Reversible Electrical Behavior with Strain for a Carbon Black-Filled Rubber

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ABSTRACT: Most unfilled elastomers exhibit a high electrical resistance. Fillers are usually added to elastomers to enhance their mechanical properties. Frequently the filler type used is an electrically conductive carbon black and the inclusion of such fillers reduces the resistivity of the elastomer compound. Previous work has shown that for elastomers containing high abrasion furnace, carbon black fillers such as N330 (or N300 series) at a volume fraction above the percolation threshold the resistivity changes with strain, the precise resistivity versus strain behavior being nonlinear and irreversible for conventional carbon black fillers. A strain-measuring device, deriving strain directly from a measure of the resistivity, requires that the behavior be reversible and reproducible from cycle to cycle. This work presents the electrical resistivity behavior of a natural rubber (NR) compound filled with Printex XE2 carbon black. This type of filler has a significantly different morphology to the N300 series blacks examined previously. The Printex was incorporated into the rubber at a volume fraction above its percolation threshold and its behavior is contrasted to that observed with N300 series carbon black-filled NR. Here, and for the first time, reversible electrical resistivity dependence with strain is reported for an elastomer filled with Printex XE2. This reversible behavior under strain opens up the possibility of applications, such as a flexible load sensor, pressure sensor, or switch. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 541–546, 2010

Key words: rubber; carbon black; filler; resistivity; modulus

INTRODUCTION

Most unfilled elastomers exhibit a high electrical resistivity. The fillers most commonly used in the rubber industry are carbon blacks. These fillers are usually added to elastomers to enhance their mechanical properties, such as strength[1] and abrasion resistance,[2] or to increase the modulus[3] or mechanical damping properties. Changes in the functional properties of a rubber, such as the electrical or thermal conductivity, because of the incorporation of different fillers have been the topic of extensive research in the past.[4–10] Also, filled elastomers show responses to external stimuli, such as temperature and pressure.[11–15] Yamaguchi et al.[16] showed that for elastomers containing N330 carbon black fillers at a volume fraction above the percolation threshold the resistivity changed with strain. The precise resistivity versus strain behavior was nonlinear and irreversible during the initial loading and then subsequent unloading. To develop a strain-measuring device, which monitors the strain directly from a measure of the resistivity requires that the behavior be reversible and reproducible from cycle to cycle. One possible way to achieve this was discovered by Busfield et al.,[17] whereby a modest swelling of the filler and rubber network with a suitable solvent resulted in a much more reversible resistivity behavior with strain. This work investigated if reversible resistivity versus strain behavior can be achieved without swelling. To do this, a different carbon black filler, Printex XE2 supplied by Evonik Degussa GmbH was compounded into rubber at a volume fraction above the percolation threshold, using the formulation shown in Table I, to investigate its electrical and mechanical behavior under repeated straining.

THE STRUCTURE OF CARBON BLACK FILLERS

Carbon black fillers are made from the partial combustion of hydrocarbons in a controlled atmosphere. The smallest individual building block is defined as a particle. Clusters of particles fuse together to form primary aggregates and these aggregates flocculate together to form larger secondary aggregates. A typical primary aggregate of Printex XE2 is shown in Figure 1(a). The aggregates are held together by Van

TABLE I
Compound Formulations Used in this Study

Ingredient	Unfilled	N330	Printex XE2
NR	100	100	100
Carbon black		50	10
zinc oxide	5	5	5
Stearic acid	2	3	2
MBTS[a]		0.6	
Anti-ozone wax	1.5		1.5
6PPD[b]	1.5		1.5
TBBS[c]	1.5		1.5
Sulphur	1.5	2.5	1.5
Volume fraction of carbon black Φ		21%	5.2%

[a] MBTS: 2,2-dibenzothiazyl disulphide.
[b] 6-PPD N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine.
[c] TBBS N-tert-butyl-2-benzothiazolesulfenamide.

