

# Effect Of Both Compression And Extension On The Electrical Resistivity Of NBR/EPDM Rubber Blend Filled With Different Types Of Carbon Black.

H.N.M. Alsuhaqqi, A.A. El-Gamel, S.A. Khairy, H.H. Hassan

Faculty of Science, Department of Physics, Cairo University, Giza, Egypt

**ABSTRACT:** Blend based on acrylonitrile butadiene rubber and ethylene propylene diene monomer rubber as 50NBR/50EPDM loaded with N-326(HAF) and N-774(SRF) carbon black fillers was prepared. The effect of each type of carbon black on the electrical resistivity of rubber blend was studied. The changes of the electrical resistivity of rubber blend during compression and extension were investigated. Based on the shell structure theory, the experimental results were explained from the view that external pressure induces the creation and annihilation of effective conductive paths, leading to the changes in the resistivity of blends.

**Keywords :** EPDM; compression; NBR; resistivity; sensor.

## 1 Introduction

Blending two or more polymers to produce new materials with mixed properties has been extensively developed in several industries [1]. The reinforcement of rubber properties by the incorporation of carbon black is due to the presence of active polar groups such as phenol, carboxyl, quinone and lactones on the carbon black surfaces [2- 3]. These polar groups on the carbon black surfaces interact with rubber and the interaction is higher with polar rubbers than hydrocarbon rubbers, which is due to polar- polar interaction [4]. The degree of reinforcement of the filled rubber depend mainly on the filler concentration and principal properties of carbon black such as particle size, surface area, aggregate structure and its distribution in rubber matrix as well as rubber-filler interaction [5]. Carbon black-filled conductive rubbers have wide applications, such as pressure sensitive sensors which can be used for shock proof switches [6], sensors for measurement of vehicle weights to collect toll tax on roads [7], and smart flexible sensors adapted to textile structures, able to measure their strain deformations [8], and tactile sensor that is thin and flexible and able to attach to a curved surface and will make the robot operate in unstructured environments [9, 10]. Electrical conductivity depends on amplitude of strain, the frequency of stress-strain cycles, and also the total number of stress-strain cycles, the nature of the polymer and the amount of the filler loading. At low strain due to rapid destruction of conductive path volume resistivity increases, but at higher strain the effect is marginal because the formation of a conductive network occurs in the system [11]. In addition, electrically conductive particle in polymer could produce flexible piezoelectric materials [12]. The correlation between the external pressure and the electrical resistivity of the composites has been intensively investigated [13-16]. Voet et al. [17] and Sircar et al. [18] studied the electrical resistance of carbon black filled styrene butadiene rubber at constant shear strain. The present work aims to study the effect of static pressure on the electrical resistivity of conductive blend of 50NBR/50EPDM rubber. We have also measured the changes in the electrical resistivity with time after the instantaneous static loading pressure was applied.

## 2 EXPERIMENTAL

### 2.1 Materials

Ethylene Propylene Diene Monomer (EPDM) with diene monomer content of 5 %, and Nitrile Butadiene Rubber (NBR) with nitrile content 34% have been blended together according to the recipe illustrated in Table (1). We have used two different types of carbon black namely, the High Abrasion Furnace black (HAF-LS or N-326) and the Semi Reinforcing Furnace black (SRF -HS or N-774). The physical and chemical properties of both blacks are listed in Table (2). All other ingredients such as sulfur, zinc oxide, stearic acid, dioctylphthalate and diphenyle guanidine are obtained from the commercial grades.

### 2.2 Samples preparation

All rubber compounds were mixed according to the ASTM D 3182 by using two-roll mill machine of 300 mm length, 150 mm diameter, and gear ratio 1.4. The vulcanization process was carried out by using an electrically heated platen press at  $153\pm 2$  °C and 4 MPa for 30 min.

### 2.3 Experimental techniques

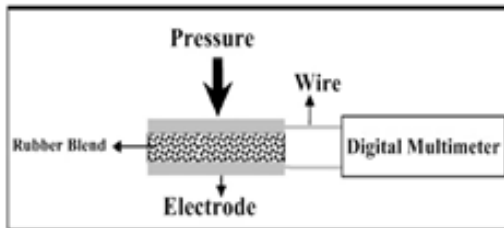
The experimental set-up for measuring the electrical resistivity of the investigated samples is shown in Fig. (1). Two iron plats were attached to the sample during the vulcanization process with good ohmic contacts and were used as electrodes. The electrical resistance was recorded by using a digital multimeter with 1% of accuracy. The electrode area is a little less than that of the sample to keep the transverse size invariant during the compression. The sample was compressed instantaneously to a certain pressure (P) by using a hydraulic press up to 10 MPa. Then the pressure was kept invariant for 1.5 hrs. blend was reinforced with different types of carbon black [100N-326, and 100N-774]. Other ingredients were used and compounded according to the recipe listed in table (1). The compounded

