JOURNAL OF APPLIED POLYMER SCIENCE VOL. VI, ISSUE NO. 24, PAGES 651-655 (1962)

Internal Field Emission in Carbon Black-Loaded Natural Rubber Vulcanizates

L. K. H. VAN BEEK

Central Laboratory T.N.O., Delft, Holland

and

B. I. C. F. VAN PUL*

Rubber Research Institute T.N.O., Delft, Holland

INTRODUCTION

The specific resistance of rubber vulcanizates varies between 10 and 10^{15} ohm-cm., depending on the presence of filler and, especially, on the type of filler. Silica and silicate-type fillers hardly influence the resistivity of natural rubber vulcanizates, but carbon black causes an increase in conductivity. How far the conductivity increases depends on the type and quantity of carbon black incorporated. The resistivities of filled rubbers are further influenced by factors such as vulcanization time, milling procedure and, consequently, dispersion of the filler, temperature history, and stress history. A discussion of these influences has been given in a review by Norman.[1]

In this paper we are chiefly interested in the current-voltage characteristics of filled rubbers. Samples were prepared which contained the same amounts of carbon black and had been subjected to the same vulcanization and milling procedure. They differed in type and dispersion of carbon black. Two types of carbon black were studied: furnace black (high-abrasion furnace black, HAF) and thermal black (medium thermal black, MT). Three different dispersions of HAF black were investigated. In vulcanizates 1A, 1B, and 1C the dispersions were good, moderate, and poor, respectively. Although the nonohmic behavior of filled rubbers is known, no interpretation has been given in the literature. It will be shown in this paper that there exists a correlation between the carbon black distribution and the current-voltage characteristics.

* Present address: Ozone Research Equipment Corporation, 3840 North 40th Avenue, Phoenix, Arizona.

PREPARATION OF SAMPLES

The compositions of the samples are given in Table I. The mixes were vulcanized at 142°C. in slabs approximately 2 mm. in thickness during the time required to reach optimal mechanical properties.

TABLE I
Composition of Samples, in parts by weight

	Sample 1 (HAF)	Sample 2 (MT)
International ribbed smoked sheet I	100	100
ZnO	5	5
Stearic acid	3	3
Sulfur	2.25	2.25
N-Cyclohexyl-2-benzothiazyl-sulfenamide	0.6	0.6
Carbon black HAF	40	—
Carbon black MT	—	40

As mentioned in the introduction, three different HAF dispersions were prepared. An idea of these dispersions may be obtained from Figures 1 and 2. The electron micrographs were taken from slices cut from samples 1A and 1C with an ultramicrotome.

CURRENT-VOLTAGE CHARACTERISTICS

Since the resistivities of the samples turned out to differ very much, two methods had to be used for measuring the current as a function of applied voltage. Sample 1A, which had the lowest resistivity, was placed in a sample holder (General Radio No. 1690-A) and the current through the sample

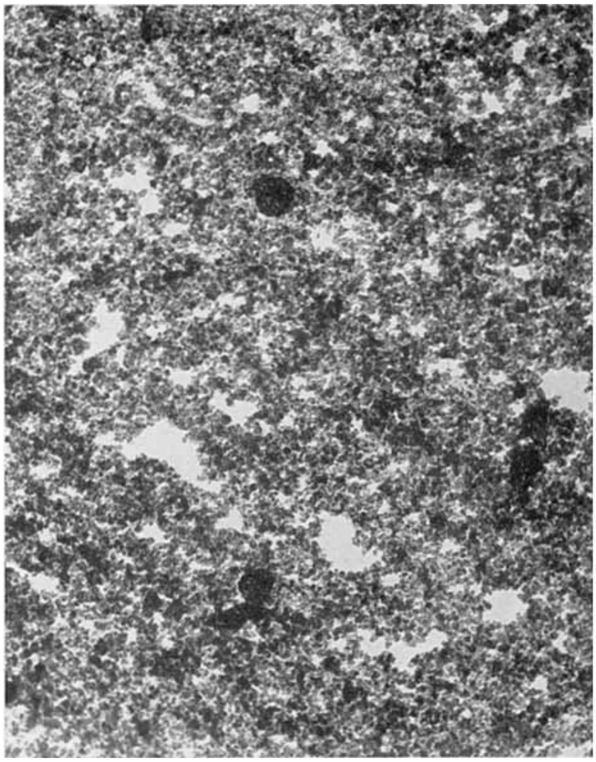

Fig. 1. Electron micrograph of a slice cut from sample 1A. Good HAF dispersion. Thickness of slice about 1200 A. (according to Dr. H. Sitte). 18,000×.

