Swelling and Electrical Properties of Rubber Vulcanizates Loaded with Paraffin Wax

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ABSTRACT: The influence of the concentration of paraffin wax on the penetration rate, P, and the average diffusion coefficient, D, of kerosene in an SBR–NR composite and also on the coefficient of viscosity were investigated. All decreased with the addition of wax. Also, the effect of the concentration of paraffin wax on both the current–voltage characteristics and the temperature dependence of the dc electrical conductivity were studied. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 3169–3177, 2001

Key words: SBR; NR; wax; swelling; electrical properties

INTRODUCTION

To control the effects of rubber aging, either waxes or chemical stabilizers are added. Waxes function as antiozonants by blooming to the rubber surface to form an inert protective film.[1]

The swelling process and its kinetics give an idea about the capacity of a crosslinked polymer in different liquids and vapor media. However, the interaction of polymeric materials with different solvents is a problem from both the academic and technological points of view.[2]

The mass and dimensions of polymer or rubber systems may be changed due to the penetration of solvents into swollen specimens. Indeed, the swelling process may lead to deformation or destruction of the sample microstructure. When a crosslinked polymer is brought into contact with a solvent, the network absorbs a certain amount of liquid, which depends strongly on the molecular weight of this liquid and the degree of the crosslinked polymer, besides the ingredients add-

ed.[3,4] The diffusion theory for elastomers[5,6] is based on the assumption that the swelling commences by absorption of liquid in the surface of the sample to a certain concentration equal to that of the whole sample at final equilibrium; then, the swelling proceeds through the depth of the swollen layers at a penetration rate, P, given by[5–7]

$$P = \frac{1}{2} \left(\frac{M_t}{t^{1/2}} \right) \frac{s}{M_e} \qquad (1)$$

where s is the thickness of the sample and M_e and M_t are the weight uptake of the liquid at equilibrium and after time, t, respectively.

The diffusion of a liquid in the bulk of the rubber depends on the homogeneity of the mix, the type of ingredients, and the way that the carbon black is aggregated.[7] The relation between the average diffusion coefficient, D, and the penetration rate, P, is given by[8]

$$D = \frac{\pi}{4} P^2 \qquad (2)$$

Table I Mix Formation of 40 HAF/(SBR-NR) Composites Loaded with Paraffin Wax

Ingredient (phr)	Concentration (phr)
SBR	50
NBR	50
HAF	40
Processing oil	10
Stearic acid	2
MBTS[a]	2
PBN[b]	1
Zinc oxide	5
Sulfur	2
Paraffin wax	0, 10, 20, 30, 40

[a] Dibenthiazole disulfide.
[b] Phenyl-β-naphthylamine.

On the other hand, there has been considerable interest in generating either conducting or semiconducting systems of conjugated polymers, in a specially well-defined pattern, on top of either an insulating or semiconducting matrix background.[9,10] In recent years, studies of the transport mechanisms in polymers have gained importance owing to the potential applications in various fields.[11] The variation of the electrical conductivity and the electric-field strength suggests a conduction mechanism in which carriers are released by thermal activation over a Coulombic potential barrier that is decreased by the applied electric field. The physical nature of such a potential barrier can be interpreted in two basic ways: It can be considered as a transfer of electrons over the barrier between the cathode and the dielectric, taking the classical image force into consideration (Schottky emission). Alternatively, charge carriers can be released due to the ionization of impurity centers in the dielectric (Poole–Frenkel effect).[12]

In the present work, the influence of the concentration of paraffin wax on both the swelling (including the penetration and diffusion of kerosene) and dc electrical properties (including the conduction mechanisms and the temperature dependence of conductivity) for styrene butadiene rubber–natural rubber (SBR–NR) vulcanizates loaded with 40 phr of HAF carbon black was studied.

EXPERIMENTAL

Material Used and Samples Preparation Technique

A masterbatch of styrene–butadiene rubber (SBR) and natural rubber (NR) with equal ratios and loaded with 40 phr (parts per hundred parts of rubber by weight) of HAF (high abrasion furnace N-330) carbon black was prepared. Different concentrations of paraffin wax were then added. All samples were prepared according to the recipes presented in Table I.

