

# Changes in Electrical Conductivity During Mechanical Deformation of Carbon Black Filled Elastomeric Matrix

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**Abstract:** Relation between electrical conductivity and mechanical behaviour was investigated during mechanical deformation followed by stress relaxation at constant deformation and by recovery after stress release. Although generally simple mechanism was expected consisting in conductivity decrease during strain followed by certain recovery during stress relaxation, rather complex behaviour was observed, depending on deformation values and type of filler used. It is believed that conductivity changes may contribute to understanding of changes in the reinforcing filler structure during mechanical deformation. The results are discussed in terms of formation, decomposition and further reforming of conductive continuous filler structures during various stages of mechanical deformation.

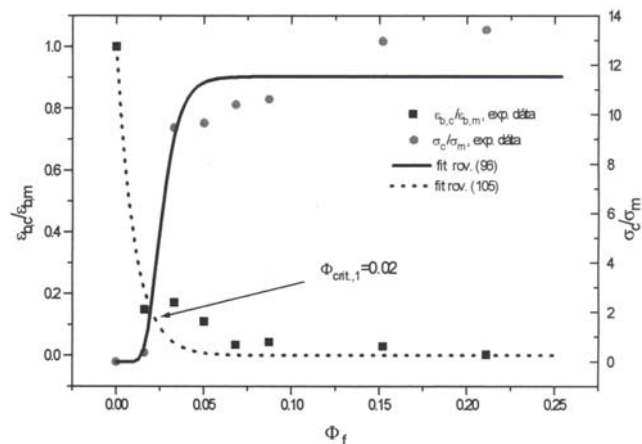
**Keywords:** Electrical properties, mechanical properties, correlation, relaxation, network structure.

## 1. INTRODUCTION

Polymer composites composed from insulating polymeric matrix and conductive filler represent an important group of materials with several interesting applications. The principle of conductivity of these materials consists in a formation of a conductive network through the material so that electrons can be easily transported from one side of the specimen to the other. This idea has been further theoretically worked out and experimentally proven by observation of so called percolation threshold, which is defined as a narrow concentration range of the filler within which the electrical conductivity increases by several orders of magnitude [1, 2]. Below the percolation threshold, at low filler content, the material exhibits low conductivity; the particles of the filler are separated and transport of electrons is difficult and slow. As the filler content increases, more and more particles form aggregates which are of anisotropic shape in case of highly conductive fillers. At certain filler concentration, the aggregate of conductive particles becomes to be continuous though the material making the electron transports rather easy. This is the concentration where percolation threshold is observed. Further increase of the filler content results in an increase of the number of conductive paths through the specimen and more electrons can be transported. However, after formation of certain, rather small number of conductive continuous paths, a kind of saturation is reached and further increase in conductivity is much less steep comparing to the region of percolation.

As said, the formation of electroconductive continuous network results in a steep increase in electrical conductivity. On the other hand, it creates a path not only for electrons in electrical field but also for cracks if the material is under mechanical stress. Therefore the highly electroconductive

composites are usually quite brittle; presumably, mechanical fracture is supported by the conductive path where catastrophic crack is formed easier compared to intact polymeric matrix, as shown by Krupa *et al.* [3], who derived an equation describing the tensile strength at break of composites using percolation concentration of the filler. The example of relations between electrical parameters and mechanical behavior is shown in Fig. (1).



**Fig. (1).** Example of relation between electrical conductivity ( $\sigma$ ) percolation threshold and mechanical properties represented by a steep decrease in elongation at break ( $\epsilon$ ) around percolation concentration of the filler ( $\phi_f$ ). Suffices m and f indicate the values for matrix and composite, respectively.

Since the nature of the percolation threshold consists in a particular structure of the electroconductive filler, changes in the electrical conductivity should be closely related to the filler supramolecular order. Therefore it is expected that generally with the progress of uniaxial strain, conductivity should decrease, due to low capability of conductive filler network to adjust to higher deformation, resulting in a de-

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struction of the continuous conductive structure, while during stress relaxation (the specimen is kept at constant nonzero deformation) the electrical conductivity might recover to certain extent or to stay constant.

