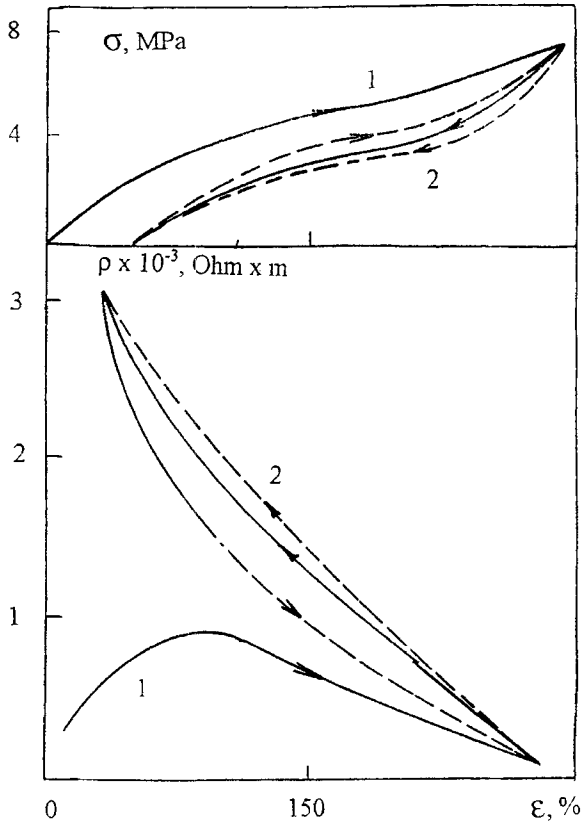


FIGURE 16 The dependence of  $\sigma$  and  $\rho$  on stretching in the cyclic regime for BSC filled by acetylene carbon black.

## 2. MECHANICAL RELAXATION AND ELECTRIC CONDUCTIVITY OF ECPC

As mentioned in the previous Section, forces raise in polymer matrix from the very beginning of deformation counteracting the external influence. Therefore, the elucidation of relaxational effects on electric conductivity is complicated during deformation of ECPCs due to overlapping of several factors.

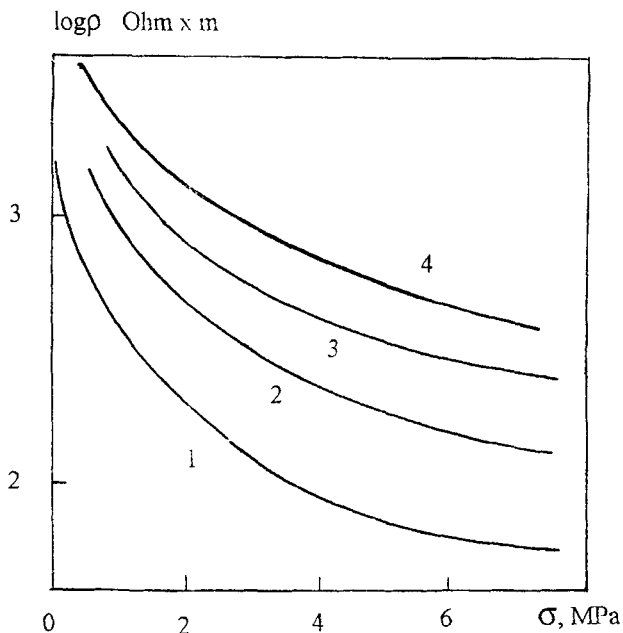


FIGURE 17 The dependence of  $\rho$  on tension of ECPC, based on BSC elastomer and acetylene carbon black, at stretching at  $E_{\infty} = 1.9(1); 3.13(2); 4.01(3); 5.91(4)$  MPa, respectively.

To study electrically conducting properties of polymer composites during their mechanical relaxation the tests were performed, which used the same composites, studied at high deformations [23].

The experiment on determination of  $\rho$  during relaxation of the mechanical tension  $\rho$  was performed as follows. A thin sheet (2 mm) sample of electrically conducting rubber was stretched on a stretching machine at a definite deformation  $\varepsilon$ . The change of  $\rho$  was recorded by an automatic recorder immediately after stretching stop. The automatic recorder scale was graduated in Ohms on time  $\tau$ , and synchronous recording of the time dependence of  $\sigma$  at fixed deformation was made according to the methodic, described above. Moreover, relaxational characteristics were recorded for the same samples after the end the 'stretching-contraction' cycle.

As Figure 18(a) shows, the values of  $\rho$  grow during relaxation of tension  $\sigma$ . In this case, the increase of  $\rho$  proceeds with higher rate in



