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

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ABSTRACT: Structural changes proceeding in composites under the effect of various mechanical deformations (stretching, compression, shear, etc.) affect the structure of an electrical conducting system. Mechanical stresses, induced by deformation of composite materials during deformation, affect both the 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 electric conductivity of materials. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 601–621, 1999

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ELECTRIC CONDUCTIVITY OF CARBON BLACK-FILLED RUBBERS UNDER STRETCHING DEFORMATIONS

Mechanical deformations that initiate intertransformations of macromolecules can affect the topology of conducting particles interacting with macromolecules. Many works have studied connections between structural features of composites and their electric conductivity at deformation.[1–3] Analysis of these shows that, to date, no systematic study has been able to explain the wide spectrum of the features of connections between structural transformations and conductivity. There is little doubt that such a situation is caused by numerous factors affecting the electric conductivity of electrically conducting polymer composites (ECPC) under mechanical tensions. Among these

factors, the following are deterministic: the type and composition of the components; their adhesion and cohesion; and the method (conditions of production of composites, the prehistory of composites). Study of the problem is complicated by one more condition: electroconducting properties of materials change inadditively with the deformation rate, exposure duration at measurements, temperature, and so forth.

Electric Conductivity of ECPC at Low Deformations

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

Behavior of the electric conductivity of organosilicon electrically conducting rubbers, based on

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

SCTV (high-molecular elastomer polydimethylvinilmethylsiloxan mm 450,000) and P357E carbon black, at low deformations, has been studied.[6] In some cases, compositions contained low-molecular elastomer SCTN polydimethylsiloxan mm 25,000. The composites were obtained using the additive vulcanization technique. Electrodes were introduced into the samples during vulcanization of rubbers. This provided reliable connection and minimal resistance of the contact. Geometrical size of the samples fitted the requirements for standard tensosensitive elements.

For 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 of sample, with geometrical sizes $1 \times 3 \times 10$ mm^3. 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 cycles. Exponential growth of curves can be explained satisfactorily by the tunneling mechanism of the charge transfer between filler particles[3] distributed in the polymer. Tunneling becomes entangled with the deformation growth because of the growth of spaces between filler particles. This leads to the growth of electric

resistance. The existence of histeresis loops on the curve (Fig. 1) is explained by an irreversible degradation of conducting bridges 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 histeresis, easily observed at cyclic one-axis stretchings. To decrease histeresis effects, we must reduce the concentration of carbon black associates. In the presence of supermolecular formations (globules),[7] this can be done by increasing uniformity of the distribution of *ingradients* in the polymer mass by reducing the 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-size globules. By varying polymer concentration in the solution, the number of large globules was expected to change. Comparison of dependences $\Delta R - \lambda$ for samples with different polymer concentrations in the solution (Fig. 2) enabled us to consider the possibility of the above-described model's application for electrically conducting rubbers.

According to experimental data, the sensitivity of electric resistance to deformations grows with

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

Table I   Electromechanical Characteristics of Rubber ECPC

Samples, Mass Parts	ρ (Ohm/m)	Homogeneity (%)	Relative Elongation (%)	Tensosensitivity Coefficient
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[a] (complete filling)				
150 : 50	0.009	0.8	150	10.0

[a] The sample was obtained by polymerization-filling technique.

polymer concentration in solution. Indeed, growth of globules formation size causes a decrease of their total surface and the square to be covered by filler particles. Thus, the probability of carbon black particles aggregation in intermediate layers is increased. The change of globule formation diameter at constant filler concentration may also cause a corresponding change of the depth of its penetration.[8] Then, the sensitivity of conductivity to deformation will increase as a consequence of reduction of the total amount of conducting chains. Considering these facts, it seems advisable to use a low-molecular elastomer as an additional component of the composite. The results of the composite obtained tests are shown in Table I.

According to the data in Table I, the inclusion of low-molecular elastomer SCTN into the composite promotes an increase of uniformity of the filler distribution within it. Apparently, application of an elastomer with low viscosity allows for 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 part of the rigid component in the elastomer matrix was shown by a significant reduction of deviations between ΔR and λ values at the beginning and 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. Thus, increased sensitivity

of conducting rubbers to deformation is possible at the application of polymers with different viscosities that have different thermodynamic affinities to fillers. Growth of tensometric parameters is also achieved by selection of an optimal polymer concentration in the solution.