The compounds were mixed according to the ASTM D 3182 method in a laboratory-sized mixing mill at a friction ratio of 1:1.19, by carefully controlling the temperature, nip gap, time of mixing, and uniform cutting operation. The temperature range for mixing was 60–70°C. The order and time periods of mixing were as follows: 0–3-min mastication; 3–6-min addition of one-third filler plus one-third oil; 6–13-min addition of one-third filler and one-third oil; 13–18-min addition
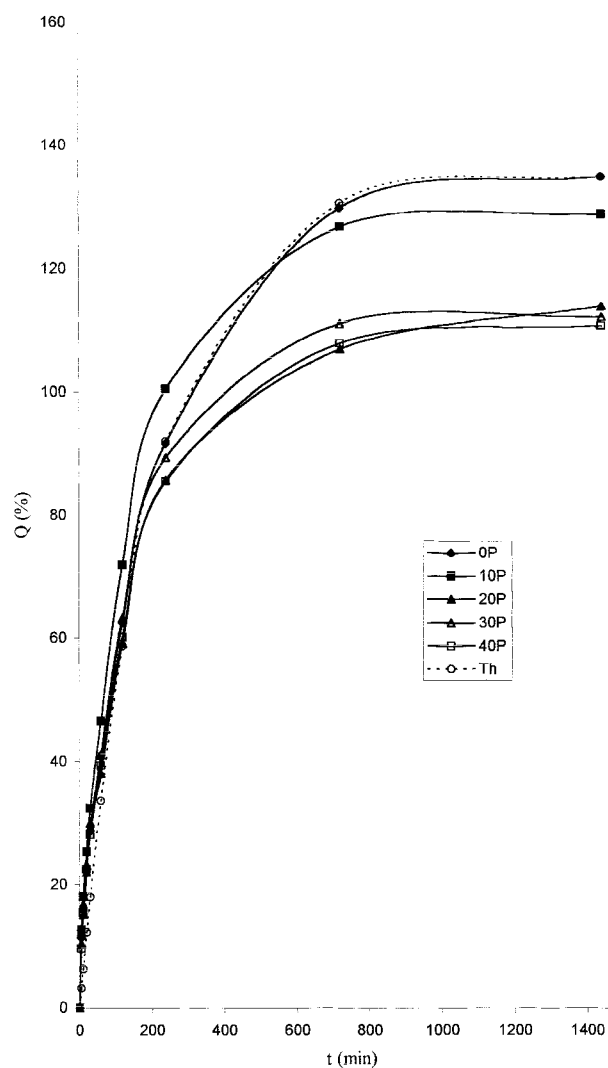

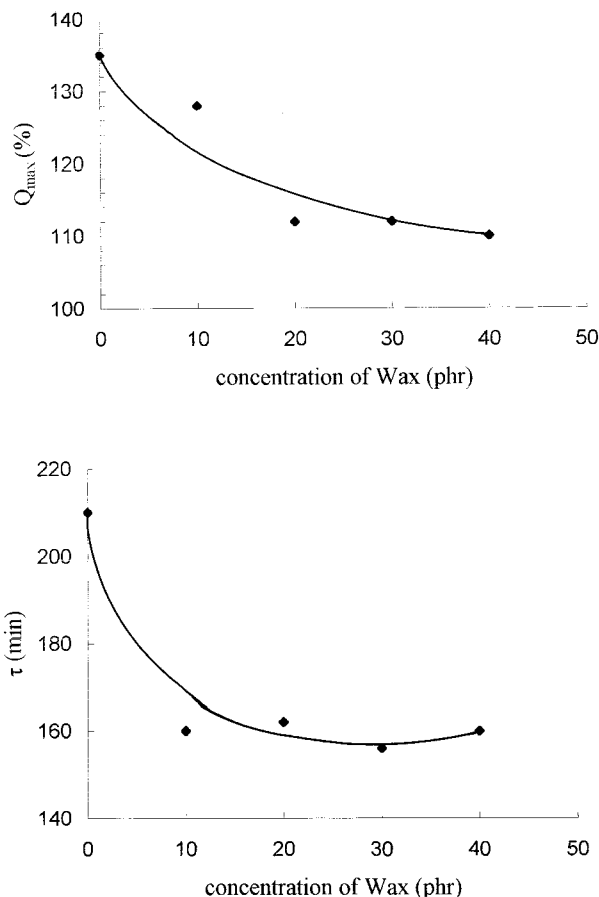**Figure 1** Dependence of the degree of swelling on time for all vulcanizates.