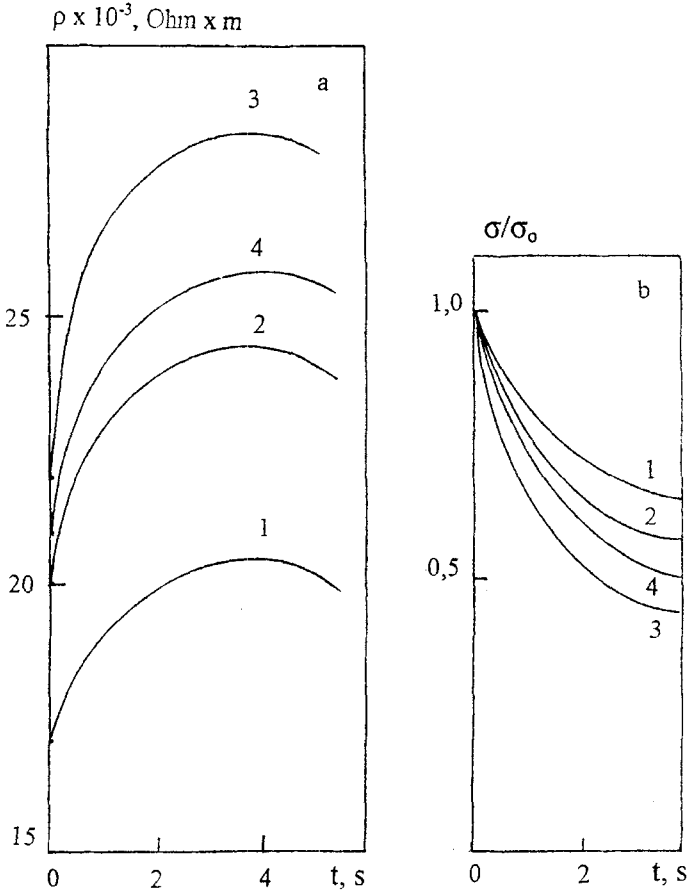


FIGURE 18 Time dependences of  $\rho$  (a) and  $\sigma$  (b) during relaxation of mechanical tension after stretching of the rubber, based on SCTV with P357E carbon black (350 mass parts) by 50 (1, 4), 100 (2), and 150% (3). The rate of elongation is 2.5 (1–3) and 5.0 mm/s (4), respectively.

rubbers, deformed at relatively high rates. Moreover, increase of the stretching rate induces acceleration of  $\rho$  increase in these materials. In this case, kinetics of mechanical tension  $\sigma$  reduction is completely coincident with the character of  $\rho$  change. This means that the sample relaxates mechanically the faster, the higher the rate of the sample deformation is (see Fig. 18(b)). Growth of  $\rho$  with time during relaxation of  $\sigma$  can be explained basing on the effect of the elastomer

molecular system disordering that occurs after deformation release [23]. In this case, internal mechanical tensions are reduced by transition of highly regulated system into lower regulated state on the present stage of deformation. Disordering in the system of macromolecules induces conducting circuit destruction, *i.e.*, growth of  $\rho$  of the material. In view of the fact that the growth of the deformation rate induces increase of structural transformation intensities in the material, it is evident that significant deformations of the conducting system will happen in the electrically conducting system interacting with the polymer matrix.

The analysis of time dependences of  $\rho$  at the relaxation of rubbers show that they are successfully described by the expression.

$$\rho = \rho_{\infty} - (\rho_{\infty} - \rho_0)e^{-t/\tau}, \quad (1)$$

where  $\rho_0$  and  $\rho_{\infty}$  are border values of  $\rho$  during relaxation under fixed stretching deformation;  $\tau$  is the relaxation time.

Equation (1) represents the solution of the differential equation, similar to that deduced by Bartenev [13] for kinetics of the polymer mechanical relaxation. According to Eq. (1) kinetics of relaxation are described by the Maxwell model:

$$\frac{d(\sigma - \sigma_{\infty})}{dt} = E_1 \frac{dE}{dt} - \frac{\sigma_1 - \sigma_{\infty}}{\tau}.$$

Taking logarithm from Eq. (1), we get:

$$\ln \frac{\rho - \rho_{\infty}}{\rho - \rho_0} = -\frac{t}{\tau}. \quad (2)$$

Thus in the case, when application of Eq. (1) to relaxation kinetics is correct, the dependence should fit a straight line in coordinates of Eq. (2).

As Figure 19 shows, time dependences by Eq. (2) are straightened. This allows to use the model of consequently connected strings and dempher (the Maxwell model) for describing kinetics of the change of  $\rho$  during relaxation of mechanical tension of electrically conducting rubber.

Relaxation times  $\tau$  for the composites of SCTV elastomer with P357E carbon black were determined [24] by tangents of straight lines

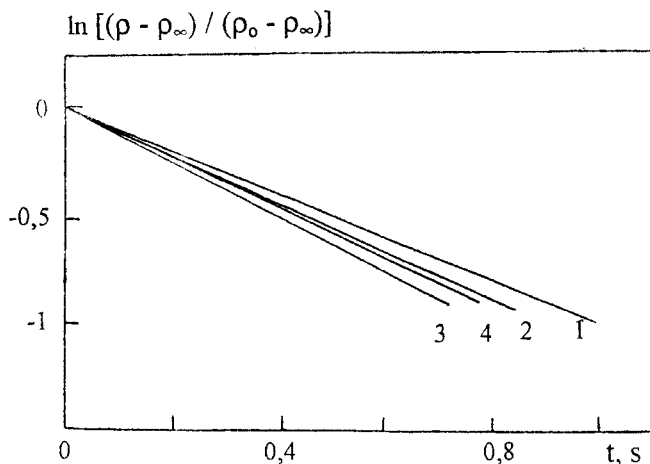


FIGURE 19 The dependence of  $\rho$  of the samples based on SCTV elastomer with P357E carbon black (50 mass parts) on time during relaxation in coordinates of Eq. (1). For curve numeration see Figure 11.

(Fig. 19). Numerical values of  $\tau'$  for other composites were obtained similarly. The results are shown in Table II.

The data shown in Table II testify that the increase of deformation of polymers leads to growth of the relaxation rate of both  $\rho$  and  $\sigma$ . This effect is strengthened at the increase of the filler concentration in the composite. For example, at comparable rates of deformation  $\rho$  of rubber containing 60 mass parts of active carbon black relaxates with higher rate than in the same rubber containing 50 mass parts of the

TABLE II Relaxational characteristics of stretched ECPC on the base of SCTV\*

Filler, mass parts	Deformation, %	Deformation rate, mm/s	Relaxation time $\tau$ , s
P357E (50)	50	2.5	1.00
	50	5.0	0.88
	100	2.5	0.91
	150	2.5	0.84
P357E (60)	30	2.5	0.60
	60	2.5	0.44
P803 (50)	100	2.5	3.84
P803 (60)	100	2.5	2.28

\* Elastomers were obtained by the additive vulcanization technique.

same carbon black. In this case, the effect of the interphase growth is observed. This growth causes an increase of conditionally equilibrium modulus of the system. In composites containing lower active carbon black (P803) relaxation times are much higher than in rubbers with active carbon blacks. This points out a relatively low adhesive interaction between the polymer and the filler in rubbers with P803 carbon black. However, weak adsorptional forces also grow at deformation (tension increases). According to the model by Alexandrov–Lazurkin [25] and the generalized model by Ferri [26] this means the leveling of local tensions in the sample. In practice, the present effect is displayed in decreasing heterogeneity of a composite material that improves some properties of materials despite some decrease of mechanical stability.

