

ELECTRICAL CONDUCTIVITY IN RUBBER DOUBLE NETWORKS*

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INTRODUCTION

The electrical conductivity of carbon-black-rubber composites is augmented by promotion of interaggregate contacts. Conventionally this is achieved by employing high concentrations of high-structure filler and by using porous "conductive" blacks^{1,2}. There is an obvious trade-off in this regard with respect to processibility and mechanical properties. Enhanced electrical conductivity has also been realized in rubber blends by means of a nonuniform distribution of the carbon black³⁻⁵.

It is known that deformation, while initially reducing the electrical conductivity of carbon-black-reinforced rubber, induces at higher strains an enormous increase in the conductivity of many filled elastomers⁶⁻¹². Tensile strains of less than 50% can be sufficient to bring about an order of magnitude enhancement. The orientation of a flexible-chain polymer can be made thermodynamically stable by incorporation of a double-network structure; that is, an elastomer is crosslinked a second time while deformed, effecting permanent orientation¹³⁻¹⁹. Although the influence of this inherent orientation is modest at equilibrium, the behavior is very sensitive to further deformation²⁰. Since inherent strains well beyond the level necessary for amplification of the electrical conductivity can routinely be achieved with a double network, such rubbers might provide enhanced electrical conductivity.

The various factors influencing the electrical conductivity of SBR containing N339 carbon black will be described. The intention of this study was to assess the utility of a double-network structure in obtaining enhanced conductivity.

EXPERIMENTAL

The rubber formulation, comprised of a commercial masterbatch (Carbomix 1848 from the Copolymer Rubber and Chemical Corporation) with added curatives, is given in Table I. Mixing was done on a two-roll mill, with continual rotation of the feed in order to minimize grain in the milled sheet. The carbon-black-agglomerate dispersion, measured by surface analysis using a profilometer, typically exceeded 98%. Initial curing was carried out for 12 min at 155°C under pressure.

Test specimens were 152 mm in length, 12.5 mm wide, and 1 to 2 mm thick. Resistivities were measured *via* leads glued 90 mm apart onto the tensile specimens, the ends of the latter coated with graphite to minimize contact resistance. An Instron 1135 with an MTS environmental chamber was used for the deformation experiments. When heating was required, the environmental chamber was flushed with nitrogen for 30 min after sample installation, with continuous purging thereafter. The heating rate was typically 4°C per min, with the subsequent cooling at 2.6°C per min on average. Elongation of the test samples (initial gauge length = 128 mm) was carried out at 50 mm/min and retraction at 5.0 mm/min unless noted otherwise. Double networks were obtained by executing a second cure cycle while the elastomer was held stretched in the Instron. An unstrained sample was always cured simultaneously to provide a control.

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TABLE I
RUBBER FORMULATION

SBR ^a	100
N339 ^a	82.5
Aromatic oil ^a	62.5
Varox DCP-R peroxide ^b	2.6
Agerite Resin D antioxidant ^b	0.5

^a Carbomix 1848 (Copolymer Rubber and Chemical Corp.).

^b R. T. Vanderbilt Co.

RESULTS

The procedure used to form a double network involves stretching of the filled elastomer, maintaining this extended state while the temperature is elevated to effect a second curing, and finally cooling and retraction of the specimen. The interest herein is in the relationship between the inherent orientation of a double-network rubber and electrical conductivity. The latter, however, is also influenced directly by various processing steps (*i.e.*, extension, stress relaxation, cyclical heating, curing, and retraction); these effects are now considered in turn.