**TABLE (1).** THE COMPOSITIONS OF EPDM /NBR RUBBER BLENDS LOADED WITH DIFFERENT TYPES OF CARBON BLACK.

Ingredient (phr) <sup>a</sup>	Samples					
	1	2	3	4	5	6
EPDM	50	50	50	50	50	50
NBR	50	50	50	50	50	50
BR <sup>b</sup>	20	20	20	20	20	20
Stearic acid	2	2	2	2	2	2
Zinc oxide	5	5	5	5	5	5
Parafin oil	10	10	10	10	10	10
DOP <sup>c</sup>	10	10	10	10	10	10
N-326 (HAF-LS)	---	0	25	50	75	100
N-774 (SRF-LS)	---	100	75	50	25	0
MBTS <sup>d</sup>	2	2	2	2	2	2
DPC <sup>e</sup>	1	1	1	1	1	1
IPPD (4020) <sup>f</sup>	1	1	1	1	1	1
Sulfur	3	3	3	3	3	3

<sup>a</sup> Part per hundred parts of rubber by weight.  
<sup>b</sup> Butadiene Rubber  
<sup>c</sup> Dioctyle phthalate.  
<sup>d</sup> Dibenzthiazyle disulphide  
<sup>e</sup> Diphenyle Guandine  
<sup>f</sup> N-(1, 3-dimethylbutyle)-N-phenylenediamine

rubbers were molded into discs of 1 x 10<sup>-4</sup> m<sup>2</sup> area and 0.01 m in height.



**Fig. 1** Sketch of experimental set-up for measuring resistance of the rubber blend.

**TABLE 2**

PHYSICAL AND CHEMICAL PROPERTIES OF THE DIFFERENT TYPES OF BLACK USED [19].

Properties	HAF-LS	SRF-HS
ASTMD Designation code no.	N-326	N-774
Particle size (nm)	29	70
Surface area (m <sup>2</sup> /g)	80	28
Oil absorption cc.g	1.17	0.67
Roughness factor	0.73	0.74
PH value	7	9
Volatile content (%)	1.50	0.50
Ash (%)	0.30	0.30
Benzene extractable (%)	0.05	0.05

LS.: Low Structure, and HS: High Structure.

**TABLE 3**

THE ELECTRICAL RESISTIVITY OF THE NBR/EPDM BLENDS WITH 100 N-326, AND 100N-774 CARBON BLACKS.

NBR/EPDM rubber blends	carbon black	Resistivity(Ω.cm)
50NBR/50EPDM	100N-774	6.15E+05
	100N-326	3.18E+03

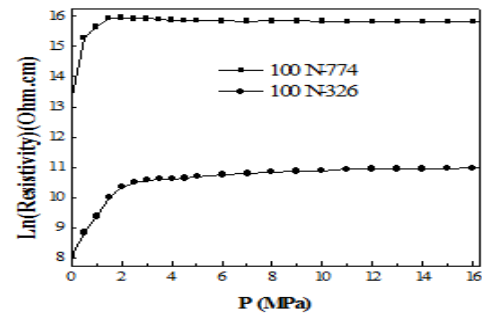
### 3 RESULTS AND DISCUSSION

#### 3.1 Electrical resistivity.

The electrical resistivity of 100N-326 carbon black filled 50NBR/50EPDM is higher than the 100 100n-774 filled the same blend. This can be attributed to the difference in size of aggregation of carbon black particles. The carbon black which has smaller aggregation can be dispersed more finely and the fine dispersion of carbon black aggregation leads to high electrical resistivity, the N-774 has smaller size of aggregation (smaller surface area) of particles than N-326, bringing about higher electrical resistivity for the blend with carbon black N-774 [20].

#### 3.2 Effect of compression on Resistivity

To analyze the changes in the electrical resistivity of (50NBR/50EPDM) rubber blend several variables are defined;  $\rho_i(o-)$  which represents the electrical resistivity of the rubber blend before the compression process.  $\rho_i(o+)$  represents the electrical resistivity at the moment immediately after the compression.  $\Delta\rho_i$  represents the instantaneous increment of the resistivity at the moment immediately after the sample loaded from 0 MPa to pressure P, and it can be expressed by  $\Delta\rho_i = \rho_i(o+) - \rho_i(o-)$ .