The investigation of relaxational processes at the end of the deformation cycle (stretching-contraction) after complete discharge of the samples showed [27] that relaxational phenomena are more complex if compared with the above described facts. First of all, the complexity is expressed in the functional  $\rho-t$  dependence starting from the complete end of the cycle (Fig. 20). Since the curves of the present figure were considered, let us mention that they, in fact, represent a superposition of at least two relaxational processes. One of these processes relates to the most linear parts of the curves, and the second one – to most curvilinear parts with limit overwhelming at  $t \rightarrow \infty$  (see Fig. 20, Curves 2 and 3). Both parts of the curves mentioned reflect regulation of the conditioning system by regulating the macromolecular part of the composite.

However, the rate of relaxation and time of reaching equilibrium values of  $\rho$  at the end of the relaxational period significantly depend on the filler concentration. For the composite containing 40 mass parts of carbon black, the process proceeds at a low rate, but the equilibrium state in it occurs rather rapidly, whereas in rubbers with 50 and 60 mass parts of P357E higher rates are observed at the initial stage of relaxation, and decelerated curve growth – on the further stages of kinetics. One more fact is characteristic for the present dependences; the difference between minimum and maximum values of  $\rho$  on the whole interval of relaxation also strictly depends on the filling degree.

Analysis of the dependences, shown in Figure 20, gives a possibility to conclude the following. Taking into account the ideas by Bartenev

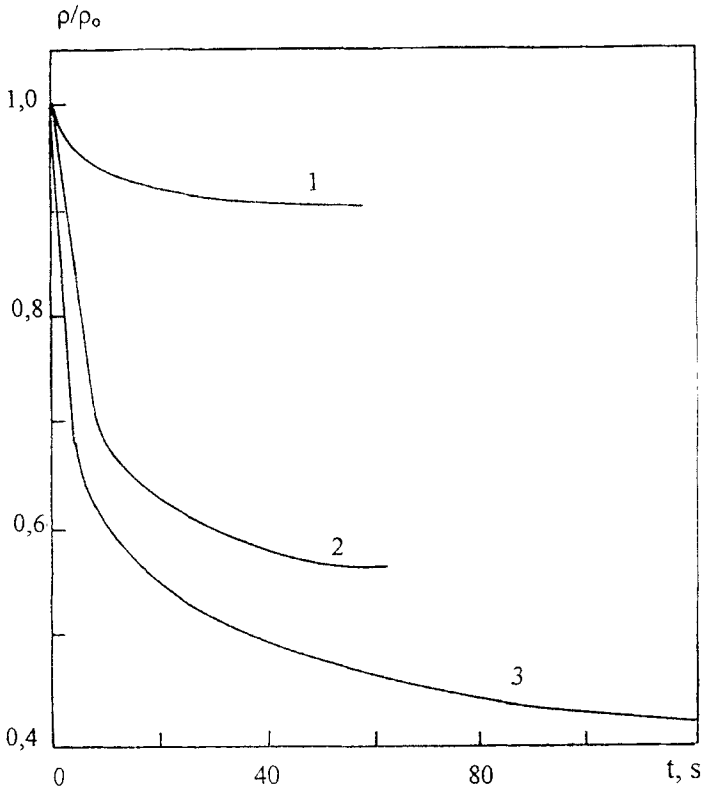


FIGURE 20 The dependence of  $\rho$  on delay after the contraction end (relaxation without loading) for rubbers, based on SCTV containing 40 (1), 50 (2) and 60 (3) mass parts of P357E carbon black, respectively. At the moment of discharge  $\rho_0 = \rho$ .

[13] and Rebinder [28] on the formation of a complex heterogeneous system after injection of active carbon blacks into a polymer, which are characterized by non-linear viscoelasticity (the processes of this type are non-linear relaxation at low deformations and non-linear viscoelasticity at high deformation, the tixotropic effect by Mallins–Patrikeev, in particular), proceeding of two physical processes at relaxation of the considered systems can be supposed.

The first process is close to the elastic range of deformation (Hooke's range) of a macromolecular system. As it is known, this process proceeds fast by both branches of the deformation cycle and is

defined by elastic properties of the composite matrix. Elastic forces rapidly drives the system into the equilibrium after external influence release. However, it is often difficult to separate this process in polymers. In the composite material electrically conducting system, connected to the adsorption forces, can clearly response to any smallest structural changes in topology of structural polymer units (globules, for example), absolutely controlled by them. In the present case, conducting system in the polymer matrix plays the role of a relay-contact scheme translating information about the state of the surrounding (polymer) medium to the 'language' of electric conductivity. Thus, the abrupt decrease of  $\rho$  values, shown in Figure 20, corresponds to reduction of conducting channels existing in tight connection with macromolecules of elastomer, elastic properties of which is often promoted by the bonds mentioned.

The second process is the reduction of initial system (before the deformation) with participation of filler particles, splitted from macromolecules during deformation (stretching) of the polymer system or absent in the adsorption connection with macromolecules during deformation (carbon black agglomerates, for example). As it is known [29], these particles decelerate regulation in the system of macromolecules, intensify internal friction and non-linear effects at high deformations, connected to it. That is why, their existence in the composite always leads to elongation of relaxational processes. Apparently, this is the reason of deceleration of restoration of the primary conducting system of the composite material. Thus, taking into account the above mentioned it becomes clear the delay of complete reduction of the equilibrium structure in high-filled polymer matrices in higher degree comparing with low-filled polymers. For the first glance, this position seems to be paradoxal. Let us remind now that according to the exponential dependence of  $\rho$  on concentration of the active filler reduction of the structure is much higher than for the composite possessing 50 mass parts of the same carbon black than for the composite with 60 mass parts of the same carbon black.