der Waals forces. The detailed morphology of carbon black structure reflects the surface area per unit mass of these filler aggregates. Fillers comprised of smaller primary particles or that form complex shapes are considered to be high structured fillers and typically exhibit increased interaction with the rubber. The different shapes and morphologies for carbon black fillers are defined in ASTM D1765.[18] In the Standard, the definition of each of the different grades of carbon black, such as N330 used here, is given. ASTM D-2414[19] describes the dibutyl-phthalate oil absorption test, which measures the amount of dibutyl-phthalate absorbed on 100 g of carbon black. The resulting dibutyl-phthalate absorption (DBPA)number is used to characterize the filler structure. This test indicates the internal void volume present in both the primary and secondary aggregate structures. Another carbon black characterisation technique ASTM D-3037[20] determines the

nitrogen surface area (NSA) by measuring the volume of nitrogen adsorbed on the filler surface. The Brunauer, Emmett, and Teller[21] model for multilayer adsorption is then used to calculate filler surface.

The average sizes measured using both the DBPA and NSA tests on the fillers used in this study are listed in Table II. Despite the particles and the aggregates being of comparable size, the surface area of the Printex is significantly greater than that of the N330 carbon black. This difference in the measured structure has been attributed by Evonik, the distributor of Printex XE2, to result from differences in the manufacturing process. Printex XE2 is made using a controlled partial oxidation of heavy oil, known as a gasification process, whereas N330 is made by oxidation of oil in a furnace. Evonik suggested that the morphology of Printex XE2 is essentially aggregates of several hollowed-out dish-shaped primary particles. The TEM image shown in Figure 1(b) shows some evidence of this. This results in a dramatic increase in the surface area to volume ratio for this type of filler and will probably increase the amount of trapped rubber held within the filler cavities.

THE EFFECT OF FILLER MORPHOLOGY ON ELECTRICAL RESISTIVITY

Typical elastomers are electrical insulators and carbon black fillers are conductive. There is a volume fraction of fillers, called the percolation threshold, which must be exceeded in order for the composite network to be conductive.[23,24] Probst's[25] data, shown in Figure 2, demonstrates that resistivity varies with volume fraction for a wide range of different carbon black fillers compounded into high-density polyethylene. As the structure and surface area of the filler increase, then the percolation threshold shifts to a lower filler volume fraction. Clearly, the precise size,
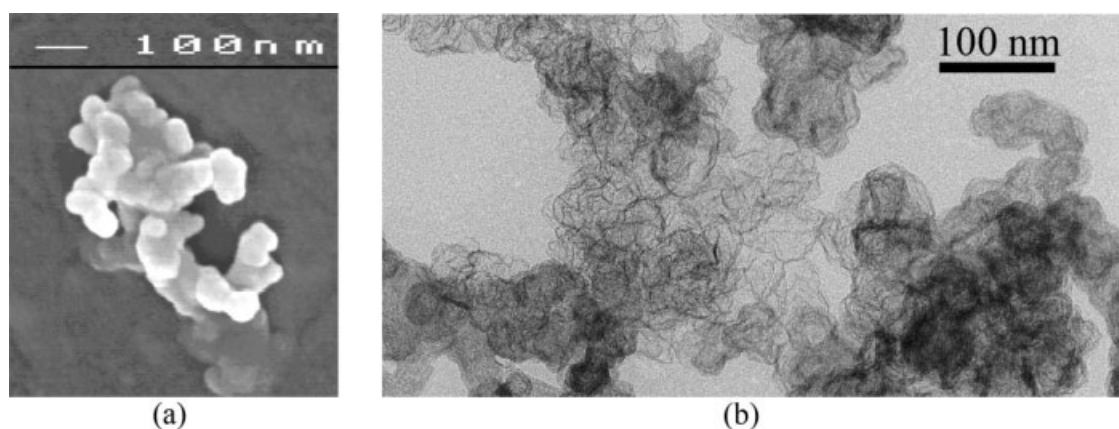

Figure 1 (a) Carbon black aggregate of Printex XE2, taken using a scanning electron microscopy technique, with a single particle highlighted by the small circle. (b) Carbon black aggregate of Printex XE2 taken using a transmission electron microscope (TEM), used to highlight the hollowed out shell-like structure.