Figure 2 Dependence of (a) the maximum degree of swelling and (b) the characteristic time on the concentration of paraffin wax.

of remaining filler and oil; 18–26-min addition of other ingredients; 26–29-min addition of paraffin wax; and 29–30-min refining through tight nip gap and dump (the nip gap was 1.5 mm). After mixing, the rubber compositions were molded in an electrically heated hydraulic press to the optimum cure using molding conditions that were previously determined from torque data using a Monsanto rheometer (R100).

Swelling Measurements

Rubber blends were weighed and inserted into test tubes containing kerosene at 30°C. The rubber blends were removed from the solvent and blotted with filter paper to remove excess solvent from the surface of the sample. The rubber blends were then weighed to an accuracy of 0.1 mg at a given time and at a fixed temperature. The degree of swelling, Q, was calculated by using the gravimetric method, where Q is given by

$$Q = \frac{M_s - M_p}{M_p} \times 100 \ (\%) \qquad (3)$$

where M_s is the mass of the sample after swelling, and M_p, the mass of the sample before swelling.

Electrical Measurements

The samples employed for conductivity measurements were shaped into circular discs, which were sandwiched between brass plates. One electrode is insulated with Teflon. An automatically controlled electric oven up to 140°C controlled the temperature.

The dc current measuring equipment comprised a digital electrometer type 616 Kiethly. Using coaxial cable, metal shielding, and a common ground loop eliminated the electrical noise.
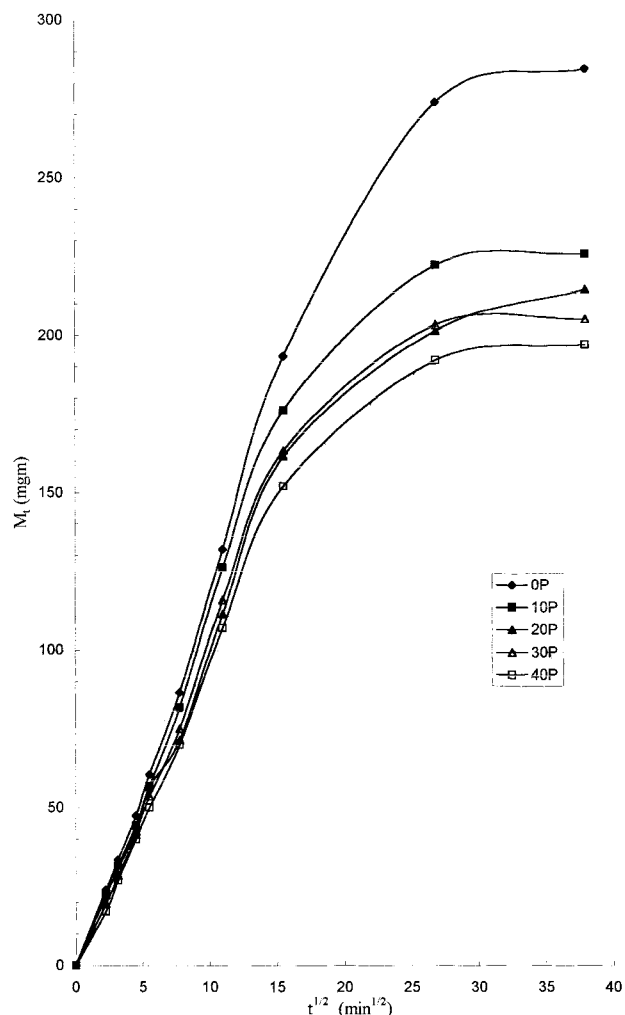