EXTENSION AND STRESS RELAXATION

In Figure 1 are representative data showing the changes in electrical resistivity when the cured SBR compound described in Table I is stretched to double its length. The origin of the decrease is not well established. It has been speculated^{6,7,10-12} that a maximum in the

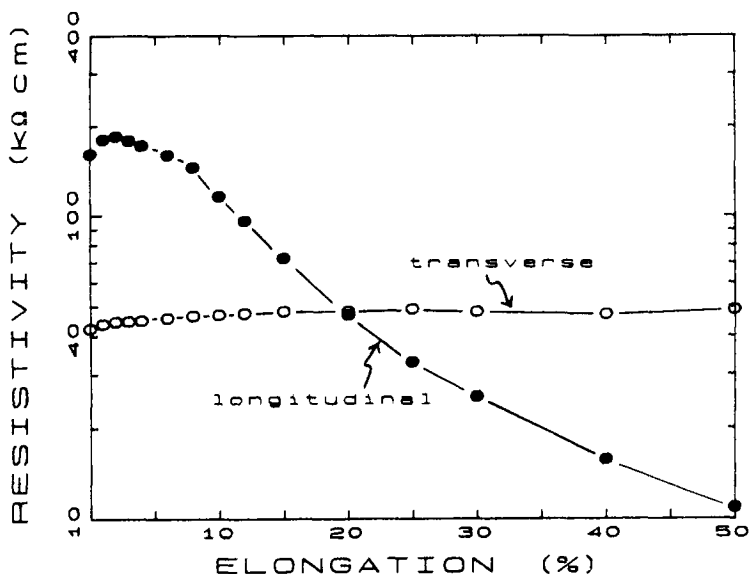


FIG. 1.—The effect of uniaxial extension on the electrical resistivity of the SBR compound containing 82.5 phr of N339 carbon black. Enhancement of the conductivity occurs primarily along the direction of the stretching. The transverse response varied with prior processing history, perhaps being dependent on the initial anisotropy of the filler phase.

resistance *versus* strain relation reflects realignment of carbon-black chains following their breakdown. This rationale does not necessarily account for resistivities greater than the initial (zero strain) level. Nevertheless, the only explanation advanced for the strain enhancement of electrical conductivity remains that of orientation of the aggregates^{6,7,10-12}. It is not obvious that an anisotropic arrangement of the anisometric, irregularly shaped carbon-black aggregates would increase their mutual contacting relative to the isotropic condition. Presumably, the motion of the aggregates during extension contributes to aggregate contacting in so far as such motion enables the formation of more extensive van der Waals bonding among the filler particles. The rubber deformation thus may serve the same role as Brownian motion does in promoting aggregate recontacting and reduced electrical resistivity during annealing at high temperature of previously deformed samples^{1,6,9}. In the absence of a driving force for carbon-black flocculation, orientation probably would not decrease the electrical resistivity, since orientation *per se* may not effect greater particle contacting. However plausible the concept that stress orients the carbon black phase^{6,7,10-12}, explicit information concerning this is scarce. Direct observation in electron micrographs of filler orientation was reported²¹, although the persuasiveness of these results has been questioned²².

Unlike resistivity along the stretch direction, the transverse resistivity is seen in Figure 1 to be relatively independent of strain. This result contradicts previous work indicating that for high-structure blacks (such as the N339 used herein), the transverse electrical resistivity will decrease with elongation^{6,11}. This discrepancy may be related to the initial degree of anisotropy of the filler, arising, for example, from processing. The transverse behavior was less reproducible from batch to batch, perhaps reflecting variations in the milling of the rubber.

In Figure 2, a comparison is shown between the electrical behavior of the filled SBR when deformed at two different rates. Of course, a faster rate engenders higher stresses, and this apparently results in more extensive breakup of the filler floc (*viz.*, in Figure 2 the more pronounced maximum in resistivity at 4% elongation)⁹. The conductivity enhancement,