The  $\rho - \tau$  dependences shown on Figure 20 reflect morphological changes in heterogeneous system. Analysis of these curves showed that exponential parts are successfully described by the (1) type of equation with the only difference that  $\rho_\infty$  is substituted by  $\rho_m$  at the end of relaxation, and  $\rho_0$  by  $\rho_1$ , corresponded to the value of  $\rho$  at crossing

exponential curve by the straight line:

$$\rho = \rho_m - (\rho_m - \rho_0)e^{-t/\tau}. \quad (3)$$

Using Eq. (3) for various composites tested, relaxation times were determined. Numerical values of them are shown in Table III.

The analysis of the data from Table III leads to the following conclusions:

1. Filler content significantly affects relaxational characteristics of the material. For example, the rubber containing 40 mass parts of P357E carbon black possesses the rate of fast relaxation about 5 times lower, and duration of slow relaxation is 4-fold lower than for analogous rubber with 60 mass parts of the same filler. The rubber containing 60 mass parts of P803 carbon black has no range of fast relaxation at all, but the same rubber displays such ranges at the filling degree of 120 mass parts of P803. The main reason of these differences is in increase of the rubber elasticity modulus with the increase of filler concentration. On the one hand, this leads to the increase of the interphase surface square, and on the other hand, to occurrence of broken polymer-filler bonds, which promote growth of internal friction and deceleration of the relaxational process in the macromolecular system. That is why, although the increase of the modulus is the reason of growth of the rate of conditionally

TABLE III Relaxational characteristics of electrically conducting rubbers based on SCTV elastomer at the end of deformation cycles

No.	Filler, mass parts	Sample prehistory		Relaxation rate, $s^{-1}$	
		Maximal deformation in the cycle, %	Deformation rate, %	Fast	Slow
1.	P357E (40)	150	2.5	$1.2 \times 10^{-2}$	7
2.	P357 (50)	150	2.5	4.0	21
3.	P357E (60)	60	2.5	$6.7 \times 10^{-2}$	28
4.	P803 (60)	200	2.5	-	6
5.	P803 (120)	150	2.5	$2.2 \times 10^{-2}$	11
6.	P357 (40)	150	2.5	$10.6 \times 10^{-2}$	48
7.	P803 (60)	150	2.5	$5.1 \times 10^{-2}$	24
8.	P803 (60) + SCTN (20)	200	2.5	$2.8 \times 10^{-2}$	16

Composites No. 1–5 were obtained by the additive vulcanization technique; Composites No. 6–8 were obtained by the peroxide vulcanization technique.

called fast relaxation, the mechanical tensions caused by accumulation of the filler particles, detached from polymer globules, leads to a noticeable increase of the slow relaxation time.

2. The effect of the filler type on proceeding of relaxational processes is also sufficient. Rubbers with active carbon blacks (P357E) display the ranges of slow and fast relaxations much more clearly, than those with low active carbon blacks (P803) even at increased concentrations. First of all, the effect of the filler type is displayed by formation of an interphase layer and is similar to the effect of the filler content. In the case of active carbon blacks, the increase of the filler–filler and polymer–filler interactions balanced by high content of low active carbon blacks, because in both cases the modulus of the material and internal friction in relaxational processes grow.
3. Comparison of characteristics of the rubber, produced by two different vulcanization techniques, shows that the rate and time of relaxation depends on vulcanization network density is not weaker than the type and concentration of the filler (compare composites 1 and 6, 4 and 7, Tab. III). Since the concentration of polymer cross-links in peroxide vulcanizates significantly prevails over the concentration of longitudinal links (by SCTV end groups) in rubbers, obtained by additive vulcanization, it is evident that the mechanical modulus of the first composites is higher than that of the second ones. This is the reason of differences in relaxational characteristics. In this case, the increase of the ‘soft phase’ in the composite by introduction of low-molecular SCTN elastomer softens relaxational processes. This is expressed by decrease of fast relaxation rate and time of slow relaxation, if compared with similar composites containing no SCTN (compare composites 7 and 8, Tab. III).

### **3. ELECTRIC CONDUCTIVITY OF ECPC UNDER COMPRESSION**

#### **3.1. All-round Compression**

Some features characterize dependences of ECPC electric conductivity on all-round compression.



The dependence of  $\rho$  on pressure at all-round compression was studied on the example of the samples, obtained by additive vulcanization technique from SCTV with different concentrations of P357E carbon black. The experiments were performed using a device of 'plunger-cylinder' type. The device scheme is shown in Figure 21 [30]. Device punches served simultaneously as contact electrodes, connected to a recorder of electric resistance of ECPCs. The results of measurements are shown in Figure 22. The dependences clearly show that under conditions of all-round compression at the increase of pressure the character of  $\rho$  changes significantly depends on the filler concentrations.

For example,  $\rho$  of the samples with low filling degree (Fig. 22, Curve 1) grows with pressure and is characterized by the S-type dependence, whereas for the samples with high filler concentrations the values of  $\rho$  decreases abruptly first, and then decrease monotonously and come out of the limits. In this case, the higher the filler concentration is, the

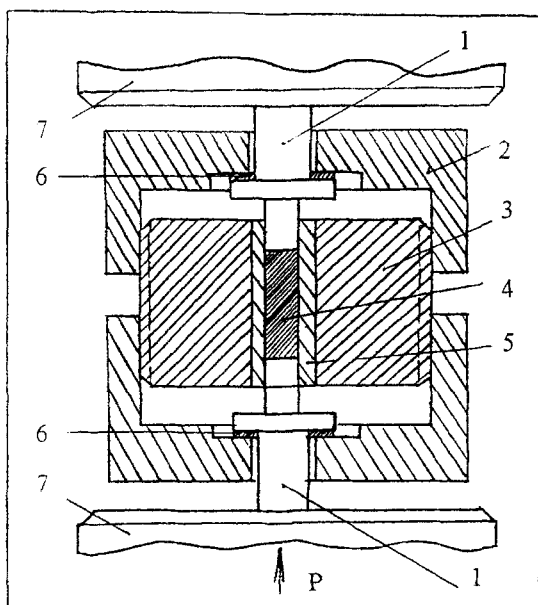


FIGURE 21 The 'plunger-cylinder' type container with pressure fixing: 1—puanson; 2—clamping nut; 3—cylinder; 4—sample; 5—textolyte socket; 6—textolyte collar; 7—hydraulic press puansons.