TABLE II
Size and Structure of the Two Carbon Blacks Used in this Study

	N330	Printex
Mean primary aggregate size (nm)	105[22]	100
Mean carbon black particle (nm)	32[22]	30[22]
Surface area/NSA[a]/m^2/gm	82[22]	600[22]
Oil absorption number/DBPA[b] (cc/100 g)	102[22]	370[22]

[a] NSA: (ASTM D 3037-88): nitrogen surface area.
[b] DBPA: (ASTM 2414): dibutyl phthalate absorption.

surface area, volume fraction, structure, and porosity of the filler aggregates all affect both the mechanical and the electrical properties of the filled rubber composite.

The effect of carbon black structure on the resistivity of the filled elastomer was studied by Janzen,[26] who proposed that the number of contact points between the filler aggregates determined the electrical conductivity. A higher DBPA reflected a higher filler structure and a lower percolation threshold. This effect is shown schematically in Figure 2 for the extreme types of filler. Janzen[26] derived the following equation

$$\phi_{crit} = 1/(1 + 4\rho_{CB}DBPA) \quad (1)$$

where ϕ_{crit} is the critical volume fraction at the percolation threshold and ρ_{CB} the bulk density of the carbon black. Therefore, the percolation threshold or the critical weight fraction is inversely related to DBPA.

Carbon blacks with a higher structure act as reinforcing fillers,[27] at the very least as a result of the increase in the volume of rubber close to a filler–rubber interface. Carbon black fillers with a smaller surface area and hence a lower structure interact to a
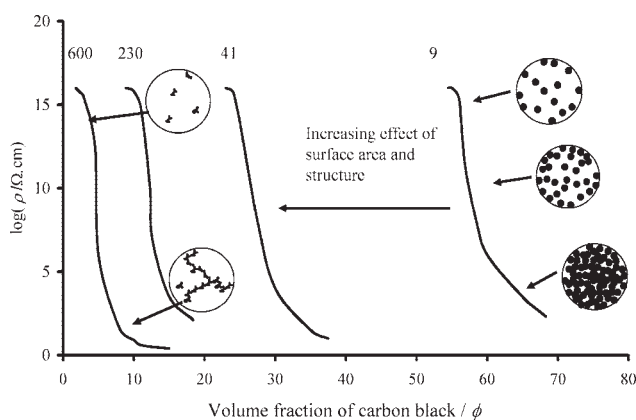
lesser extent with the polymer and modify the mechanical and electrical properties less.[28]

EXPERIMENTAL METHOD

Formulations for the different elastomer compounds used in this investigation are given in Table I. The matrix rubber used was natural rubber (NR). The amount of carbon black incorporated being sufficient to ensure that the compound was conductive in the unstrained state. For the tensile tests, the mix was cured into approximately 1-mm thick sheets at 160°C for 15 min, the process temperature and time having been identified using a rheometer to ensure that a complete cure cycle was attained. Once cured, the test samples were carefully removed without being strained and cooled to room temperature.