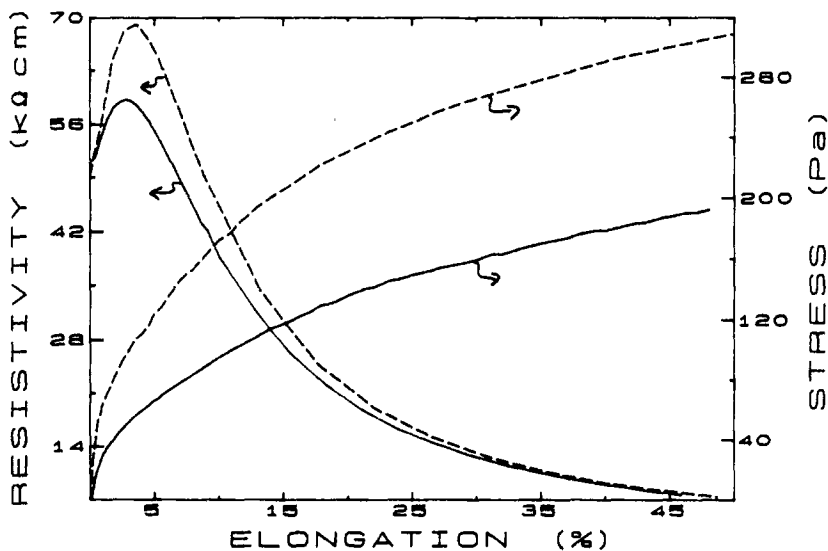


Fig. 2.—The effect of stretching the SBR rubber at nominal elongation rates of 0.033 min^{-1} (—) and 0.33 min^{-1} (---). The higher stresses associated with the higher deformation rate causes an increase in the maximum resistivity seen at low strains; however, the conductivity enhancement occurring at higher elongation is surprisingly unaffected by strain rate. The differences between these data and the results in Figure 1 are due to batch-to-batch variations of the rubber.

however, is seen in Figure 2 to be relatively independent of the stress. The transient orientation of the polymer chains is higher at higher strain rates, yet this does not promote greater orientation of the filler phase (at least to the extent it is reflected by the conductivity). This result may be due to competition between destruction and reformation of the filler contacts.

At low strains where the electrical resistivity increases upon deformation, under constant stress the resistivity can increase, decrease, or remain constant with time²³. The behavior during the constant-stress period has been correlated with the change in resistance upon removal of the stress²³.

At the higher strains at which the resistivity is diminished, different behavior might be expected. If the decrease is due to filler orientation, relaxation of the polymer chains after cessation of the deformation should cause the resistivity to rise. In Figure 3 is shown the change in resistivity with time after stretching the SBR to various strains. These data illustrate the presence of two competing mechanisms, both transpiring during stress relaxation. At low strains where breakup of the floc is dominant, reformation during the constant-strain period reduces the resistivity. At higher elongations, sufficient for a decreased resistivity, stress relaxation of the rubber effects an increased resistivity, which may be ascribed to a reduction in the filler orientation. The aggregate interaction brought about by orientation of the polymer chains (*via* a putative alignment of the carbon black) diminishes as the chain orientation relaxes. It is interesting, however, that a slower rate of deformation did not engender higher resistivity at high strains (Figure 2).

The largest changes in resistivity during stress relaxation never exceeded about 200%, whereas stretching decreases the resistivity more than a factor of five (Figures 1 and 2). Hence, notwithstanding the decline in electrical conductivity during stress relaxation, its strain enhancement remains substantially greater than the initial conductivity of the unstrained sample. This is a useful result in relation to the utility of double networks.