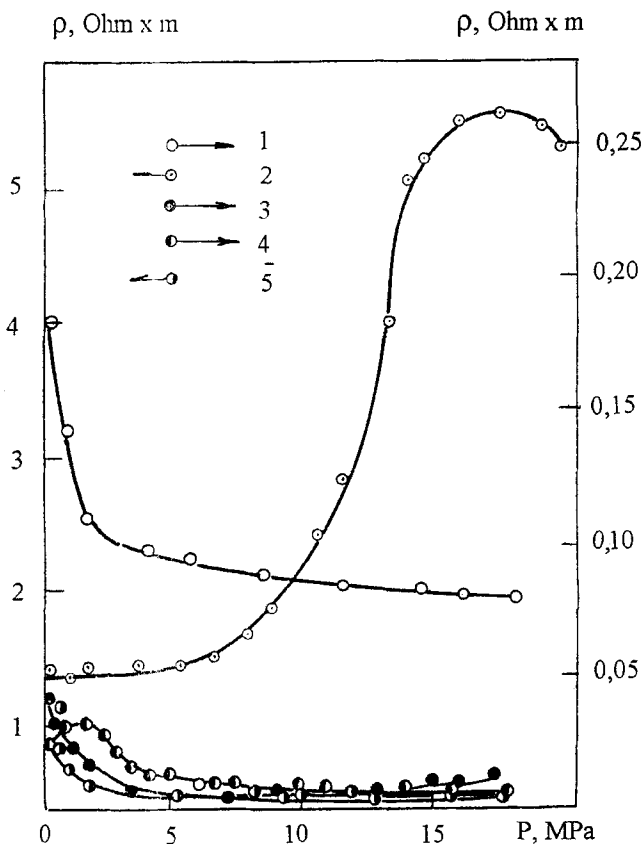


FIGURE 22 Baric dependence of  $\rho$  for SCTV-based ECPCs with P357E carbon black concentration of 20(1), 30(2), 40(3), 50(4) and 60(5) mass parts under the all-round compression.

initial fall of  $\rho$  is displayed much more clear virtually until border values at lower pressures.

The results obtained can be explained in terms of changes of secondary carbon black conducting systems during compression, and the same reasonings can be used in practice, which were mentioned above under consideration of stretching deformations of rubber ECPCs. In particular, degradation of so-called 'transient' structure, the secondary carbon black structure formed by van-der-Waals forces, happens at low deformations that leads to growth of  $\rho$ . Drawing together of carbon black aggregates and formation of new conducting

channels happens as the pressure is increased due to reduction of the sample volume (generally, by means of the free volume decrease). However, in accordance with the known dependence of compressibility of solids on external pressure, characterized by overwhelming, the process of drawing together of carbon black aggregates at high pressures should also be overwhelmed. The opposite view of conductivity curves for rubbers containing 20 mass parts of a filler to those for rubbers with higher concentration of the same filler is explained by a difference in levels of 'reservation' or compensation of destroyed conducting channels by newly formed conducting bridges, stimulated by volumetric compression of the samples. In the samples with comparatively low filling degree the reservation is so low due to low density of the conducting system that the degradation prevails over the competing process of restoration. That is why, the general tendency to  $\rho$  decrease in the compressed state of ECPCs is displayed in composites with relatively low filling degree at higher pressures, than in composites with higher filling degree.

### 3.2. Uniaxial Compression

Contrary to the all-round compression of ECPCs, qualitatively different action is observed in investigations of the  $\rho$  dependence on deformation under the conditions of uniaxial compression. Thus, the experiments performed in vulcanizates SCI-3, SCD, SCI + SCD (1:1), SCN-26M and nairit A, containing acetylene carbon black, have shown that  $\rho$  of all samples at uniaxial compression increases with pressure [31] (Tab. IV).

According to the data from Table IV, the sample resistance at compression significantly increases first, and then abruptly decreases. In this case, pressure effect on  $\rho$  decreases with its value coming closer to definite border values with the filler content growth.

At a cyclic loading of the mentioned vulcanizates a residual effect is displayed that points out proceeding of irreversible structural changes in the samples leading to the resistance increase. However, this process is saturated with growth of the number of compression-rest cycles. In this case, a significant role is played by the type of elastomer, and the boundary loading value. In particular, the higher the elastomer-filler interaction is, the weaker is the change of  $\rho$ , and the saturation time

TABLE IV Uniaxial compression effect on  $\rho$  of vulcanizates

Elastomer	Filler content %	$\rho$ (Ohm $\times$ m) at compression pressure, MPa			
		Atmosphere pressure	0.1	0.5	1.5
SCI-3	30	2.1	47.8	51.2	1250
	50	0.18	0.6	2.2	3.8
	70	0.06	0.12	0.31	0.32
	100	0.04	0.05	0.08	0.07
SCD	30	3.2	26.3	360	423
	50	0.2	0.5	0.8	1.2
	70	0.07	0.09	0.13	0.13
	100	0.04	0.04	0.05	0.05
SCD-26M	30	9.7	152	1210	5200
	50	0.4	1.0	6.6	16.6
	70	0.09	0.16	0.56	0.67
	100	0.04	0.06	0.07	0.06
Nairit A	30	10.8	203.8	2010	6250
	50	0.5	2.8	7.2	12.3
	70	0.1	0.2	0.6	0.6
	100	0.03	0.05	0.07	0.06

grows with the limit pressure increase (Figs. 23 and 24). Similar results were obtained in works [31–34]. Basing on the experimental results shown in Table IV and Figures 23 and 24 a conclusion can be made that at uniaxial compression conducting channels degradation occurs in the composites due to appearance of shift deformations in the material mass, which cause mutual translation of filler particles in the polymer matrix (together with segments of macromolecules) in normal direction to the compression axis.