Electric Conductivity of ECPC at High Deformations

The effect of high deformations of various types has been studied previously.[9–13] The models that explain the character of electric conductivity dependence on stretching and the compression deformations of these materials are known. However, little attention has been given 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 effect of stretching deformations (stretching–contraction) in the range of $0 < \varepsilon < 150\%$ has been studied.[12] 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 sinchronously: electric resistance of the sample R; mechanical tension σ; elongation at stretching ε; time of deformation at three rates of stretching t; change of the cross section square of the sample S. The device scheme for studying ρ and σ dependences on deformation of stretching ε are shown in Figure 3.

Data in Figures 4–6 show that the character of ρ change of samples in the form of the blade, the active part of which had a sizes $2 \times 5 \times 50$ mm^3 depends significantly upon both the value of the

Figure 3   The measuring scheme for ρ dependence of ECPCs on mechanical load under various temperatures; see text for details.

change of initial lengths of the samples at deformation and type, and the concentration of the filler. For example, if ρ of the rubber with relatively low concentration of P357E carbon black initially grows little at elongation and then decreases (Fig. 4), in the case of related composites containing the same filler in higher contents, the ρ–ε dependence grows monotonously until elongation end (Fig. 6). Significant differences are also observed in the ρ–ε 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, in addition to the factors already mentioned, the production technique plays a role of the same importance in determining deformation dependence of electrically conducting properties of filled rubbers. The ρ–ε dependences, recorded for rubbers obtained by the peroxide vulcanization technique (Fig. 8), show that differences in the processes of structurization—formation of a vulcanized network, in particular—lead to quantitative changes of ρ values at stretching.

The character of dependences shown in Figures 4–8 can be explained, if electrically conducting polymer composites represent 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 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

Figure 4   The ρ–ε 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').

interacting with macromolecules. Breaks of some chains of conducting particles leads to weakening of an infinite cluster and results in the increase of ρ. At further increase of deformation, the opposite processes can proceed in the materials. At elongation, the cross-section square of the sample decreases. This results in 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 by means of completion of carbon chains, randomly oriented in space, and their convergence according to the scheme shown in Fig. 9. Thus, two competing processes proceed at rubber stretching: degradation and formation of conducting chains. The change of ρ of the material depends upon prevailing process.

The process of longitudinal conducting chains breaks (ρ increases) because of the sample elongation along the stretching direction, and in-

ρ x 10⁻³, Ohm x m

Figure 6 The $\rho-\varepsilon$ 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′).

ρ x 10⁻³, Ohm x m

Figure 5 The $\rho-\varepsilon$ 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′).

crease 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 why ρ grows at stretching. The growth of ρ at stretching of rubbers increases with the filler content (Fig. 6). Horizontal parts of the curves in Figures 5 and 6 seem to correspond to the equality of the probabilities of degradation proceeding and the formation of conducting chains. Therefore, it can be suggested that in a definite range of deformation, ρ does not depend upon it. It is evident that setting the equilibrium between destructive and reductive processes depends upon correlation of in-

Figure 7 The ρ–ε dependence for the rubber based on SCTV at P803 carbon black concentration of 60 (1), 80 (2), and 100 (3) mass parts, obtained by additive vulcanization.

Figure 8 The ρ–ε dependence for the rubbers based on SCTV and P803 carbon black (60 mass parts) (1), and SCTV and P357E (40 mass parts) (2), obtained by peroxide vulcanization.

teraction forces between components of the homogeneous polymer system.

The concentration effect is also displayed at different rates of deformations of materials. It is possible that at a relatively low rate of stretching of the rubbers containing 40 mass parts of carbon black, relaxational processes in the material, which promote setting of a quasistable structure of the conducting system (stable for the current value of the stretching degree ε), follow the rubber deformation. At high rates of stretching, the formation of a quasistable conducting system is somewhat delayed. Thus, the character of the dependence changes. This means that a maximum occurs on the ρ–ε dependence curve, corresponding to the initial stage of deformation of the sample. In the samples with a 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, ρ of all samples grows first and then decreases to definite values passing the maximum. A similar effect was observed in Boomstra and Dannenberg[15] for elastomer-based

rubber. Growth of ρ at the beginning of contraction is explained by destruction of conducting chains as a result of disordering of macromolecules and their globule formations.