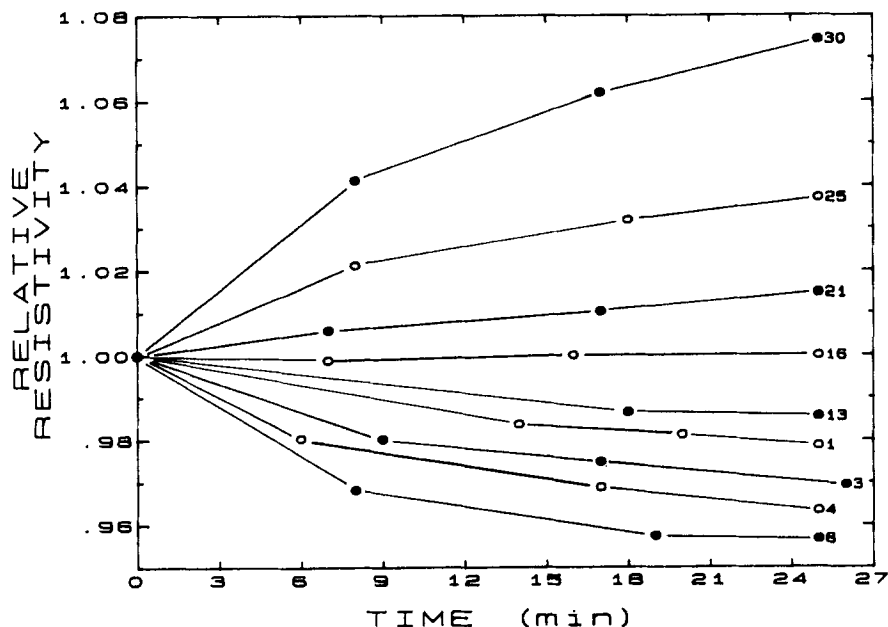


FIG. 3.—Changes in the resistivity (normalized by the zero-time values) measured after imposition of tensile strains of various magnitudes (as indicated at the right side of each curve) on the SBR cured once. At the lower elongations associated with resistivity increases, the resistivity declines upon relaxation. At higher strains, which induce resistivity decreases, relaxation causes an increase in resistivity as a constant strain is maintained.

TEMPERATURE

The principal mechanism for electron transport in rubber containing carbon black in concentrations beyond the percolation threshold is quantum mechanical tunneling across or thermally activated hopping over the insulating polymer medium^{24,26}. The barrier to the tunneling is reduced by thermal fluctuations (*cf.* Johnson noise), conferring a temperature dependence to the conductivity^{24,25}. In competition with this thermal activation is thermal expansion of the tunneling gaps between the filler aggregates. These competing effects can give rise to a maximum in the electrical response *versus* temperature relation⁸. Interestingly, maxima have been reported in the temperature dependence of both the conductivity^{25,26} and the resistivity²⁷⁻²⁹. Some of these differences are related to the filler concentration^{30,31} or to the presence of crystallinity in the rubbers exhibiting the resistivity maxima³².

Displayed in Figure 4 is the electrical resistivity of the carbon-black-reinforced SBR measured one week after mixing on a two-roll mill. As the temperature is increased, there is a modest increase in resistivity, followed at roughly 80°C by a marked decrease. Lowest resistivity is obtained at the highest temperature utilized (*circa* 150°C). When the sample is held at high temperature, there is some continued reduction in resistivity (about 40% over several hours time). Similar behavior is exhibited by samples taken from the same milled sheet, but subjected to one hour of molding under pressure at room temperature prior to the electrical measurements (see Figure 4). These results are consistent with previous findings that, with exception of extremes in molding pressures³³, the electrical conductivity is insensitive to molding⁸. Most interestingly, the low resistivity attained *via* heating in both cases is retained almost unchanged upon cooling back to room temperature; moreover, the resistivity remains nearly invariant to further thermal cycling. After the initial heating, the resistivity changed less than 30% over the temperature range from 30° to 150°C when measurements were carried out within several hours of the initial heating.