The measurements of the electrical resistivity in tension were performed using a rectangular test piece. The standard size adopted for each specimen was 80 × 25 × 1 mm. The electrical resistivity was measured using a four-point contact method shown in Figure 3 to eliminate the effect of contact resistance. The current was measured in series with the circuit. The voltage was measured between the two central contact points and it was ensured that only a
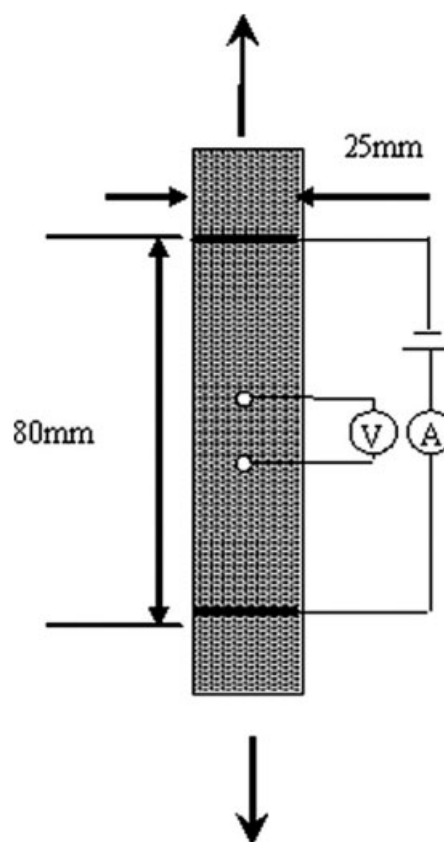

Figure 2 Electrical resistivity versus volume fraction for a range of different carbon blacks in high-density polyethylene (Probst, 1984). The numbers given indicate the nitrogen surface area (m^2/g) for the different fillers.

Figure 3 A schematic showing the four-point contact method used to measure electrical resistivity under strain.
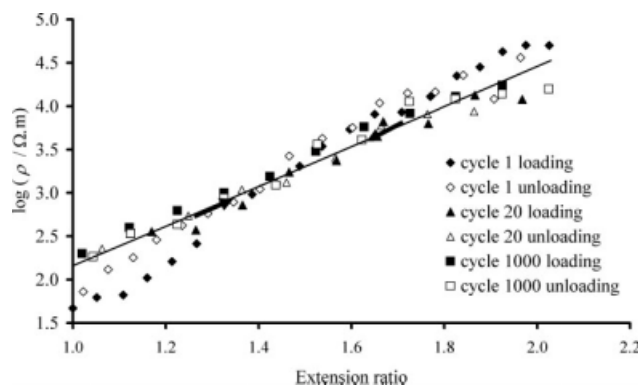
Figure 4 Electrical resistivity versus extension ratio data for Printex filled NR at a filler volume fraction of 5.2% under cyclic tensile strains.

tiny current passed through this path. Each resistance measurement was made in the range of 5–30 Volts. The electrical contacts were spring-loaded brass clamps. The current flow through the specimen was measured using an Hewlett Packard 34401A ammeter. The voltage was measured using an ALTAI HC-779 Voltmeter. Samples were generally extended in a screw-driven tensile test machine in discrete steps, initially of 1 mm at an average strain rate of 0.02/min (up to a strain of 0.1), 2 mm at an average strain rate of 0.04/min (for strains from 0.1 to 0.25) and 10 mm at an average strain rate of 0.2/min (for strains above 0.25). All readings were made within 10 s of each elongation step to standardize the effect of stress relaxation. The resistance of the carbon black filled elastomer R can be determined from Ohm's law

$$R = V/I_e \qquad (2)$$

where V is the potential difference measured between the two probes of brass, which are the contact points, and I_e the current flowing through the carbon black-filled elastomer. From this, the electrical resistivity ρ can be calculated as

$$\rho = RA/l \qquad (3)$$

where A is the instantaneous cross-sectional area, equal to A_0/λ, where A_0 is the initial cross-sectional area and λ the tensile extension ratio in the test piece, measured using a video capture system, and l the distance between the measuring points on the brass probes. A linear voltage versus current plot indicated that over the voltage and strain ranges used, both compounds exhibited Ohmic behavior.

RESULTS AND DISCUSSION

Figure 4 shows how the electrical resistivity for Printex XE2 changed under repeated straining up to an extension ratio of 2. At only 10 weight parts per

hundred rubber (which is equivalent to a volume fraction of 5.2%), the filled elastomer conducted well in the unstrained state. Clearly, for this filler, the percolation threshold was at a volume fraction below 5.2%. This reduction in the percolation threshold with geometric shape factor of the filler was anticipated following Probst[25] (Fig. 2).