Development of new methods for characterization of conductive polymeric composites are of interest if electrical conductivity can be measured under dynamic conditions during deformation. The primary goal is to reveal correlations between the two factors.

The papers dealing with the correlation of electrical conductivity and mechanical properties are rather rare in the literature, so are the papers describing measurements of electrical conductivity under dynamic conditions. Rather detailed and comprehensive study was done by Radusch *et al.* [4, 5] who used measurement of electrical conductivity for determination of the degree of homogenization during mixing of a conductive filler into polymeric matrix in an internal laboratory mixer.

The effect of the addition of short carbon fibres (SCF) on the mechanical and electrical properties of conductive polymer composites (CPC) with poly(ester) and poly(epoxy) matrices has been studied by Feller *et al.* [6]. The reinforcement effect of (SCF) filled thermosets depends on the nature of the matrix. Up to 3% v/v, a good correlation is found between resistivity and relative Young's modulus. The fact that resistivity can be correlated to relative Young's modulus for SCF content below the plateau shows the ability of electrical techniques to be a non-destructive method for the evaluation of SCF composites mechanical properties.

## 2. METHODS

Styrene-butadiene synthetic rubber (SBR) Kralex 1500 (Kaucuk, Kralupy, Czech Republic) based vulcanizates were used as the polymeric elastomeric matrix. Two grades of carbon black (CB) were used as the electroconductive fillers, namely Chezacarb A<sup>+</sup> (Unipetrol RPA, Czech Republic, dibutylphthalate absorption 365 – 395 ml/100g, iodine absorption 1010 – 1140 mg/g) and Vulcan 7H-N234 (CS Cabot, Valašské Meziříčí, Czech Republic, iodine absorption 115 – 125 mg/g, oil number 120 – 130 ml/100g).

Composition of the rubber mixture is given in Table 1 below and the curing times in Table 2.

**Table 1. Composition of the Rubber Mixture for Testing**

Component	phr	Source
SBR	100	Kaucuk, CR
CB	Various	
ZnO S6	3	SlovZink, SR
Stearin	1	Setuza, CR
Sulfenax CBS/MG	1	Istrochem, SR
Sulphur	1.75	Siarkopol, PL

The concentration range of CB was derived from requirement of sufficient conductivity (being too low for blends containing 5 wt % of Chezacarb or 25 wt % of Vulcan) on one hand and deformation at break above 400 %, on the other hand, so that experiments could be proceed until

400 % without fracture of the specimen. The strain at break was lower than 400 % for vulcanizates containing more than 40 wt % of Vulcan or more than 10 wt % of Chezacarb.

**Table 2. Curing Times for Blends with Different CB Content, Curing Performed at 150 °C and Pressure 20 MPa**

CB Type	CB Content wt%/phr	Curing Time Min
Chezacarb	7.5 / 11.8	44.5
	10 / 15.7	42.5
Vulcan	30 / 47.0	36.0
	35 / 54.9	36.25
	40 / 62.7	38.0

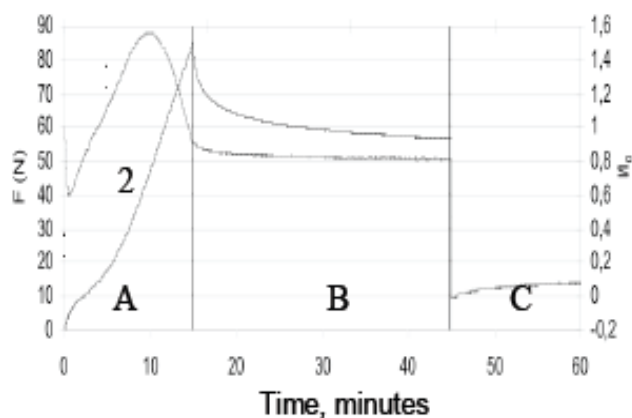
The blends were mixed in 30 ml mixing chamber of Plastograph Brabender PLV 151 in two stages, first at 50 rpm and 100 °C for 10 minutes, followed by 8 minutes at 90 °C and 40 rpm. Final homogenization was done in a roll mill. The samples were vulcanized in a laboratory press under conditions specified in Table 2. The curing times were determined using rheometer RPA as the  $t_{90}$  time needed for achieving 90 % of maximum torsion. Samples for simultaneous measurement of stress – strain curve and electrical conductivity contained two Cu wires for attaching the contacts of the multimeter APPA 305.