**Fig. 2** The Ln(Resistivity) Versus P for 50NBR/50EPDM filled with two different typrs of carbon blacks.

The experimental phenomena can be explained and described by analyzing the changes in the conductive network of the rubber blend as follows. It was pointed out that, the blend is a three dimensional conductive network composed of rubber macromolecule and carbon black [21]. The electrical resistivity of the blend is decided by the changes in the conductive car-

bon black network. When the gap between carbon black particles is small enough, the tunneling effect occurs, inducing the formation of local conductive path (LCP). If LCP penetrates insulating matrix, an effective conductive path (ECP) is formed, thus contributing to the conductivity of the blend, the external pressure changes ECP, leading to the changes in the resistivity of the blend. During the process of instantaneous compression the conductive network is changed by the movement of the polymer segments and the changes in the uniaxial size of the blend, leading to the change in the electrical resistivity of the blend. The electrical resistivity of carbon black is far less than that of the rubber; therefore, the electrical resistivity of the blend loaded with carbon black is decided by the electrical resistivity of the insulating films between adjacent conductive particles, which are related to the changes in ECPs under the compression process. Fig. 2 depicts the  $\ln(\text{resistivity})$  as a function of compression,  $P$ . One notices that the effect of compression on the resistivity predominates up to certain  $P$ , after that the resistivity becomes compression independent. This may be attributed to the fact that two phenomena occur in the system during compression: breakdown of the existing conductive network and formation of a new one. At low compression the breakdown process is more prominent compared to the formation process and the net result is a reduction in the number of conductive networks. At higher compression, when the strain is high, some carbon black rearrangements also take place leading to the formation of new conductive networks. Thus at high compression the formation and breakdown of conductive networks balance each other, resulting in marginal change in the resistivity against compression [22].

### 3.3 Effect of compression on the time dependence of electrical resistivity

Fig. (3:a,b) shows the time dependence of the electrical resistivities of the (50NBR/50EPDM) rubber blend loaded with different ratios of carbon black filler (100N-774), and (100N-326), respectively after loading with different static pressure values;  $P = 5 \text{ MPa}$ ,  $10 \text{ MPa}$ , and  $15 \text{ MPa}$ . The electrical resistivities of the rubber blend increases instantaneously at the moment immediately after the sample is loaded from  $0 \text{ MPa}$  to a certain pressure  $P$ . After which the electrical resistivity decreases exponentially with time under the constant pressure  $P$ . It is noticed that, as the compressive pressure  $P$  increases the electrical resistivity increases. The instantaneous increment of the electrical resistivity  $\Delta\rho_i$ , increases or (decreases) with the increase of the instantaneous loading pressure for the blend loaded with 100 N-326 or (100N-774) as shown in Fig. (4). As shown in Fig. (3:a-b), the electrical resistivity increases instantaneously when the sample is compressed. This experimental phenomenon indicates that the breakdown process is more prominent compared to the formation process and the net result is a reduction in the number of conductive networks.

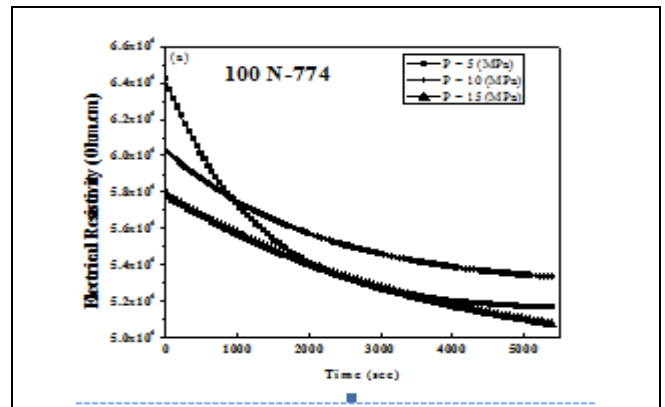


Fig. 3:a The electrical resistivities versus time for the rubber blend (50NBR/50EPDM) with 100N-774 carbon black at different