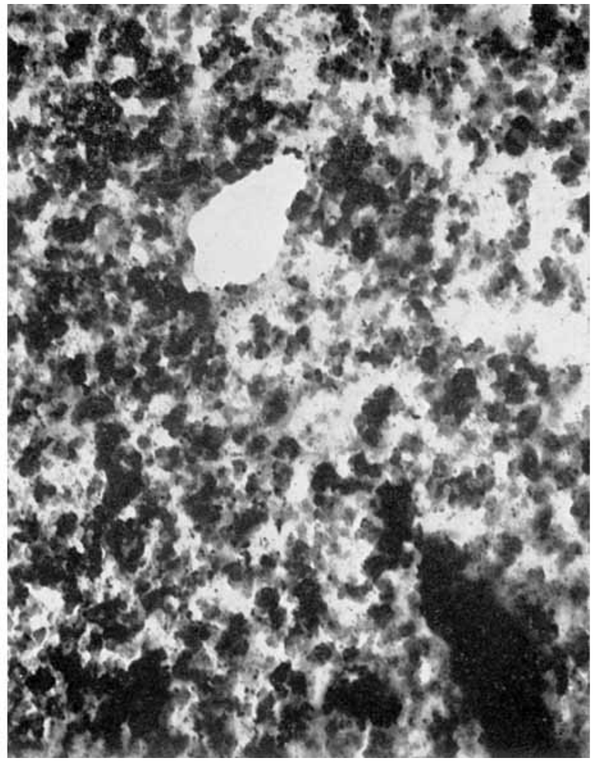

Fig. 2. Electron micrograph of a slice cut from sample 1C. Poor HAF dispersion. Slice thickness same as in Fig. 1. 19,000×.

was measured with a microammeter (Hewlett-Packard). For the other samples the voltage/current ratios were determined with a megatrometer (Mid-Eastern Electronics, Model 710). Contact resistances were reduced to a minimum by coating the faces of a sample with colloidal graphite (aquadag). Although, as Norman[1] has pointed out, coating with aquadag is in itself not adequate to avoid contact resistances, our samples cut from the slabs were found to have very high surface conductance. This conductive surface ensured good contact with the electrodes, as was confirmed by the fact that all samples showed ohmic behavior at low voltages (< 25 v. for samples 1C and 2, < 3 v. for samples 1A and 1B). The samples had diameters of about 2 cm. and they were about 0.2 cm. thick. The following values of V/i ratios give an idea of the resistivities:

Sample no.	V/i
1A	8×10^3 (25 v.)
1B	2×10^6 (25 v.)
1C	7×10^{11} (25 v.)
2	4×10^{14} (500 v.)

Although all samples contained the same percentage of carbon black, their resistivities differed very much. In order to understand these differences it is useful to consider some basic properties of carbon black and the way in which it is distributed in the rubber vulcanizates.

Carbon black has high conductivity, although not as high as graphite. It consists of spherical particles in which submicrocrystals of graphite are orientated at random. Thus the x-ray pattern is diffuse. In a good dispersion of HAF black the particles are found not to be randomly distributed but to be arranged in long chains. This type of chain formation is called "structure." Evidence of the existence of structure in carbon black was obtained by the oil-absorption method.[2,3] Structure may also be present in rubber vulcanizates, as can be demonstrated by the 300% modulus and sometimes by the tear strength (Delft method). A direct confirmation of the existence of structure in sample 1A is provided by the electron micrograph of Figure 3. On the other hand, hardly any structure is found in the poor HAF dispersion of sample 1C (Fig. 2). Here separate clusters of carbon black are imbedded in the rubber medium.