Because the length of samples is restored, the process of restoration of broken conducting chains

Figure 9 Scheme of carbon black channels decomposition before (a) and after (b) elongation.

and ρ reduction is increased. Therefore, at sample contraction, a maximum appears on the ρ–ε dependence curve. However, rubbers with a 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 the 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 ρ–ε 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 the relaxational processes in deforming systems are displayed, because 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 are 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, split from macromolecular formations (globules), can exit from the conducting system and increase the total resistance of the material. Moreover, these particles can become the source of destruction of other conducting bridges, which survived from degradation as a result of chaotic translations of these particles in the polymer matrix, and contribute into the resistance increase (growth of ρ at contraction). These processes are the main cause of histeresis phenomena occurring at cyclic loads. Based on this, the existence of a definite correlation between two histeresis phenomena would be expected: mechanical tension–deformation, and specific electric resistance–deformation. To explain such a correlation, the σ–ε dependences were composed for rubbers containing 40 and 50 mass parts of the filler (Figs. 10 and 11). Comparison of dependences ρ–ε and σ–ε (Figs. 4, 5, 10, 11) shows that the conclusion is qualitatively supported by the example considered: histeresis phenomena in the ρ–ε dependence are proportional to those in the σ–ε 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.

Figure 10 The dependence of mechanical tension on 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′).

These rubbers contained SCTN elastomer, in some cases.

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 seen that the ρ–ε dependence begins growing only after the concentration increase of low-structurized carbon black. The experimental data allow us to suggest that the increase of total surface of the polymer–filler interphase leads to coming closer to the structural effects caused by low- and high-structurized carbon blacks attributable to an increase of low-structurized carbon black concentration. First, this affects the composite density and mobility of macromolecular segments. As a result, the decrease of segmental mobility by formation of intensive cross links (at peroxide vulcanization), which promote an increase of the equilibrium material modulus, the obstacles for the orientation effect manifestation appear. Change of the microstructure because of cross-link formation in the vulcanizate promotes the opposite change of ρ at deformation of rubbers obtained by two different vulcanization methods,

Figure 11 The dependence of mechanical tension on 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′).

but possessing an 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 ρ–ε dependence, contrary to the same composites obtained by additive vulcanization (weak vulcanization network). Figure 10 shows that ρ of both rubbers decreases with ε growth. In this case, the density of vulcanization network seems to compensate relatively low filler concentration.

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

Study of the stretching effect by 200% in a cyclic regime (stretching–contraction) on natural rubber vulcanizates with 50 mass parts of channel carbon black and vulcanizates of BSC elas-

tomer with five mass parts of HAF carbon black[17] showed that, on the initial cycle, ρ increases first, until elongation reaches 50–60%. Then it decreases and becomes fivefold lower at the elongation of 200%, than at the initial moment. Contraction of the sample causes a sharp increase of ρ. After discharge, it is found to be 100-fold higher than its initial value. In further cycles, ρ 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, a difference is observed in the quantitative data, which are deformation ranges, corresponding to degradation or orientation of carbon black bridges, different 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 the existence of anisotropy. Figure 12 shows curves created from the results of measuring longitudinal and transverse resistance of natural rubber vulcanizates

Figure 12 Change of ρ longitudinal (dotted lines) and transverse (continuous lines) in two "stretching–contraction" cycles.

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

with channel carbon black. The measurements were made before deformation, during deformation at elongation by 50, 100, and 200%, following a 15 minutes "rest" after each deformation mentioned. The difference observed in the change of ρ shows the effect of orientation of carbon black particles at high deformations.

Anisotropy of ρ may occur as a consequence of carbon black chain orientation. In this case, longitudinal resistance can either be lower or higher than the transverse one, or their ratio is changed at stretching. Figure 13 shows the dependencies 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 ρ on the initial cycle is lower than the transverse one.

At high elongations, two effects overlap: the orientation of resistant primary structures; and the 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 ρ, but is weakly expressed in low structural types.