The measurement of electrical properties was done in parallel with recording the stress – strain curve. Because of changing dimensions of the specimen during measurement, instead of the conductivity, the electrical current passing through the specimen at chosen constant voltage was measured and expressed as relative value being the ratio of current measured at certain deformation over that passing through undeformed sample in the beginning of the experiment at zero deformation. The typical course is seen in Fig. (2). During the first 15 minutes, the sample was deformed by uniaxial stress up to relative deformation 400 % (uniaxial drawing stage, region A in Fig. 2). It has to be stressed that in no case fracture of the sample occurred. After reaching this deformation, the movement of the clamps was stopped and the sample was held under 400 % deformation for 30 minutes while stress decrease was recorded (stress relaxation stage, Fig. 2, region B). Then the load was released and the sample shrank elastically to almost original length (recovery stage, certain small permanent deformation was observed, region C in Fig. 2). Relative current passing through the sample was recorded during all three stages.

Typically the scheme of mechanical treatment was repeated twice with the same sample, so that in the repeated run of deformation – relaxation – recovery the sample was not intact but the effect of previous deformation run was investigated.

## 3. RESULTS

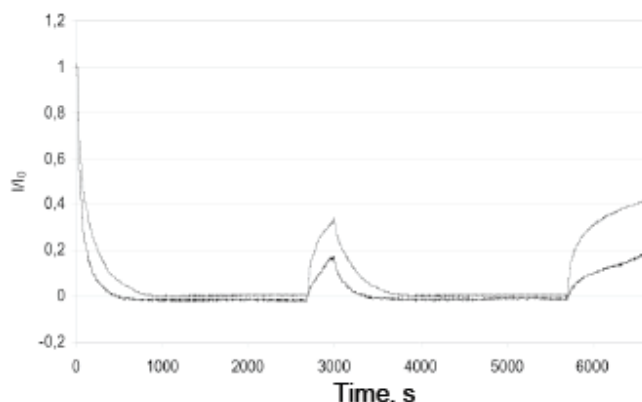
The two types of carbon black in vulcanizates were compared regarding the effect of concentration and nature on changes of electrical current with deformation. The courses of dependences of relative current on deformation are shown in Figs. (3 and 4). The deformation status is characterized by



**Fig. (2).** Typical dependence of parallel measurement of stress - strain curve (2, time is proportional to the deformation) and electrical relative current (1) in dependence on time of the experiment. The phases of the mechanical loading **A** - uniaxial drawing, 0 – 15 minutes, **B** - stress relaxation, 15 – 45 minutes, deformation is constant **C** - recovery, rest of the experiment.

the time of the experiment, where the first part up to 900 seconds represents monotonous deformation under uniaxial stress, part between 900 and 2700 seconds belongs to stress relaxation (recording changes of stress with time at constant deformation), and the last part includes stress release and 300 seconds of recovery. After that run, the second run proceeds which consists of the same set up except for the last recovery stage which lasts for 900 seconds instead of 300.

In the Fig. (3) the change of relative current values is shown with rising deformation – stress relaxation - recovery for two vulcanizates filled with different Chezacarb content. The shape of the curves is almost identical regardless of the CB concentration. During deformation quite extensive decrease in conductivity was observed, followed by a modest increase during the relaxation stage. The recovery stage is characteristic by the increase in the relative current, although the values after 5 minutes were far below the original current passing through the vulcanizate before the deformation.