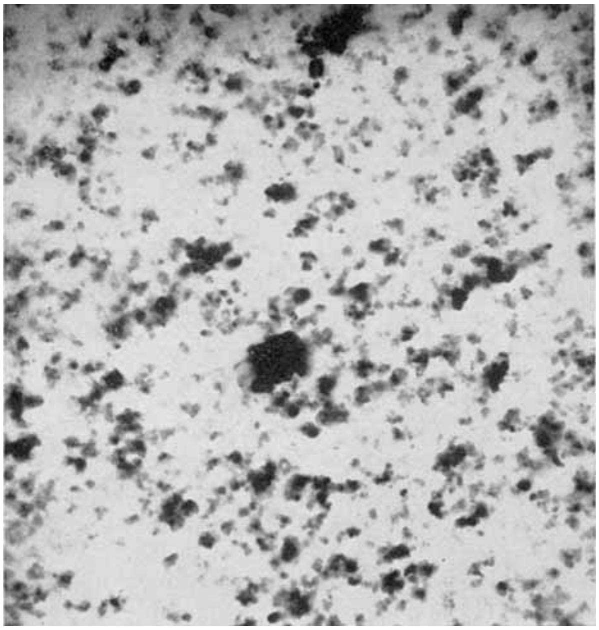

Fig. 3. Electron micrograph of a very thin (about 800 A.) slice cut from sample 1A. 11,500×. Good HAF dispersion. The square-edged crystal is ZnO.

Sample 1B takes an intermediate position. These observations explain the differences in the resistivities found.

The existence of long conducting chains in sample 1A is responsible for its low resistivity. The absence of long-range structure in sample 1C causes a very high resistance. That the occurrence of structure also depends on the type of carbon black is demonstrated by sample 2 which contains MT black in good dispersion. Fig. 4 shows that this type of black does not give rise to structure. The particles are separately imbedded in the rubber medium. The complete absence of any structure causes an extremely high resistance.

As a consequence of the presence of conducting particles in an insulator, local discontinuities in field strength are to be expected. In narrow insulating gaps between conducting areas of carbon black, very high field strengths may develop. This led to the assumption that internal field emission might explain the nonohmic behavior of black-loaded rubber vulcanizates.

Internal field emission is a general term describing a number of processes which have in common that electrons have a finite probability of crossing forbidden zones. A special case of internal field emission is the tunnel effect. Tunnelling occurs when two conductors are separated by a narrow insulating gap. Such a system seems to be very much the same as that observed in the electron micrographs of Figures 2 and 4. Since the theories on internal field emission strictly apply to crystal lattices only, there is no need to give a detailed description. A review of these theories was recently given by Chynoweth.[4] He points out that all theories have in common that the emission current is described by an expression of the form:

$$i = AV^n \exp\{-B/V\} \quad (1)$$

A, B, and n are constants; n usually lies between 1 and 3. A is a function of the tunnelling frequency, i.e., the number of attempts to penetrate the gap per second. The factor $\exp\{-B/V\}$ represents the transition probability or barrier transparency. It follows that the transition probability increases when the voltage is raised.

In order to study the applicability of eq. (1) to rubber samples, the constant A was evaluated from the experimental data. This enabled us to plot $V \log (i/A)$ against $V \log V$. An example is given in Figure 5. This may be compared with the nonohmic i-V characteristic shown in Figure 6. It is seen from Figure 5 that a straight line is obtained above a certain limiting voltage. These voltages, together with the constants in eq. (1), are summarized in Table II.