Apparently, such deformations result rather significant structural changes, which cause restoration of the initial structure and properties of ECPCs to be probable only at durable storage of samples at room temperature (acceleration of restoring processes is observed at increased temperatures).

### 3.3. Compression at High Pressure

In the works made by Enikolopian *et al.* [35–40] for compression of various ECPCs by high pressure a sequence of unusual phenomena was observed that gave a new approach to interpretation of the conductivity mechanism of electrically conducting composites. Let us discuss them more thoroughly.

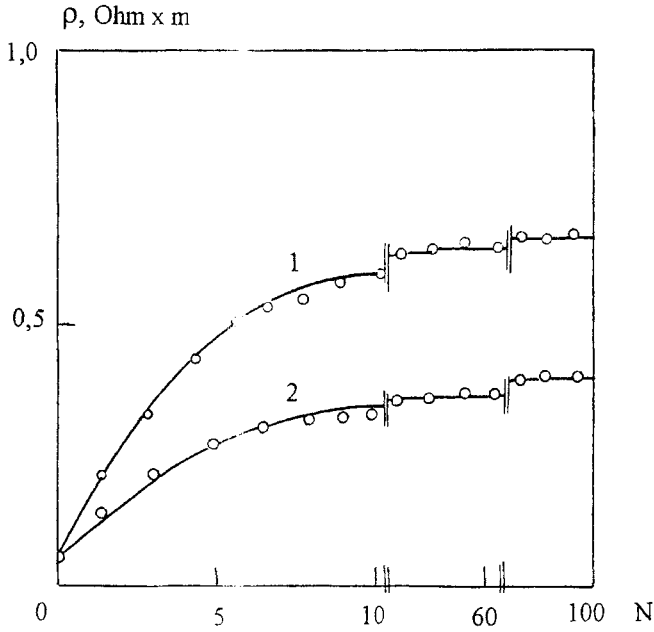


FIGURE 23 Pressure effect on the dependence of  $\rho$  on the number of cycles in ECPC based on SCD with acetylene carbon black (70 mass parts).

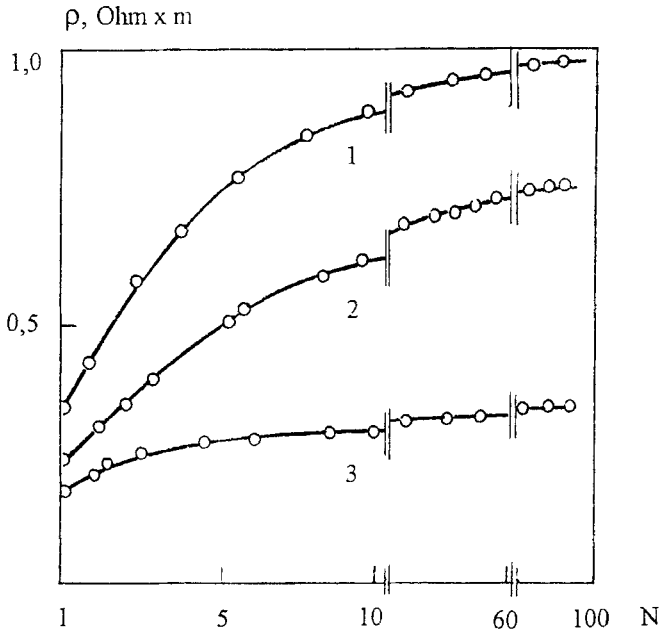


FIGURE 24 Cyclic compression effect on  $\rho$  for ECPCs based on nairit (1), SCN-26M (2), and SCD + SCI-3 mixture (3) with acetylene carbon black.

Uniaxial compression of thin films from some polymers by up to 1500 MPa pressure gave an abrupt decrease of electric resistance of these polymers by several degrees at a definite critical pressure [35]. In this case, changes in resistance  $R$  occurred in accord with the curve shown in Figure 25. Analysis of the phenomenon observed showed that a significant decrease of the polymer electric resistance was not induced by the known metal-insulator transition due to Mott's definition [39]. A jump of  $R$  values was observed in 2–30  $\mu\text{m}$  thick films of PP, PTPE, PA, Lavsan. Puansons of the 'Bridgeman anvil' type were used as electrodes [40]. Puansons were polished with roughness of 1  $\mu\text{m}$ . In this case, the accuracy of measurement did not yield from 12%. Figure 25 presents the  $R - P$  dependence being of practically reversible character. It has been found that the  $P_{cr}$  values significantly depend on the film material. The phenomenon observed in the work [35] the authors devoted to injection of electrons from a metal into a polymer due to decrease of the conductivity zone bottom in dielectrics, stimulated by high pressure. The present suggestion was used by the authors for explanation of anomalous effects in the conductivity of ECPC based on various polymers.