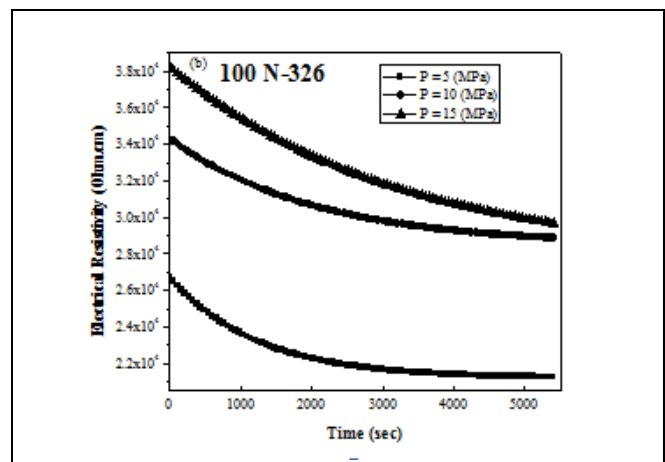


Fig. 3:b The electrical resistivities versus time for the rubber blend (50NBR/50EPDM) with 100N-326 carbon black at different compression pressure 5 MPa, 10 MPa, and 15 MPa.

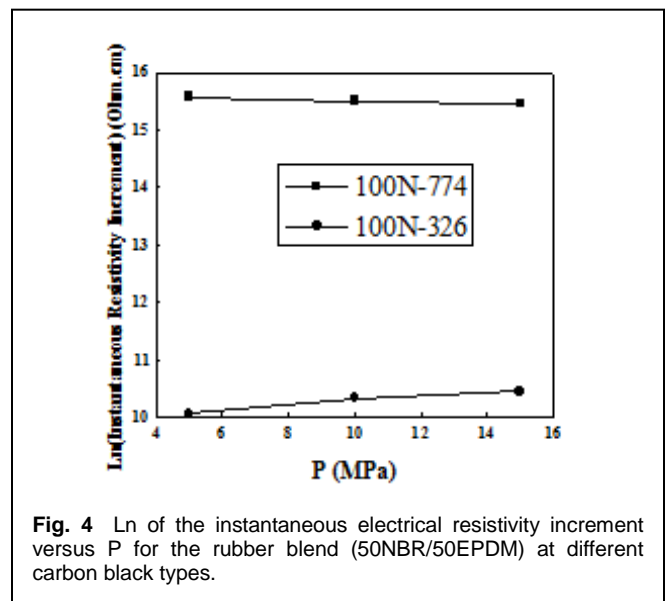


Fig. 4  $\ln$  of the instantaneous electrical resistivity increment versus  $P$  for the rubber blend (50NBR/50EPDM) at different carbon black types.

It is noticed also that, the electrical resistivity decreases with time after the rubber blend is loaded. This result indicates that

some carbon black rearrangements also take place leading to the formation of new conductive networks. The conductive network gets more and more unstable with time under the constant pressure. As shown in Fig. (4), the instantaneous increment of the resistivity increases or (decreases) with the increase of the instantaneous pressure. This result indicates that the extent of the changes in the conductive network increases or (decreases) with the increase of the instantaneous loading pressure.

### 3.4 Effect of extension on the time dependence of electrical resistivity

As seen from figures (5:a,b) the electrical resistivity of the strained sample suffers an abrupt increase at  $t = 0$ , followed by a gradual decrease with time to reach its equilibrium (steady) value  $\rho_0$ , after sufficiently long time. Such  $\rho(t)$  dependence might be interpreted in terms of the stress-relaxation theory of polymer. The conductive sample may be represented by the three-element mechanical model consisting of spring S1 in parallel with a non-Newtonian Maxwell unit with spring S2. In this model S1 represents the rubber chains, while the S2Maxwell unit represents the carbon black particles in the viscous rubber matrix. When the strain is suddenly applied, the dashpot starts to slip under the effect the applied stress and two springs are extended, which means an uncoiling of the rubber chains, and thus the sample acquires its maximum strain. This results in an increase in the average distance between carbon particles or even temporal breakdown of the carbon black structure, with explain the abrupt increase of  $\rho$  at the moment the strain is applied. After straining is stopped instantaneously, stress relaxation at constant strain begins. Because of the extension is kept constant during stress-relaxation, the elongation of the spring S1 is also constant, consequently the stress acts on it remains unchanged. As the dashpot slips, the stress acting on spring S2 decreases. The time-dependent flow, which occurs in the Maxwell unit, decreases the total stress in function of time.