The second effect is observed for all types of the filler. The ratio of these two effects is the reason for the 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 was studied by the replica technique, used in electron microscopy. It was found that the replica, depicted from the sample preliminary stretched by 350%, contains much more technical carbon, than nonstretched one. For BSC vulcanizates, filled by Cetjen EC carbon black, the change of longitudinal ρ 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 ρ.[18] Previous deformation, conducted 15 min before the next one, increases ρ 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—an effect similar to the Mallins–Patrikeev effect[19] at mechanical loading of elastomers. Moreover, previous deformation can affect the disposition of the maximum on stretching–ρ curves. At repetitive deformation, ρ starts its reduction at the elongation lower than in the first cycle. These data show that the preservation of the residual orientation of the conducting system happened in the first cycle.[3] It was mentioned above that the change of ρ can depend upon the deformation rate. For example, for the BSC–HAF system, the structure is able to restore after the 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 a decrease of ρ. Figure 14 shows the curves of stretching–ρ dependences of natural rubber vulcanizates with different filling degrees by acetylene carbon black, obtained at a high rate of deformation.[19] At growth of the filling degree, the curves become 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 rates from 0.5 to 30%, the curves are qualita-

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.

tively similar, until the elongation reaches 150–200%. At higher elongation, they are raised sharper at lower deformation rates. These results are contrary to the above-mentioned data.[20] An explanation of this difference should be sought in both applications of different types of carbon blacks and in a significant (by 2–4 deg) difference in the deformation rates.

It is also interesting to study the effect of the crosslinking degree of vulcanizates on the character of deformation curves, calculated for the real size of the sample. The thickness of vulcanization network was characterized by a relative equilibrium modulus E_∞.[19–21] The thickness was regulated by the vulcanization duration change. Most of the curves shown in Figure 15 reach their maximum on the initial stage of deformation and their minimum at high deformation. Existence of the maximum and its value depend upon E_∞.

There are no maxima and minima at low density of vulcanization network ($E_\infty = 1.3$ MPa). The higher the values of E_∞ 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 ρ and the mechanical tension σ. They show that at any moment of deformation, growth of mechanical tension is followed by reduction of ρ and opposite, excluding only the first cycle of stretching. The histeresis of the material electric conductivity coincides with the histeresis of mechanical tensions.

The curves of ρ 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_∞, show that, under the same mechanical tension, the samples with more dense vulcanization network possess higher electric resistance ρ (see Fig. 17).[21]

The square of the histeresis loop is stabilized at increasing the number of "stretching–contraction" cycles. In this case, the square of histeresis loop decreases. Reduction happens so abruptly, the higher is the crosslinking degree of vulcanizates. For example, NC with 60 mass parts of acetylene carbon black ATG-70 possesses reduction of the histeresis loop square by 4–5 times at the increase of E_∞ from 1 to 2.5 MPa. The de-

Figure 15 The dependence of resistance at break σ (curves 1', 2', 3', 4') and ρ (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.

Figure 16 The dependence of σ and ρ on stretching in the cyclic regime for BSC filled by acetylene carbon black.

crease of the histeresis loop square also happens at growth of the filler concentration.[22]

MECHANICAL RELAXATION AND ELECTRIC CONDUCTIVITY OF ECPC

As mentioned in the previous section, forces rise in the 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 because of overlapping of several factors.

To study electrically conducting properties of polymer composites during their mechanical relaxation, tests were performed that used the same composites, studied at high deformations.[23] The experiment on determination of ρ during relaxation of the mechanical tension σ was performed as follows. A thin sheet (2 mm) of electrically

conducting rubber was stretched on a stretching machine at a definite deformation ε. The change of ρ was recorded by an automatic recorder immediately after the stretching stopped. The automatic recorder scale was graduated in Ohms on time τ, and sinchronous recording of the time dependence of σ at fixed deformation was made according to the method described above. Moreover, relaxational characteristics were recorded for the same samples after the end of the "stretching–contraction" cycle.