A jump-like reversible decrease of  $R$  was observed for ECPC based on polypropylene (PP) and copper powder (Fig. 26) [39]. Therefore,  $\rho$  of the material changed proportionally to the square film thickness. Temperature dependence of conductivity of ECPCs under pressure was also unusual.  $R$  does not change at temperature increase up to a definite value. At higher temperatures the  $R - T$  dependence obtains the view characteristic for classic semiconductors

$$\gamma = \gamma_0 \exp\left(-\frac{\Delta E}{kT}\right).$$

In accordance with the model suggested in [40] low conductivity of ECPCs (metal-filled composites, in particular) at  $P < P_{cr}$  is provided by existence of a potential barrier between metal particles and polymer molecules, which occurs in the case if the work function of electrons yielding from metal exceeds the energy corresponding to the conductivity zone bottom position in insulator,  $E_c$ . Using thermodynamic approach, developed in the work [41], the height of this barrier can be expressed *via*  $W_m$  according to the expression:

$$U_b = W_m - A - E_p, \quad (4)$$

$R \times 10^6, \text{ Ohm}$

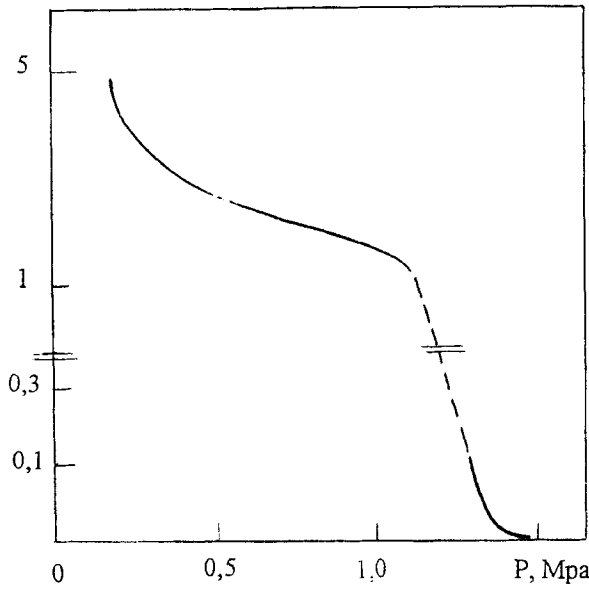


FIGURE 25 The dependence of thin PP films resistance on pressure.

$\log R, \text{ Ohm}$

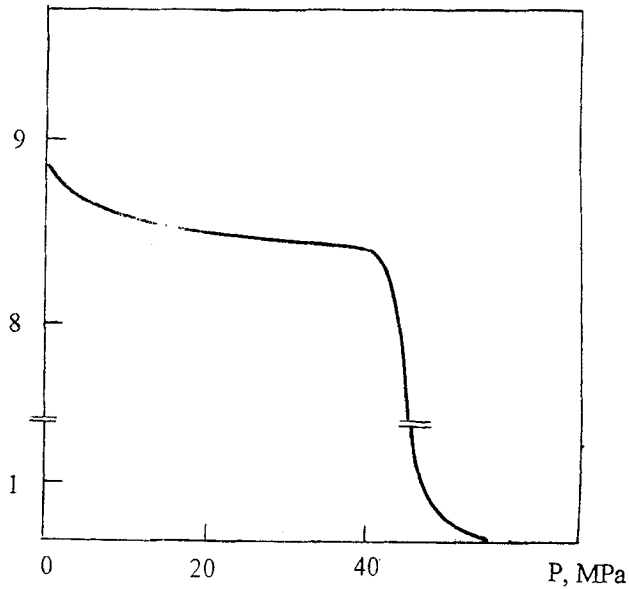


FIGURE 26 Dependence on pressure of electric resistance of ECPCs based on PP and copper powder (2 mass parts).

where  $E_p$  is the polarization energy of insulator;  $A$  is the energy of affinity to electron. At typical values used in Eq. (4) the barrier height on the metal-insulator interface is so high that electrons are able to overcome it only in the case of obtaining an accessive energy by means of photothermal or any other type of excitation. Since the self-conductivity of polymer is low, and electron transfer from metal is rather difficult due to the above mentioned reason, the whole system possesses comparatively low conductivity, not exceeding that of a semiconductor. But the position of the polarization energy,  $E_p$ . Therefore, at  $P = P_{cr}$ , when  $E_p = W_m - A$ , the potential barrier metal-insulator disappears. In this case, the picture of energy zones becomes profitable for injection of carriers. This leads to an abrupt decrease of electric resistance at  $P = P_{cr}$ .

One of probable approaches to direct experimental testing of testing of theoretical interpretation of the effect discussed was suggested in the work [40]. It concerns the study of effects of various fillers on  $P_{cr}$  of one and the same polymer matrix. In the case of suitability of Eq. (4),  $P_{cr}$  should be so higher, the higher the  $W_m$  value is. To check the jump-like model of the  $R$  change experiments were conducted in the systems of polytetrafluoroethylen (PTFE) with 10 mass parts of fillers: graphite, zinc, aluminum, copper, and nickel, the  $W_m$  values of which were 3.8; 4.3; 4.4; 4.6 and 5.1 eV, respectively, with the particle size of 0.1  $\mu\text{m}$ . The  $P_{cr}$  value was determined due to the methodic discussed in the work [38]. The  $P_{cr} - W_m$  dependence curve for the PTFE - filler system is shown in Figure 27 [41]. In this case,  $P_{cr}$  grows with  $W_m$ . As  $W_m = A - E_p$  at  $P_{cr} = P_{atm}$ , extrapolation of the dependences obtained to their cross point with the straight line, parallel to the abscissa axis and located at  $10^{-7}$  MPa from it, allows to determine the  $(A - E_p)$  values, found for PTFE as 3.5 eV. This value allows to calculate the potential barrier height  $U_b$ , by Eq. (4). Estimation of  $U_b$  gives the following values: -0.3 for graphite, -0.8 for zinc, -0.9 for aluminium, -11 for copper, and 1.5 eV for nickel.