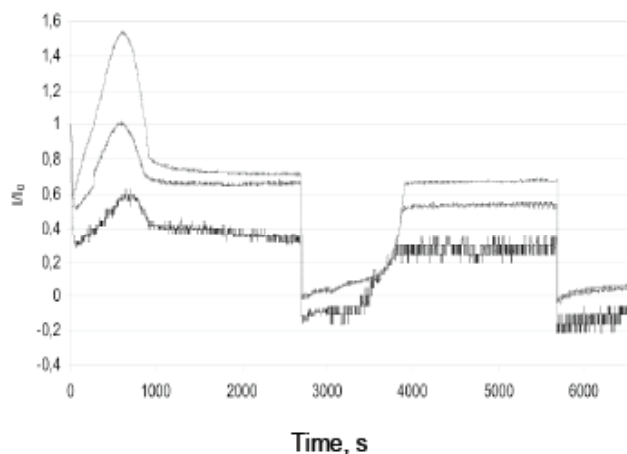


**Fig. (3).** Changes in normalized electrical current values ( $I$ ) for the vulcanizates of SBR filled with Chezacarb carbon black 10 wt % (upper curve) and 7.5 wt % (lower curve) during whole deformation – relaxation – recovery cyclus, repeated twice.

Second run with the same sample is more or less the same, although the starting current values after 5 minutes

recovery is much lower compared to that of the original undeformed sample. Relaxation stage leads to certain modest increase in current values while final 30 minutes recovery shows rather substantial current increase. This course also indicates that 30 minutes is much below the time required for reasonable recovery, since the rising tendency of the curve after 30 minutes recovery is obvious.

In the Fig. (4) the same dependence is shown for three vulcanizates filled with various concentrations of Vulcan N 234. It is seen that the shape of the relative current dependence is completely different compared to the materials filled with Chezacarb A+.



**Fig. (4).** Changes in relative current passing through the vulcanizates of SBR filled with Vulcan N 234 carbon black 40 wt % (upper curve), 35 wt % (middle curve) and 30 wt % (lower curve) during whole deformation – relaxation – recovery cyclus, repeated twice.

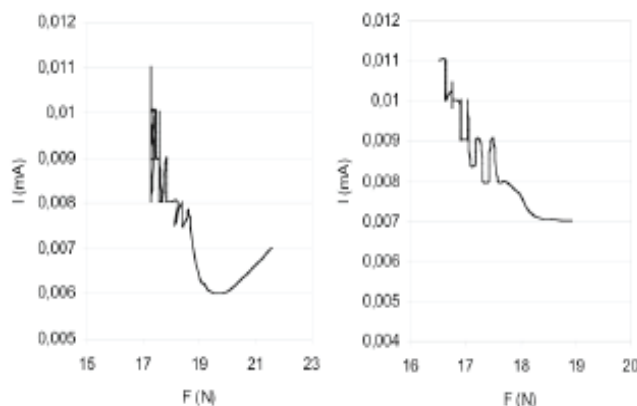
The current values, after first decrease within the strain of up to about 20 %, start to rise, reaching maximum at about 300 % of relative deformation. The value of relative current depends very much on the CB content and for the highest filler amount the current is by 50 % higher compared to the initial value before deformation. After that, the deformation drops down. This decrease continues also during the first relaxation stage. The increase during the recovery stage is rather modest, compared to the materials filled with Chezacarb. After the stress release, first, an immediate drop in relative current values occurs followed by small increase during recovery stage.

Certainly the most interesting seems to be the second run, which is completely different from both the first run of the same sample and the both runs for the Chezacarb filled vulcanizates. The current values increase from very beginning of deformation and a modest increase is observed also for the relaxation stage. The immediate current drop was observed also for the second run after releasing the stress; again the following recovery is rather modest.