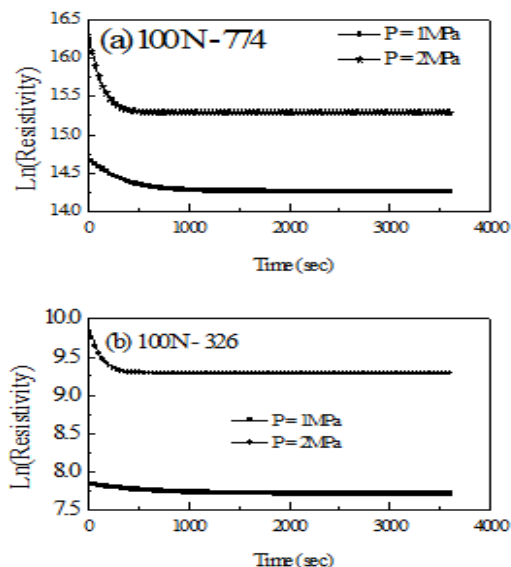


Fig. 5:a,b The time dependence of Ln(Resistivity) for (50NBR/50EPDM) with different types of carbon black at different values of extension  $P = 1$ , and  $2$  MPa.

## 4 CONCLUSION

The electrical resistivity of 100N-326 filled 50NBR/50EPDM is lower than the electrical resistivity of 100N-774 filled the same blend owing to its small particle size. The electrical resistivity of the pressure sensitive rubber blend (50NBR/50EPDM) filled with different types of carbon blacks increases suddenly when compressed and then decreases with time. The same behavior was observed in the case of extension. The instantaneous increment of the resistivity, increases for 100N-326 filled the blend with the increase of the instantaneous pressure, and decreases for the 100N-774 filled the blend with the increase of the instantaneous pressure. The electrical phenomena aforementioned are caused by the changes in the effective conductive paths.

## References

- [1] T. M. Nair, M. G. Kumaran, and G. Unnikrishnan 2004. *J. Appl. Polym. Sci.*, 93: 2606.
- [2] S. Wolff, M.J. Wang, E.H. Tan, 1994. *Kautsch. Gummi Kunstst*, 47: 780-798.
- [3] S. Wolff, M.J. Wang, E.H. Tan, 1993. *Rubber Chemistry and Technology*, 66: 163-177.
- [4] G. Kraus, 1978. *Rubber Chemistry and Technology*, 51: 297-321.
- [5] F. El-Tantawy, N. Dishovsky, 2004. *Journal of Applied Polymer Science*, 91: 2756-2770.
- [6] L. Krupa, I. Novak, I. Chodak, 2004. *Synthetic Metals*, 145: 245-252.
- [7] R. H. Norman, 1970. *Conductive rubber and plastics*. Elsevier, London.
- [8] C. Cochrane, V. Koncar, M. Lewandowski, C. Dufour, 2007. *Sensors*, 7: 473-492.
- [9] M. Shimojo, A. Namiki, M. Ishikawa, R. Makino, K. Mabuchi, 2004. *IEEE Sensors Journal*, 4: 589-596.
- [10] M. Inaba, Y. Hoshino, K. Nagasaka, T. Ninomiya, S. Kagami, H. Inoue, 1996. 'Proceedings of the IEEE/RSJ International Conference of Intelligent Robots and Systems, Dayton, USA' Vol. 2: 450-457.
- [11] K.P.Sau, T.K.Shaki, D. Khastgir, 1998. *Composite Part A*, 29:363.
- [12] N. Hu, Y. Karube, C. Yan, Z. Masuda, and H. Fukunaga, 2008. *Acta. Mater.*, 56: 2929.
- [13] X. Wang, and D.L. Chung, 1998. *Compos.*, 29B: 63.
- [14] J. N. Aneli, G.E. Zaikov, and L.M. Khananashvili, 1999. *J. Appl. Polym. Sci.*, 74: 601.
- [15] X. S. Wen, Y. C. Xu, and X.S. Yi, 2004. National Defense Industry Press, Beijing.
- [16] X. L. Tao, Y. Pan, and Q. Zheng, 2001. *J. Appl. Polym. Sci.*, 79: 2258.

- [17] A Voet, F.R. Cook, and A.K. Sircar, 1971 Rubber Chem. Technol., 44: 175.
- [18] K. Sircar, A. Voet, and F.R. Cook, 1971. Rubber Chem. Technol., 44: 185.
- [19] M. Blow, 1971. "Rubber Technology and Manufacture", Institute of Rubber Industry, London.
- [20] N. Ando, M. Takeuchi, 1998. Thin Solid Films, 334: 182.
- [21] L..H.Wang, T.H. Ding, and P. Wang, 2009. Carbon, 47: 3151.
- [22] A M. Y. El-Lawindy, W.E.. Mahmoud, and H..H..Hassan, 2003. Egypt. J. Sol., 26: 43