The initial loading cycle was somewhat unique. However, and for the first time, beyond the first cycle, all subsequent loading cycles were indistinguishable. In addition, the difference between the first cycle and the subsequent ones were only modest. The resistance increased monotonically with strain and recovered to somewhat more than the original value after the strain was removed. During the first loading cycle, the resistivity increased by 3 orders of magnitude at an extension ratio of 2. This was similar to the behavior described by Zhang et al.[13] for a polyurethane elastomer filled with carbon nanotubes. This behavior was contrasted with the electrical behavior of a N330 black-filled elastomer under strain, which had previously been investigated by Yamaguchi et al.[16] and Busfield et al.[17] and was repeated here. Figure 5 shows for the N330 filler in its virgin first cycle that the resistivity increased up to an extension ratio of 1.2. This initial increase in resistivity has been attributed[16] to the breakdown of the agglomerate structure in the rubber, which was thought to result in a net reduction in the number of conduction paths made through the sample. When the applied tensile strain increased above this strain, the change in resistivity with strain reached a plateau. This had been attributed to result from the orientation effects of filler under strain and also the effect of the reformation of some conduction paths. The orientation effects were presumed to result from shaped particles aligning in the direction of the principle strain. When the load was removed, the resistivity did not return to its
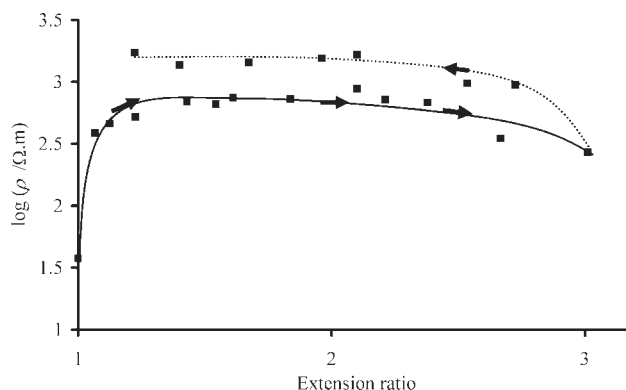

Figure 5 Electrical resistivity versus extension ratio data for the first strain cycle for N330 black at a filler volume fraction of 21%.

original value but increased yet further. This indicated that a permanent breakdown of filler agglomerate structure had occurred.

Figure 6 shows the stress versus extension ratio data for the N330 filled rubber. Printex had a similar unstrained resistivity to the N330 filler at a fifth of the volume fraction. This contrasts with the increase in the stiffness compared with the unfilled NR, which was higher for the N330 carbon black. The hysteresis was also lower for the Printex XE2 filler compared with the N330 carbon black. This suggests a higher surface area per unit mass for Printex XE2 creates a large trapped volume of rubber that is unable to move, which is mostly enclosed in a conducting carbon black shell. This results in the small volume of Printex XE2 having a more dramatic effect on the electrical properties than on the mechanical. The TEM in Figure 1(b) suggests that the individual particles are hollowed out "bowl-shaped" shells. This filler morphology will result in a large volume of rubber becoming entrapped inside the hollowed out shell. The effective filler volume fraction is, therefore, much larger than the simple volume of filler added.