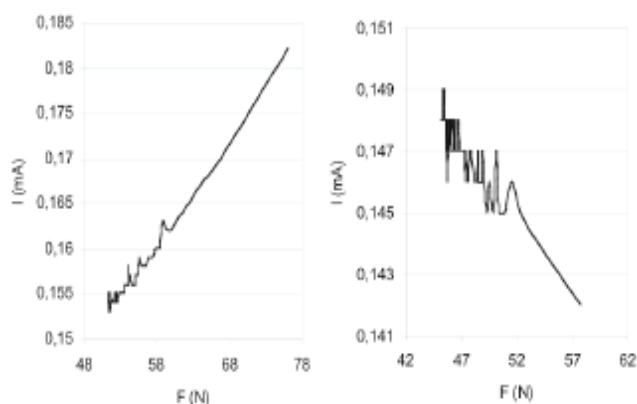
The relaxation performances of various vulcanizates can be compared in more detailed way according to Figs (5 and 6), where stress during relaxation is plotted against corresponding electrical current. It has to be realized that regarding time scale the stress always decreases, i.e. in the Figures the time scale is not always situated from the right to the left.

Only two examples are shown here; the other vulcanizates filled with the same type of CB behave similarly re-

garding the tendency and the shape as the ones plotted in Figs. (5 and 6). Of course the absolute values are different.



**Fig. (5).** The correlation between stress (F) and electrical current (I) during stress relaxation stage for the vulcanizate filled with 10 wt % of Chezacarb, first run (left), second run (right).



**Fig. (6).** The correlation between stress (F) and electrical current (I) during stress relaxation stage for the vulcanizate filled with 40 wt % of Vulcan N 234, first run (left), second run (right).

It is clearly seen that in the case of Chezacarb filled SRB an increase in the relative current values has been found for both the first as well as second run. Different behaviour was observed for Vulcan N 234 filled vulcanizates (all concentrations, as indicated above). Relaxation in the first run resulted in a decrease in conductivity, while opposite course was found for the second run.

#### 4. DISCUSSION

As said, all conductivity changes should be interpreted in terms of either formation of new conductive paths by the conductive filler particles (conductivity increase), destruction of the existing paths (decrease), or reformation of previously present but decayed conductive structures (increase). Uniaxial strain will primarily result in a decay of conductive paths. This happens for the Chezacarb filled SBR. However, different, more complex course was observed for Vulcan filled vulcanizates. First decrease up to 10 / 20 % deformation can be certainly explained by decay of part of the conductive paths, namely those which are not very strong and oriented mainly in the direction of the stress. After that phase, an increase in deformation is observed. This is suggested to occur because of a presence of many anisotropic

aggregates of CB oriented randomly. During drawing, the elastomeric chains are oriented in stress direction and force the aggregates to be oriented in the same way. Thus many new conductive paths are formed. At high enough drawing degree (about 300 % in our case) most of the aggregates are oriented and their destruction at continuing deformation is the prevailing process.

During relaxation stage generally the elastomeric chains move partially to their original more coiled shape. This generally results in reformation of previously broken paths and increase of the conductivity. The last stage, i.e. recovery results in all cases in an increase of conductivity. In this case the material returns suddenly to its original shape (small permanent deformation is neglected in these considerations). This leads to immediate break of many conductive paths and their partial reformation with time in case of Vulcan BC, while in case of much stronger Chezacarb, moreover present in much smaller amount, no extensive decay of conductive paths are expected and only their reformation, by the way in higher extent compared to Vulcan N 234, is proposed.

The difference in behavior between Chezacarb and Vulcan filled vulcanizates is explained by

1. much smaller percolation concentration of Chezacarb
2. stronger filler - filler interactions (higher filler surface, oil absorption etc.) of Chezacarb particles resulting in stronger filler structure
3. presumably smaller and less anisotropic aggregates of Chezacarb BC.

#### 5. CONCLUSIONS

The parallel measurement of electrical conductivity and mechanical stress strain curve is presented as a possible method for estimation of the structure of filler network during deformation. The differences were recorded between the SBR filled with two different grades of carbon black. The attempt to explaining the differences was done in terms of formation, destruction and reformation of conductive paths.

#### ACKNOWLEDGEMENTS

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