As Figure 18a shows, the values of ρ grow during relaxation of tension σ. In this case, the increase of ρ proceeds with a higher rate in rubbers, deformed at relatively high rates. Moreover, the increase of the stretching rate induces acceleration of ρ increase in these materials. In this case, kinetics of mechanical tension σ reduction is completely coincident with the character of ρ change. This means that the sample relaxes mechanically the faster and higher the rate of the sample deformation (see Fig. 18b). Growth of ρ with time during relaxation of σ can be explained based on the effect of the elastomer molecular system disordering that occurs after deformation release.[23] In this case, internal mechanical tensions are reduced by the transition of a highly regulated system into a lower regulated state on

Figure 17 The dependence of ρ 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.

Figure 18   Time dependences of ρ (a) and σ (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.

the present stage of deformation. Disorder in the system of macromolecules induces conducting circuit destruction; that is growth of ρ of the material. In view of the fact that the growth of the deformation rate induces an 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 dependencies of ρ at the relaxation of rubbers shows that they are successfully described by the expression:

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

where ρ_0 and ρ_∞ are border values of ρ during relaxation under fixed stretching deformation and τ is the relaxation time.

Eq. (1) represents the solution of the differential equation, similar to that deduced by Barte-

nev[13] for kinetics of 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:

$$\ln \frac{\rho - \rho_\infty}{\rho - \rho_0} = -\frac{t}{\tau} \tag{2}$$

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

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

Relaxation times τ for the composites of SCTV elastomer with P357E carbon black were determined[24] by tangents of straight lines (Fig. 19). Numerical values of τ' for other composites were obtained similarly. The results are shown in Table II.

The data in Table II show that the increase of deformation of polymers leads to the growth of the relaxation rate of both ρ and σ. This effect is strengthened at the increase of the filler concentration in the composite. For example, at compa-

Figure 19   Dependence of ρ 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.

Table II Relaxational Characteristics of Stretched ECPC on the Base of SCTV[a]

Filler, Mass Parts	Deformation (%)	Deformation Rate (mm/s)	Relaxation Time (τ, 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

[a] Elastomers were obtained by the additive vulcanization technique.

rable rates of deformation, ρ of rubber containing 60 mass parts of active carbon black relaxes at a higher rate than in the same rubber containing 50 mass parts of the same carbon black. In this case, the effect of the interphase growth is observed. This growth causes an increase of the 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 of Alexandrov–Lazurkin[25] and the generalized model of 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, the complexity is expressed in the functional ρ–t dependence, starting from the complete end of the cycle (Fig. 20). Because the curves of the figure were considered, we should 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, to the most curvilinear parts with an overwhelming limit at $t \rightarrow \infty$ (see Fig. 20, curves 2 and 3). Both parts of the curves

mentioned reflect regulation of the conducting system by regulating the macromolecular part of the composite.

However, the rate of relaxation and time of reaching equilibrium values of ρ at the end of the relaxational period significantly depend upon 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 of the present dependences: the difference between minimum and maximum values of ρ on the whole interval of relaxation also depends upon the filling degree.

Analysis of the dependences, shown in Figure 20, make it possible to conclude the following. Taking into account the ideas by Bartenev[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 nonlinear viscoelasticity (the processes of this

Figure 20 The dependence of ρ 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 $\rho_0 = \rho$.

type are nonlinear relaxation at low deformations and nonlinear 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 in both branches of the deformation cycle and is defined by elastic properties of the composite matrix. Elastic forces rapidly drive the system into 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 respond to the smallest structural changes in topology of structural polymer units (globules, for example), and is absolutely controlled by them. In the present case, the 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 ρ values, shown in Figure 20, corresponds to reduction of conducting channels existing in tight connection with macromolecules of elastomer, the elastic properties of which is often promoted by the bonds mentioned.

The second process is reduction of the initial system (before deformation) with participation of filler particles, split 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 is known,[29] these particles decelerate regulation in the system of macromolecules and intensify internal friction and nonlinear effects at high deformations connected to it. That is the reason their existence in the composite always leads to elongation of relaxational processes. Apparently, this is also the reason for deceleration of restoration of the primary conducting system of the composite material. Thus, the delay of complete reduction of the equilibrium structure in high-filled polymer matrices proceeds to a higher degree than that of low-filled polymers. At first glance, this seems paradoxal. Remember that, according to the exponential dependence of ρ 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 the heterogeneous system. Analysis of these curves showed that exponential parts are successfully described by the eq. (1), with the difference that ρ_∞ is substituted by ρ_m at the end of relaxation, and ρ_0 by ρ_1 correspond to the value of ρ at crossing the 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. Their numerical values are shown in Table III.