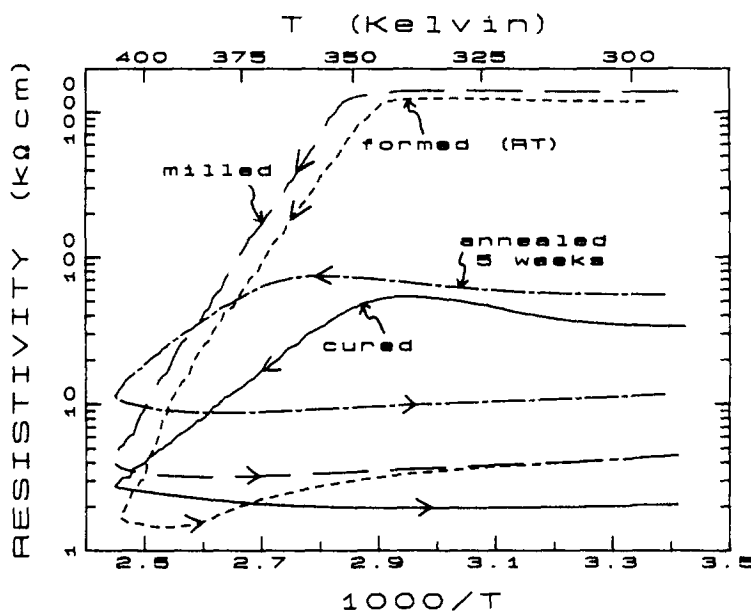


FIG. 4.—The effect of heating followed by a cooling cycle (designated respectively by arrows) on the resistivity of the filled SBR one week after milling. Curing (12 min at 155°C) induces some loss of resistivity, after which the behavior is similar to that exhibited by the samples that had not been previously exposed to heat. After the initial heating, the resistivity is relatively insensitive to further temperature cycling. The resistivity over this temperature range remains essentially equal to that measured during the cooling cycle. The subsequent temperature dependence of the resistivity after 5 weeks annealing at room temperature is shown. Some sensitivity to temperature has been recovered.

The irreversibility of the behavior seen in Figure 4 implies that the temperature dependence is not due to thermal activation of electron transport, nor is thermal expansion of the tunneling gaps of prime significance. As reflected in the increase in low-strain dynamic modulus with inverse temperature³⁴⁻³⁸, the interaggregate contacts proliferate as the temperature is reduced, and this enhancement of the filler contacting can contribute to the temperature dependence of the electrical conductivity. However, the effect of heating on conductivity observed herein does not reflect such an equilibration in the concentration of particle contacts. As described by equilibrium models³⁶, such accretion in carbon-black flocculation would be reversible.

It has been reported that heating carbon-black-filled rubber after mill mixing produces a large reduction in electrical resistivity^{6,33}. Milling disrupts the carbon-black floc, with subsequent heating evidently facilitating its recovery. The flocculated structure is destroyed mechanically whenever the applied stresses overcome the van der Waals forces responsible for mutual bonding of the particles. This confers a strain dependence to the mechanical properties³⁸⁻⁴². The strain amplitude at which the dynamic modulus indicates filler-phase disruption is not very sensitive to temperature, suggesting that the conditions necessary for breakup of the carbon-black floc are essentially independent of the mechanical response of the polymeric phase^{38,41,42}. However, if disruption of the filler phase has transpired, the ensuing recovery is affected by temperature. The processing (both mixing and forming) of filled rubber, as well as dimensional changes associated with thermal cycling during vulcanization, may disturb the flocculate structure. A portion of the resistivity decrease in Figure 4 is certainly due to reformation of the carbon-black contacts disrupted by the processing.

Note that if the rubber is cured (actually it was determined that it only needs to be subjected to high temperature) during molding, the initial plateau seen in the resistivity at temperatures lower than 80°C is lower in magnitude (Figure 4). Interestingly, the cured rubber still exhibits a significant temperature dependence through the first heating, even though the cure time was comparable to the thermal-cycle time. Similarly to the previously unheated compounds, it was found that the resistivity of the cured rubbers, after they have been heated once while suspended in the Instron, were unaffected by further temperature changes.

For all processing histories (milled, milled and formed at room temperature, or milled then formed at high temperature), long-term annealing restores a temperature dependence to the electrical resistivity, albeit of somewhat lesser degree than originally. Results are shown in Figure 4 for the cured sample after 5 weeks annealing at room temperature. Since the enhanced conductivity achieved by heating is reduced by aging, it is evident that not all of the original temperature dependencies in Figure 4 can be attributed to accelerated recovery of the carbon-black floc. The minimum that has been reported in the resistivity with temperature after RT aging of milled rubber⁴³ was not observed herein.

RETRACTION

Although the electrical conductivity increases when a filled rubber is sufficiently stretched, the conductivity enhancement is not stable. When the rubber returns to an unstressed condition, the conductivity decreases⁶⁻⁹. In fact, as seen in the data in Tables II and III, after retraction, the filled rubber exhibits significantly greater electrical resistivity than the initial level. Although some of the resistivity gain is lost over time, the resistivity after a large extension remains significantly greater than originally, even after annealing at room temperature for over one month. This result implies that, not only is the aggregate interaction promoted by high strains reversible, there occurs a concomitant permanent destruction of the filler structure. The irreversible changes in resistivity effected by large deformation have been ascribed to breaking of "strong reticulate carbon-black aggregates"⁹, but no direct evidence for this exists. The recoverable portion of the conductivity reflects losses due to debonding of the interaggregate contacts. Note that the results in Tables II and III were