Figure 3 Dependence of the weight of the specimen on the square root of time for all vulcanizates.
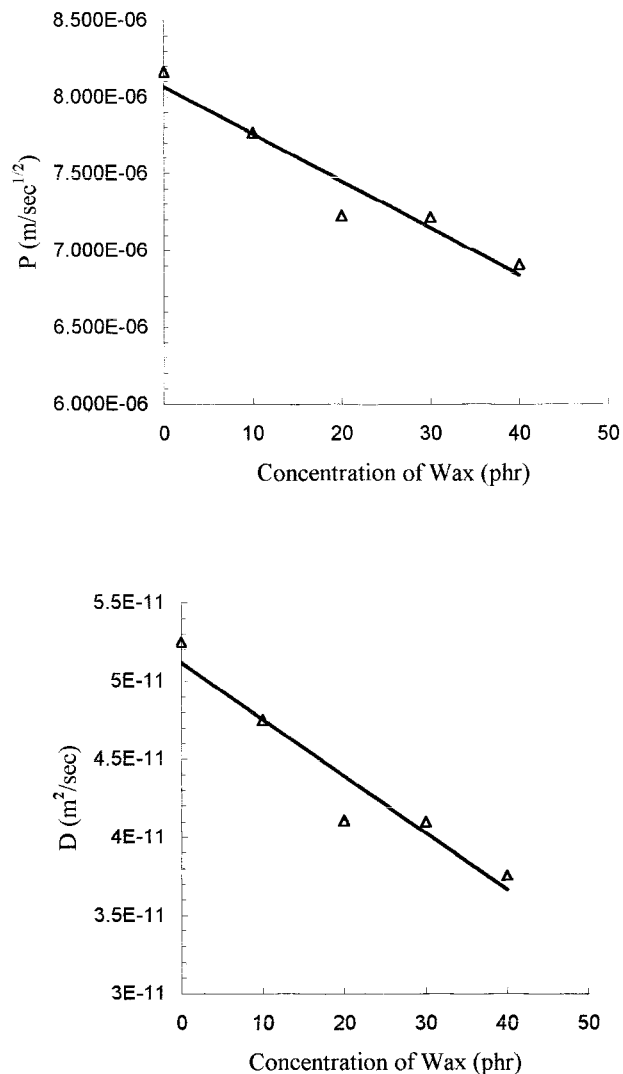
Figure 4   Dependence of the penetration rate and the average diffusion coefficient on the concentration of wax for all samples.

The thermal oxidative aging was carried out in an oven at 70°C for 50 days.

RESULTS AND DISCUSSION

Swelling

Figure 1 shows the dependence of the degree of swelling, Q (%), on the time of swelling, t, in kerosene for 40 HAF/(SBR–NR) vulcanizates loaded with different concentrations of paraffin wax. The general behavior of the curves in this figure may be approximated by an exponential function of the form
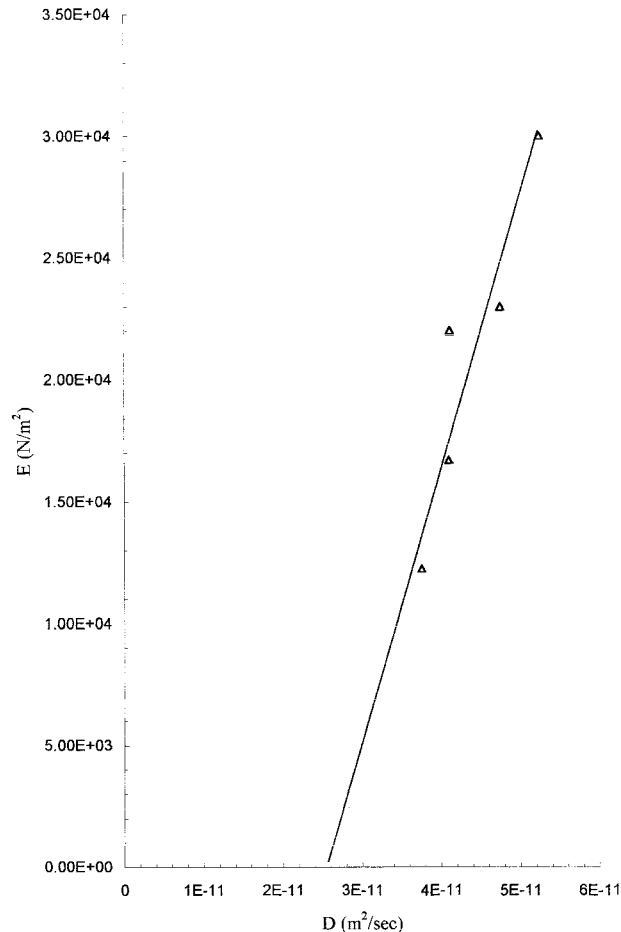