Analysis of the data in Table III leads to the following conclusions. First, filler content significantly affects relaxational characteristics of the material. For example, the rubber containing 40 mass parts of P357E carbon black possesses a rate of fast relaxation about five times lower, and duration of slow relaxation is 4-fold lower than for analogous rubber with 60 mass parts of the same filler. 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 for these differences is in increase of the rubber elasticity modulus with the increase of the filler concentration. On one hand, this leads to an increase of the interphase surface square, and on the other, 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 the reason, although increase of the modulus is the reason for growth of the rate of conditionally 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. Second, 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. 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 is balanced by high content of low active carbon blacks, because, in both cases, the modulus of the material and internal friction in relaxational processes

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	1.2×10^{-2}	7
2	P357 (50)	150	2.5	4.0	21
3	P357E (60)	60	2.5	6.7×10^{-2}	28
4	P803 (60)	200	2.5	——	6
5	P803 (120)	150	2.5	2.2×10^{-2}	11
6	P357 (40)	150	2.5	10.6×10^{-2}	48
7	P803 (60)	150	2.5	5.1×10^{-2}	24
8	P803 (60) + SCTN (20)	200	2.5	2.8×10^{-2}	16

[a] Composites no. 1–5 were obtained by the additive vulcanization technique; composites no. 6–8 were obtained by the peroxide vulcanization technique.

grow. Third, comparison of characteristics of the rubber, produced by two different vulcanization techniques, shows that the rate and time of relaxation depends upon the vulcanization network density and is not weaker than the type and concentration of the filler (compare composites 1 and 6, 4 and 7, Table III). Because the concentration of polymer crosslinks 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 one. This is caused by 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 a decrease of the fast relaxation rate and time of slow relaxation, as compared with similar composites containing no SCTN (compare composites 7 and 8, Table III).

ELECTRIC CONDUCTIVITY OF ECPC UNDER COMPRESSION

All-Round Compression

Some features characterize dependences of ECPC electric conductivity on all-round compression. Dependence of ρ on pressure at all-round compression was studied in the samples obtained by additive vulcanization technique from SCTV with

different concentrations of P357E carbon black. The experiments were performed using a "plunger–cylinder"-type device. The device scheme is shown in Figure 21.[27] Device punches served simultaneously as contact electrodes, connected to a re-

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 Pressure dependence of ρ 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.

corder of electric resistance of ECPCs. Results of the measurements are shown in Figure 22. The dependencies clearly show that under conditions of all-round compression, at the increase of pressure, the character of ρ changes significantly, depending on the filler concentration. For example, ρ of the samples with low filling degree (Fig. 22, curve 1) grows with pressure and is characterized by the S-type dependence; whereas, for samples with high filler concentrations, the values of ρ decrease abruptly first, and then decrease monotonously and come out of the limits. In this case, the higher the filler concentration, the initial fall of ρ is shown much more clearly, virtually reaching 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 reasons can be used in practice. These 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 lead to growth of ρ. Drawing together of carbon black aggregates and formation of new conducting channels happens as the pressure is increased because of 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 volumeric compression of the samples. In samples with comparatively low filling, the degree of reservation is so low because of the low density of the conducting system, that the degradation prevails over the competing process of restoration. That is why the general tendency to ρ decrease in the compressed state of ECPCs is displayed in composites with a relatively low filling degree at higher pressures, than in composites with a higher filling degree.

Uniaxial Compression

Contrary to the all-round compression of ECPCs, qualitatively different action is observed in investigations of the ρ dependence on deformation under 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 ρ of all samples at uniaxial compression increases with pressure[30] (Table IV).