TABLE II
EFFECT OF RETRACTION ON ELECTRICAL RESISTIVITY

Elongation, %	Longitudinal resistivity		Transverse resistivity		Resistivity anisotropy
	k Ω -cm	Relative	k Ω -cm	Relative	
0	37.0	1.	105.9	1.	0.35
100 ^a	1.9	0.05	8.5	0.08	0.22
0 ^a	515.2	14.	561.9	5.3	0.92
0 ^b	222.9	6.0	173.3	1.6	1.29

^a Initially upon elongation or retraction.

^b 112 hours after retraction.

obtained at elongations for which the conductivity is enhanced; the strain is well below the level associated with a precipitous drop in conductivity. This latter effect is related to fracture of polymer chains adhered to the carbon black¹¹. Obviously, any deleterious effects on conductivity of high elongation and retraction will be detrimental to the use of double networks to achieve enhanced electrical conductivity.

From Table III it is noted that relaxation in the strained state is associated with resistivity increases, while the resistivity decreases during relaxation after retraction. These results are consistent with the data in Figure 3 described above. Processing of filled rubber often imparts an anisotropy to the mechanical response. This grain is also manifested in directional electrical properties. As illustrated in Table II, significant resistivity anisotropy was observed, even though the rubber had been rotated ninety degrees prior to each pass through the two-roll mill. Uniaxial extension to 100% elongation magnifies this anisotropy, presumably due to further orientation of the filler phase. The effect of strain on transverse electrical resistivity was not reproducible, perhaps being dependent on the initial degree of this grain. Interestingly, retraction of the filled rubber removes much of the original anisotropy (Table II).

DOUBLE NETWORKS

The formation of a double network involves several steps which directly affect the electrical properties of filled rubber. Mixing, and to a lesser extent, forming of the rubber lower the conductivity. Heating (Figure 4) and extension (Figures 1 and 2) elevate the conductivity, while relaxation (Figure 3) and retraction (Table II and III) cause a reduction. Of interest

TABLE III
EFFECT OF RETRACTION ON ELECTRICAL RESISTIVITY

Time, min	Elongation, %	Longitudinal resistivity	
		k Ω -cm	Relative
0	0	33.8	1.
11	50	4.3	0.13
2795	50	8.3	0.25
2799	0	>770	>22
3050	0	630.5	19.
8525	0	261.5	7.7

herein is the net result of this combination of processes. As shown in Tables II and III and in agreement with earlier literature⁹, a tensile-retraction cycle confers permanently lower conductivity, notwithstanding the highly conductive intermediate state attained during extension. This suggests that a double network will enable improved conductivity only if the residual (permanent) strain produced is sufficient to induce a conductivity enhancement large enough to overcome the loss due to the tensile retraction.

To create the double network, cured rubber was elongated and then heated to a temperature (155°C) sufficient for further curing. An unstrained specimen was cured simultaneously to provide a control. The resistivity during the second curing was similar to the data shown in Figure 4; however, the stretched rubbers exhibited maxima in their resistivity at temperatures 10 degrees higher. This shifting of the maximum due to extension has been seen previously²⁰.

Second curing of the stretched elastomer results in a permanent set (unrecoverable strain), the magnitude of which scales with the degree of elongation during the second cure (Figure 5). The slope of the curve in Figure 5 depends primarily on the relative crosslink concentrations of the first and second networks¹⁸⁻²⁰, these were maintained constant herein. Similar to rubbers with single networks, the electrical conductivity is diminished by retraction. Higher extension is known to effect greater loss of conductivity upon retraction^{6,8}. This effect was also observed with the double-network rubbers up through 30% residual strains (Figure 6). As a consequence, the electrical conductivity ultimately realized in the rubbers with double networks was always less than that of rubbers crosslinked only in a state of ease.