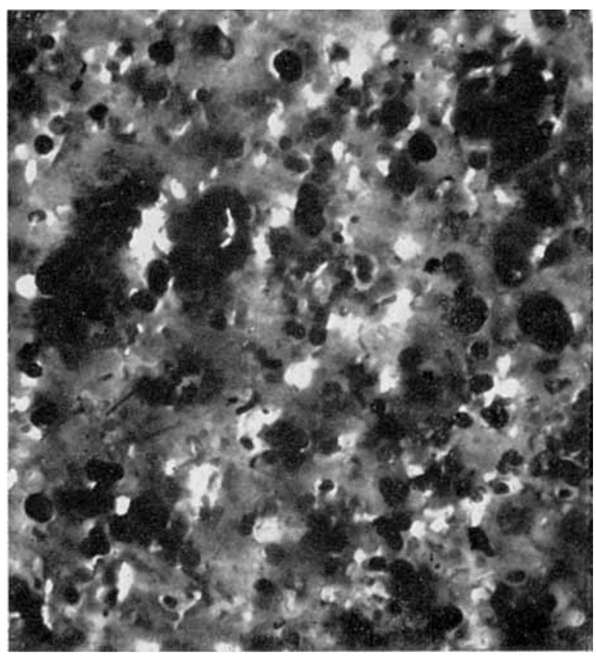

Fig. 4. Electron micrographs of a slice cut from sample 2. Good MT dispersion. Thickness of slice about 8000 A. 5,100×.

TABLE II
Values of A, B, and n from eq. (1) and Limiting Voltages

Sample no.	Temp., °C.	A	B, v.	n	Limiting voltage, v.
1A	20	6.3×10^{-5}	−0.6	1.73	?
1B	40	10^{-8}	2.5	1.93	15
1C	20	8×10^{-11}	290	2.10	200
2	20	2.8×10^{-14}	130	1.54	250

The measurements of samples 1A, 1C, and 2 were carried out at room temperature. Sample 1B showed no tunnel effect at 20°C., but tunnelling appeared to set in at 15 v. at 40°C. The effect of temperature on the observed behavior is the subject of further studies and will, for this reason, not be discussed in this paper.

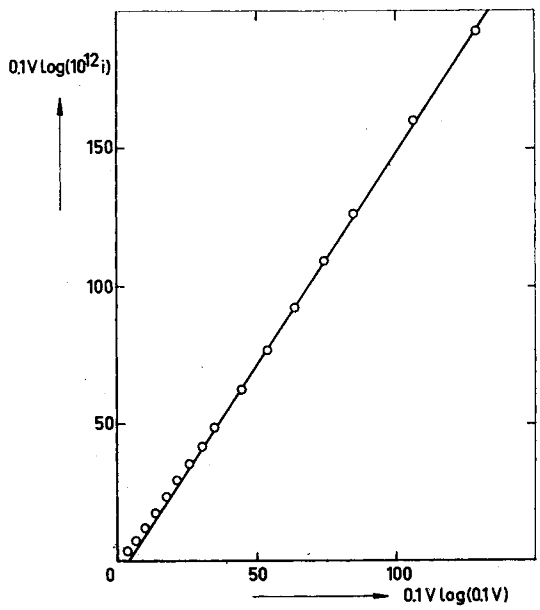

Fig. 5. Dependence of $V \log (i/A)$ upon $V \log V$ for sample 2, according to internal field emission theory.

It follows from Table II that sample 1C and 2 obey eq. (1) above a limiting voltage of 200 and 250 v. respectively. According to Chynoweth,[4] internal field emission becomes important when the field strength across a gap is about 10^6 v./cm. This would correspond to gap widths of 2 and 2.5 μ for samples 1C and 2. It is seen from the electron micrographs that these widths are of the right order of magnitude and also that the width for 1C is larger than that for sample 2. In the case of sample 1B the much smaller limiting voltage is

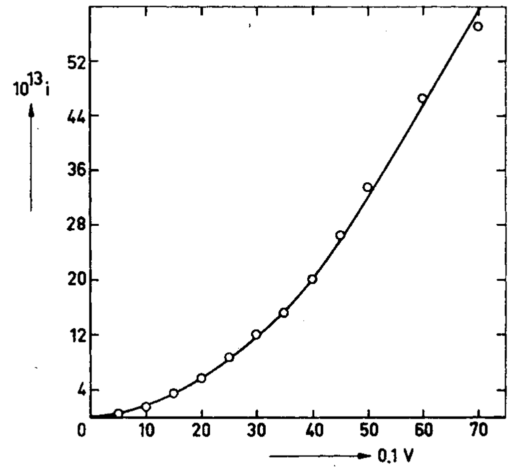

Fig. 6. Current-voltage characteristic for sample 2, showing nonohmic behavior.

acceptable, because the gaps are much narrower owing to better dispersion of the filler.