The resistivity behavior of Printex XE2 was virtually reversible with strain, suggesting that the filler network was not permanently altered under strain. The reversibility in resistivity probably resulted from the high structure and surface area of the carbon black and indicates that after the first cycle there is only limited further breakdown in filler aggregate structure under cyclic loading. This might arise because the surface area of the filler had increased with the effect of increasing the surface attraction to the rubber to the extent that the rubber could hardly slide over the surface of the filler under strain. Therefore, the weak van der Waals forces that hold the filler network structure might be able to reform
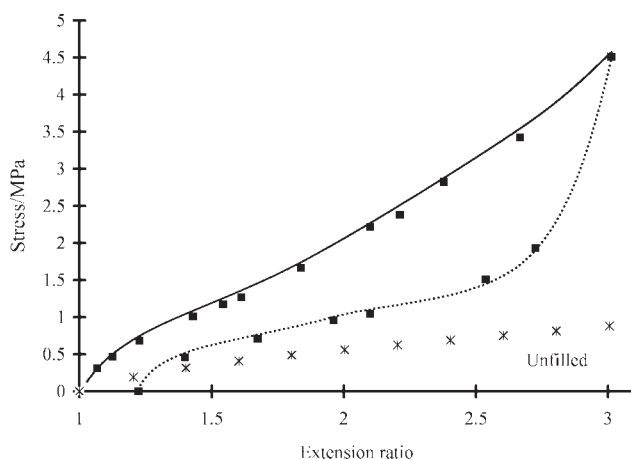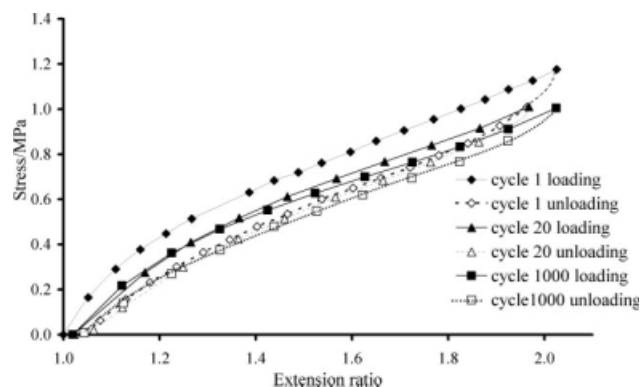

Figure 7 Cyclic tensile stress versus extension ratio data for Printex-filled NR at a filler volume fraction of 5.2%.

each time that the rubber was relaxed. Figure 7 shows the stress versus extension ratio behavior for the Printex XE2 filled elastomer. At a relatively modest volume fraction of just 5.2%, Printex XE2 has the dramatic effect of doubling the stiffness of the initial loading curve compared with an unfilled material with a broadly similar cross-link density.

The reversibility in the electrical resistivity behavior of Printex XE2 is a significant finding because it suggests that devices can be made that will be able to reliably measure forces and strains from the changes to the electrical resistivity. This might allow a whole new generation of smart rubber devices to be developed.

CONCLUSIONS

The contrasting behavior of Printex XE2 filled NR with the N330 carbon black-filled NR materials indicates that filler properties, such as surface area and structure, have a significant effect on the resistivity behavior of an elastomer under a tensile strain, both in the first loading cycle and then under repeated loading.

Printex has a very high surface area and structure. The TEM in Figure 1(b) suggests that the individual particles are hollowed out ''bowl shaped'' shells. This filler morphology will result in a large volume of rubber becoming entrapped inside the hollowed out shell. The effective filler volume fraction is, therefore, much larger than the simple volume of filler added. This results in a very low percolation threshold at a filler volume fraction below 5.2%. It is thought that the significant increase in the area of the filler rubber interface results in a more reversible behavior in the electrical and mechanical behavior under strain. This reversible behavior of Printex XE2 under strain has potential application in a wide range of smart rubber strain measuring devices, whereby the changes in electrical properties can be

Figure 6 Stress versus extension ratio data for the first strain cycle for N330 at a filler volume fraction of 21%.

easily related to changes in the strain seen in the elastomer. The reversible nature also suggests that only limited slippage occurs at the rubber filler interface in the case of the Printex XE2 filler.

The N330 carbon black has behavior consistent with that described by Yamaguchi et al.[16] The irreversible change in electrical resistivity behavior under strain also supports the theory that under repeated cyclic deformation, the filler particles rearrange themselves within the elastomer matrix.

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