Evidently the realization of higher electrical conductivity by virtue of a double-network structure requires the production of larger residual strains. The orientation induced in the filler phase must be sufficient to compensate for the disruption in the agglomerated carbon black occasioned by the extension and retraction. It is tempting to infer from Figure 6 that this competition between agglomerate destruction and orientationally enhanced particle contacting is beginning to favor the latter at residual strains beyond about 30%. Although achieving higher permanent set with double networks is certainly feasible²⁰, in the present work, the use of elevated temperature to effect the second crosslinking restricts the range of attainable residual strains. The upper limit for the strain during second curing was about

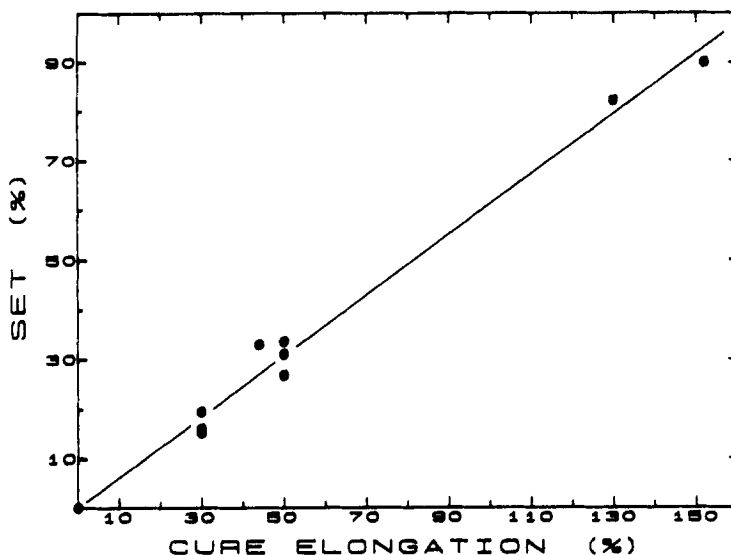


FIG. 5.—The unrecoverable strain in the SBR after it had undergone an initial cure in an unstrained condition, followed by a second curing at the indicated strain. This set is a measure of the inherent strain in the double-network elastomer.

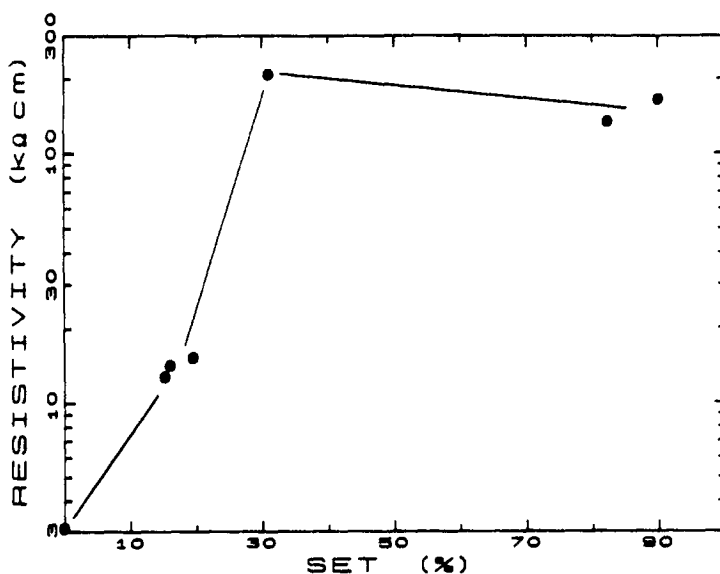


FIG. 6.—The equilibrium resistivity obtained in the SBR compound as a function of the residual strain imparted by the double network. Most of these data are the average of three experiments. The datum for zero residual strain represents the control specimens, which were cured both times in the unstrained state. The decline at high residual strain suggests that attaining conductivities greater than that of the single network may be achievable at higher degrees of inherent orientation.

150% elongation, beyond which fracture of the test specimens became evident. Certainly lower temperature curing, for example by radiation, is attractive for future pursuit of double-network elastomers.

Analogous to the results in Figure 6, it was found previously that in the absence of additional deformation, the inherent orientation of double-network rubbers had a surprisingly modest effect on their behavior²⁰. The earlier work indicated, however, that double-network rubbers are very sensitive to strain. In Figure 7 is shown a comparison of the effect of strain on electrical resistivity for two rubbers of equivalent crosslink density. While the double-network rubber initially has higher resistivity, its resistivity changes more drastically with extension. Consequently, higher conductivity can eventually be realized in the double-network rubber.