Sample 1A had a negative B value and this should mean that the barrier transparency would decrease when the voltage were raised. This is a very improbable situation and it must be concluded that internal field emission was negligible. Calculation of B from the experimental data showed that B was not constant in the voltage range studied, but decreased slowly from about +1 to −1. Because the resistivity of sample 1A is low, accurate measurements could be made only in the 1–10-v. range. The possibility that tunnelling would occur above 10 volts may not be excluded.

For practical purposes it would be extremely useful to have a method for describing the degree of dispersion. There is an indication in Table II that the degree of dispersion can be described in terms of the constants n and B. Especially n proved to be a very reproducible quantity.

We wish to thank Mr. H. J. van der Vossen (Central Laboratory T.N.O.) for resistance measurements and Mr. W. Adriaansen (Rubber Research Institute, T.N.O.) for cutting slices with the ultramicrotome.

References

1. Norman, R. H., *Conductive Rubber*, Maclaren, London, 1957.
2. Schweitzer, C. W., *Proc. I.R.I.*, **2**, 77 (1955).
3. *Cabot Carbon Blacks under the Electron Microscope*, 2nd ed., Ed. Cabot Corp.
4. Chynoweth, A. G., *Progr. in Semi-conductors*, **4**, 95 (1960).

Synopsis

The nonohmic behavior of carbon black-loaded natural rubber vulcanizates was studied. Three samples contained high-abrasion furnace black (HAF) in good, moderate, and poor dispersion. Another sample contained a good dispersion of medium thermal black (MT). The nonohmic behavior of the poor HAF dispersion and that of the MT dispersion could be interpreted as due to internal field emission across insulating gap widths of 2 and 2.5 μ. The existence of such gaps was confirmed by electron micrographs. No clear evidence of internal field emission could be obtained for the good and moderate HAF dispersions where, according to electron micrographs, the gaps are much narrower. There is some indication that the degree of dispersion can be correlated with field emission characteristics.

Résumé

Nous avons étudié la déviation à la loi d'Ohm du noir animal contenu dans le caoutchouc naturel vulcanisé. Trois échantillons contenaient du noir animal résistant à haute température (HAF) avec une dispersion bonne, moyenne et mauvaise. Un autre échantillon contenait une bonne dispersion de noir à résistance thermique moyenne (MT). La déviation à la loi d'Ohm de la dispersion (MT) pourrait être due à l'émission d'un champ interne a travers un intervalle d'isolement large de 2 à 2.5 μ. L'existence d'une tell lacune a été confirmée par micrographie électronique. Aucune évidence certaine de l'émission du champ interne n'a pu être obtenue dans les dispersions HAF bonne et moyenne, où en accord avec les micrographies électroniques, les lacunes sont beaucoup plus rapprochées. Certaines indications montrent que le degré de dispersion peut être relié aux caractéristiques de l'émission du champ.

Zusammenfassung

Es wurde das nicht-ohmsche Verhalten von russgefüllten Naturkautschukvulkanisaten untersucht. Drei Proben enthielten hoch reibungsbeständigen Ofenruss (HAF) in guter, mässiger und schlechter Dispersion. Eine andere Probe enthielt eine gute Dispersion von mittlerem thermischen Russ (MT). Das nicht-ohmsche Verhalten der schlechten HAF-Dispersion und der MT-Dispersion konnte durch eine innere Feldemission über isolierende Spaltweiten von 2 und 2,5 μ erklärt werden. Das Bestehen solcher Spalten wurde durch elektronenmikroskopische Aufnahmen sichergestellt. Keine eindeutige Bestätigung für die innere Feldmission konnte bei guten und mässigen HAF-Dispersionen erhalten werden, wo die Spalten nach der elektronenmikroskopischen Aufnahme viel enger sind. Es weist einiges darauf hin, dass der Dispersionsgrad in Korrelation zur Feldemissionscharakteristik steht.

Received July 25, 1961