Introduction Mechanical stresses, induced by deformation of the composite materials, affect both the molecular and super-molecular structures of the polymers [1-3]. Structural changes occurring in composites produced by various mechanical deformations (stretching, compression, shear, etc.) affect the structure of an electrically conducting system. As a consequence, they affect the substructure and filler particles bound to it [4-6]. It is evident that in the case of conducting polymer composites mechanical deformation influences on the electrical conductivity of materials. Results and discussion It is well known that forces formed in polymer matrix from the very beginning of deformation counteracting the external influence. Therefore, the elucidation of relaxation effects on electric conductivity is complicated during deformation of ECPC due to overlapping of several factors. 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 [7]. The experiment on determination of electrical volumetric specific resistance r during relaxation of the mechanical tension s was performed as follows. A thin sheet (2 mm) sample of electrically conducting rubber based on polydimethylmethylvinilsiloxan (industrial type –SKTV) was stretched on a stretching machine at a definite deformation e. The change of r was recorded by an automatic recorder immediately after stretching stop. The automatic recorder scale was graduated in Ohms on time t, and synchronous recording of the time dependence of s at fixed deformation was made. Moreover, relaxation characteristics were recorded for the same samples after the end the ‘stretching-contraction’ cycle. As Fig.1a shows, the values of r grow during relaxation of tension s. In this case, the increase of r proceeds with higher rate in rubbers, deformed at relatively high rates. Moreover, increase of the stretching rate induces acceleration of r increase in these materials. In this case, kinetics of mechanical tension s reduction is completely coincident with the character of r change. This means that the sample relaxes mechanically the faster, the higher the rate of the sample deformation is (Fig. 1,b). Growth of r with time during relaxation of s can be explained basing on the effect of the elastomer molecular system disordering that occurs after deformation release. 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 r 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 r at the relaxation of rubbers show that they are successfully described by the expression: , (1) where r0 and r¥ are border values of r during relaxation under fixed stretching deformation; t is the relaxation time. Fig. 1 - Time dependences of r (a) and s (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 Eq. (1) represents the solution of the differential equation, similar to that [1] deduced for kinetics of the polymer mechanical relaxation. According to Eq. (1) kinetics of relaxation are described by the Maxwell model [2]: . Taking logarithm from Eq. (1), we get: . (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 Fig.2 shows, time dependences by Eq. (2) are straightened. This allows to use the model of consequently connected strings and damper (the Maxwell model) for describing kinetics of the change of r during relaxation of mechanical tension of electrically conducting rubber. Relaxation times t for the composites of SCTV elastomer with P357E carbon black were determined by tangents of straight lines (Fig. 2). Comparison of mechanical relaxation characteristics with analogical ones obtained for electrical conductivity of same materials leads to conclusion that the mechanical and electrical conductivity relaxations are in good correlation. Moreover by means of electrical conductivity there are possible to obtain in the solid polymers new relaxation phenomena invisible for other methods. Fig. 2 - The dependence of r of the samples based on SCTV elastomer with P357E carbon black (50 mass parts) on time during relaxation in coordinates of Eq. (1). Numeration of curves coincides with one presented on Fig. 1 Table 1 - Relaxation characteristics of stretched ECPC on the basis of SCTV* Filler, mass parts Deformation, % Deformation rate, mm/s Relaxation time t, 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. The data shown in Table 1 testify that the increase of deformation of polymers leads to the growth of the relaxation rate of both r and s. This effect is strengthened at the increase of the filler concentration in the composite. For example, at comparable rates of deformation r of rubber containing 60 mass parts of active carbon black relaxes with 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 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 point out a relatively low adhesive interaction between the polymer and the filler in rubbers with P803 carbon black. However, weak absorption forces also grow at deformation (tension increases). The investigation of relaxation processes at the end of the deformation cycle (stretching-contraction) after complete discharge of the samples showed that relaxation phenomena are more complex if compared with the above described facts. First of all, the complexity is expressed in the functional r-t dependence starting from the complete end of the cycle (Fig. 3). Since the curves of the present figure were considered, let us mention that they, in fact, represent a superposition of at least two relaxation processes. One of these processes relates to the most linear parts of the curves, and the second one - to most curvilinear parts with limit overwhealming at t ® ¥ (see Fig. 3, curves 2 and 3). Fig. 3 - The dependence of r 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 r0 = r 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 r at the end of the relaxation 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 r on the whole interval of relaxation also strictly depends on the filling degree. Analysis of the dependences, shown in Fig. 3, gives a possibility to conclude the following. Taking into account the ideas by Bartenev /1/ 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 [6], 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. Table 2 - Relaxation characteristics of electrically conducting rubbers based on SCTV elastomer at the end of deformation cycles* Filler, Sample prehistory Relaxation time, s No mass parts 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 ¾ 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 * Composites No. 1 - 5 were obtained by the additive vulcanization technique; Composites No. 6 - 8 were obtained by the peroxide vulcanization technique. ** SCTN –low molecular (M.m. about 25 000) elastomer. 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 r values, shown in Fig. 3, 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, 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 relaxation 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 paradox. Let us remind now that according to the exponential dependence of r 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 r - t dependences shown on Fig. 3 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 r¥ is substituted by rm at the end of relaxation, and r0 by r1, corresponded to the value of r at crossing exponential curve by the straight line. Using Eq. (1) for various composites tested, relaxation times were determined. Numerical values of them are shown in Table 2. The analysis of the data from Table 2 shows that: 1. Filler content significantly affects relaxation 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 the 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 relaxation process in the macromolecular system. That is why, although the increase of the modulus is the reason of 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. 2. The effect of the filler type on proceeding of relaxation 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 is balanced by high content of low active carbon blacks, because in both cases the modulus of the material and internal friction in relaxation 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, Table 2). 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 relaxation characteristics. In this case, the increase of the ‘soft phase’ in the composite by introduction of low-molecular SCTN elastomer softens relaxation 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, Table 2). Conclusion The measure of the mechanical relaxation processes in the electrical conducting polymer composites, particularly in conducting rubbers, may be investigated by study of time-dependent processes of electrical conductance, because the behaviour of the conducting system is directly depended on any changes in polymer matrix.