SUMMARY

The consequences on electrical conductivity of the various processing steps used to form a double-network rubber are summarized in Table IV. Although the objective was not achieved herein, the potential for using double-network rubbers to attain enhanced conductivity remains. Alternate procedures enabling residual extensions exceeding 100% are suggested for future work. Specific conclusions drawn from this study are as follows:

1. The time dependence of the electrical resistivity after imposition of a tensile strain depends on the magnitude of the strain. The observed behavior is consistent with breakup of carbon-black floc at low strains (with concomitant reduction in conductivity) and with promotion of interparticle contacting at higher strains. The latter engenders enhanced longitudinal conductivity. The enhancement may be due to orientation of the filler phase, but this remains speculative. The effect of deformation on the transverse resistivity could not be reproducibly characterized.

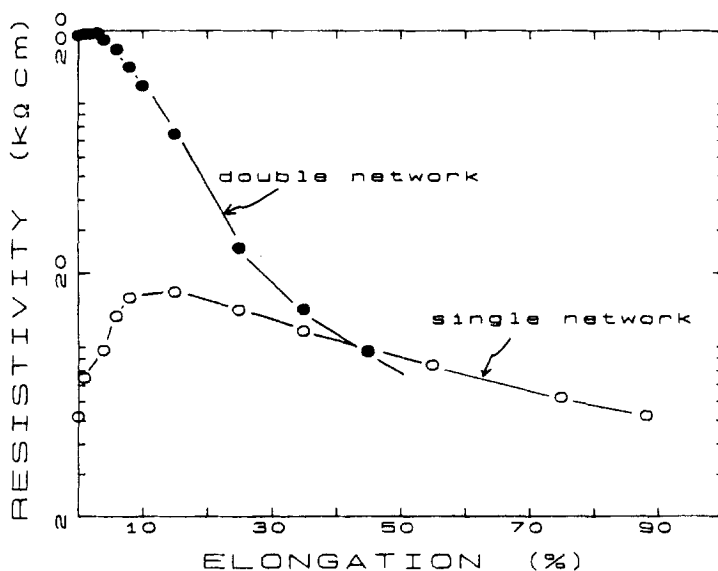


Fig. 7.—A comparison of the dependence on strain of the resistivity of a conventionally cured SBR with that of an SBR containing a double network. The residual elongation of the latter was 30%. Both rubbers were subjected to the same thermal history. The greater sensitivity to deformation exhibited by the sample that was in a strained condition during the second curing is an intrinsic feature of rubbers containing double networks.

2. The rate dependence of the electrical resistivity was also dependent on the magnitude of the rubber deformation. At the low strains associated with disruption of the filler phase, higher rates (stresses) increase the maximum in the resistivity. At higher elongations for which the resistivity declines, the effect of deformation velocity is less apparent.

3. Subjecting a filled rubber to heating after mixing reduces the electrical resistivity. The irreversible portion of this reduction is attributed to an acceleration in the recovery of an equilibrium level of filler-particle contacts. The resistivity acquires an invariance to temperature after the initial heating that persists for at least several hours.

4. The fact that extension followed by retraction of a carbon-black-reinforced elastomer results in a permanent increase in electrical resistivity negated in this work the possibility of achieving enhanced electrical conductivity *via* a double-network structure.

5. Consistent with the strain optical properties, orientational crystallization behavior, and stress-strain response previously found for unfilled rubbers containing a double-network structure²⁰, carbon-black-reinforced double-network rubbers exhibit electrical resistivities more sensitive to strain than conventionally cured elastomers.

TABLE IV
SUMMARY OF EFFECTS ON ELECTRICAL RESISTIVITY
OF DOUBLE-NETWORK FORMATION

Process	Electrical resistivity
Mixing	Increases
Thermal curing	Decreases
Extension	Decreases
Stress relaxation	Increases
Second thermal curing	Decreases
Retraction	Increases

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