According to the data from Table IV, the sample resistance at compression significantly increases first, and then abruptly decreases. In this case, the pressure effect on ρ 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 shown that indicates the 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, the weaker is the change of ρ, and the saturation time grows with the limit pressure increase (Figs. 23 and 24). Similar results have been obtained elsewhere.[31–34] Based on the experimental results shown in Table IV and Figures 23 and 24 we can conclude that, at uniaxial compres-

Table IV   Uniaxial Compression Effect on ρ of Vulcanizates

Elastomer	Filler Content (%)	ρ (Ohm $\times$ m) at Compression Pressure, MPa			
		Atmosphere Pressure	0.1	0.5	1.5
SCI-3	30	2.1	47.8	512	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

sion, conducting channels degradation occurs in the composites because of the 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 a direction normal to the compression axis. Apparently, such deformations result in rather significant structural changes, which cause restoration of the initial structure and properties of ECPCs to be probable only with durable storage of samples at room temperature (acceleration of restoring processes is observed at increased temperatures).

Figure 23 Cyclic compression effect on ρ for ECPCs based on nairit (1), SCN-26M (2), and SCD + SCI-3 mixture (3) with acetylene carbon black.

Figure 24 Pressure effect on the dependence of ρ on the number of cycles in ECPC based on SCD with acetylene carbon black (70 mass parts).

R x 10^6, Ohm

Figure 25 Dependence of thin PP films resistance on pressure.

Compression at High Pressure

In studies of Enikolopian et al.[35–40] concerning compression of various ECPCs by high pressure, a sequence of unusual phenomena was observed, which gave rise to a new approach for interpretation of the conductivity mechanism of electrically conducting composites.

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 accordance with the curve shown in Figure 25. Analysis of the phenomenon showed that a significant decrease of the polymer electric resistance was not induced by the known metal insulator transition attributable to Mott's definition.[39] A jump of R values was observed in 2 to 30-μm thick films of PP, PTPE, PA, Lavsan. Puansons of the "Bridgeman anvil" type were used as electrodes.[40] Puansons were polished to a roughness of 1 μm. In this case, the accuracy of measurements did not move from 12%. Figure 25 presents the R–P dependence as a practically reversible character. It has been found that the P_{cr} values significantly depend upon the film material. This phenomenon was observed in the work[35] the authors devoted to injection of elec-

trons from a metal into a polymer because of the decrease of the conductivity zone bottom in dielectrics, stimulated by high pressure. The present suggestion was used by the authors to explain anomalous effects in the conductivity of ECPC based upon various polymers.

A jump-like reversible decrease of R was observed for ECPC based upon polypropylene (PP) and copper powder (Fig. 26).[39] Therefore, ρ 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 a 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($\Delta E/kT$)].

In accordance with the model suggested in Vereshchagin et al.,[40] low conductivity of ECPCs (metal-filled composites, in particular) at $P < P_{cr}$ is provided by the existence of a potential barrier between metal particles and polymer molecules, which occurs if the work function of electrons yielding from metal exceeds the energy corresponding to the conductivity zone bottom position in insulator E_c. Using a thermodynamic approach (see [44]) the height of this barrier can be expressed via W_m, according to the expression:

$$U_b = W_m - A - E_p \qquad (4)$$

logR, Ohm

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

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

where E_p is the polarization energy of insulator, and 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 by obtaining accessive energy by means of photothermal or other type of excitation. Because the self-conductivity of polymer is low, and electron transfer from metal is rather difficult because of the above-mentioned reason, the whole system possesses a 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 probable approach to direct experimental testing of the theoretical interpretation of the effect discussed was suggested in Vereshchagin et al.[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 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 polytetraphtorethylen (PTPE) 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 particle size of 0.1 μm. The P_{cr} value was determined according to the method discussed in the Enikolopyan et al.[38] The $P_{cr} - W_m$ dependence curve for the PTPE–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 for determination of the $(A - E_p)$ values, found for PTPE as 3.5 eV. This value allows us 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 aluminum, -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, gives the 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 sufficient to know how the high-frequency component of dielectric permeability ε of PTPE changes with compression. This follows from the connection of ε to the polarization energy by the Born formula in the first approximation[45]:

Figure 28 The dependence of ε on pressure for PTPE-based ECPC.

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

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

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

$$\varepsilon = \varepsilon_0 + \varepsilon_1 P^{1/2} \tag{6}$$

which 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:

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

where a is the constant, dependent on r. Figure 29 shows good coincidence between the theoretical and experimental data. Thus, results of experimental and theoretical works considered above probably show sufficiently well that mechanical deformations, in general, considerably affect the 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 a modification of conducting particles distribution and a change of the middle distance between them in composites.[43-48]

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