The data on  $U_b$  and  $P_{cr}$  values, when the barrier at the metal-insulator interface practically disappears, give a possibility to obtain the  $(dU_b/dP)$  values by the curve  $U_b = f(P_{cr})$  characterizing changes of the conductivity zone bottom position in the polymer during compression. On the other hand, the  $(dU_b/dP)$  value can be obtained theoretically, if the dependence of the polarization energy on pressure is known. To conduct such a tests it is enough to know how the high-



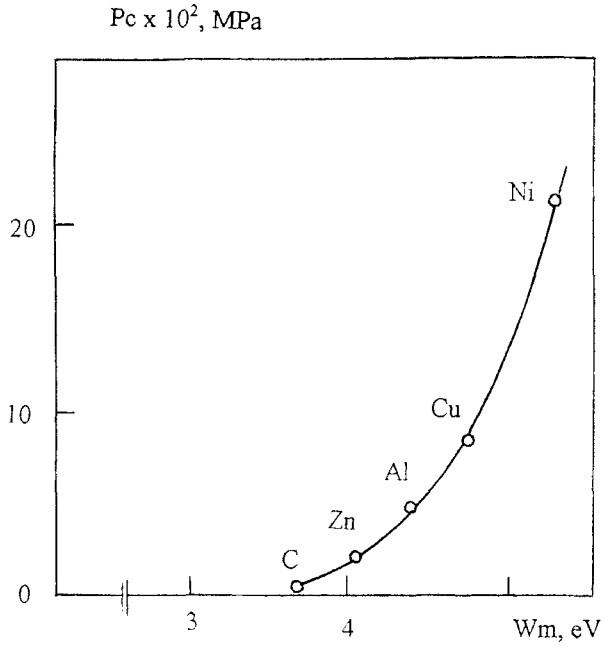


FIGURE 27 The  $P_{cr} - W_m$  dependence for PTPE-based ECPCs with copper and graphite.

frequent component of dielectric permeability  $\varepsilon$  of PTPE changes with compression. This follows from connection of  $\varepsilon$  to the polarization energy by the Born formula in the first approximation [42]:

$$E_p = \frac{e^2}{2r} \left( 1 - \frac{1}{\varepsilon} \right). \quad (5)$$

Here  $e$  is the electron charge;  $r$  is the effective distance between molecules of dielectric (in this interval  $r$  weakly depends on pressure). Comparison of the theory with the experiment is shown in Figure 28. The curve is approximated well by the formula

$$\varepsilon = \varepsilon_0 + \varepsilon_1 P^{1/2} \quad (6)$$

that contains two empirical parameters:  $\varepsilon_0 = 3.22$  and  $\varepsilon_1 = 0.11$ . Taking into account Eqs. (5) and (6), Eq. (4) will obtain the following

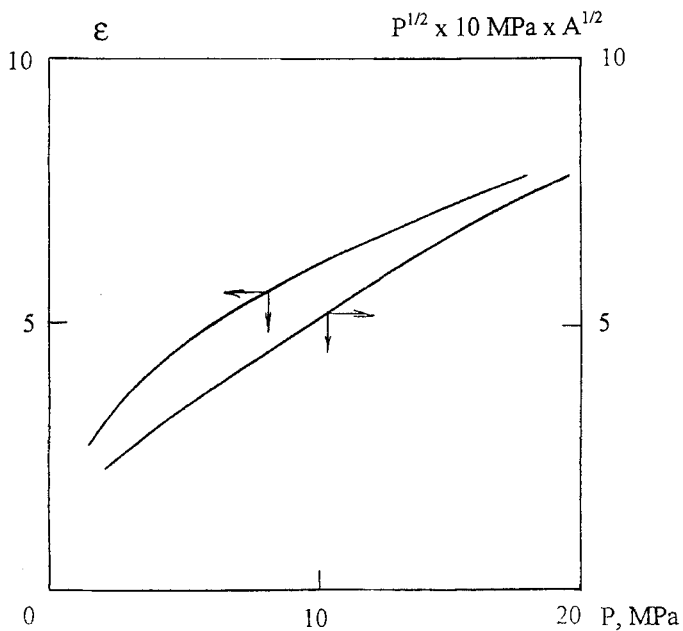


FIGURE 28 The dependence of  $\epsilon$  on pressure for PTPE-based ECPC.

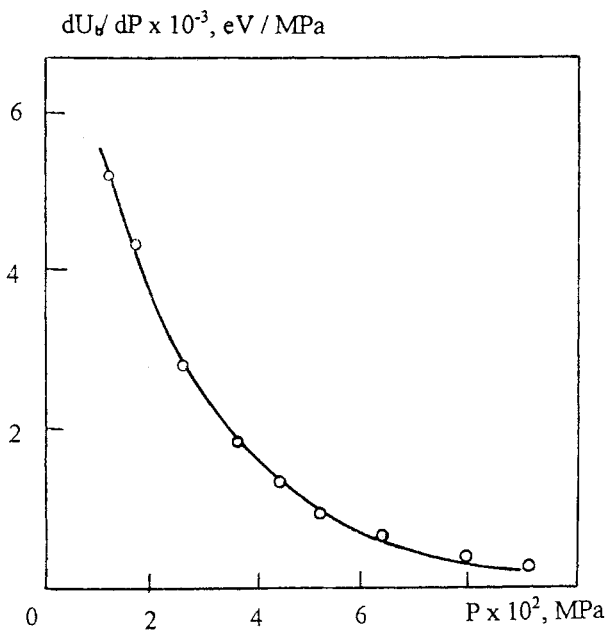


FIGURE 29 The  $(dU_b/dP)$  dependence on pressure for the PTPE + filler system. Points show experimental data, the continuous line displays theoretical calculations.

view:

$$\frac{dU_b}{dP} = \frac{a\varepsilon_1}{P^{1/2}(\varepsilon_0 + \varepsilon_1 P^{1/2})^2}, \quad (7)$$

where  $a$  is the constant, dependent on  $r$ .

Thus, above considered results of experimental and theoretical works probably showed sufficiently well, that mechanical deformations in general effect existantly on conducting properties of ECPC. The volume of this effect is defined mainly by depth of structural transformations in the polymer matrix at mechanical deformations. These transformations lead to modification of conducting particles distribution and change of the meadle distance between them in composites.

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