Figure 5   Relation between the Young's modulus and the average diffusion coefficient for all samples.

$$Q(t) = Q_m\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \tag{4}$$

where Q_m is the maximum degree of swelling and τ is a characteristic time which depends on the concentration of paraffin wax. Figure 2(a,b) shows the dependence of both Q_m and τ on the concen-

Table II   Calculated Values of b' and the Coefficient of Viscosity η for all Vulcanizates

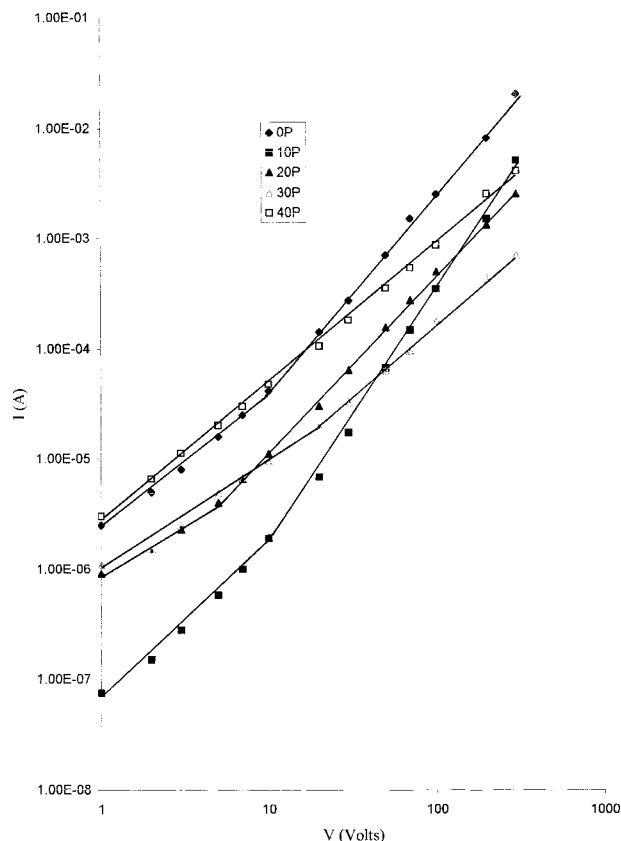| Concentration of Wax (phr)	b' (Pa s)	η_τ (Pa s)
0	4.5×10^{10}	1.3×10^8
10	3.8×10^{10}	2.3×10^8
20	4.23×10^{10}	2.28×10^8
30	3.21×10^{10}	1.6×10^8
40	2.58×10^{10}	1.2×10^8

Figure 6 Current–voltage characteristics for all vulcanizates.

tration of the wax. It is obvious that both of them decrease as the concentration of wax increases, which may imply that paraffin wax is a solvent-hating agent.

The increase in weight due to swelling was plotted against the square root of time as shown in Figure 3. The slopes of the straight lines obtained at the early part of the curves were calculated. Using eqs. (1) and (2), the penetration rate and the average diffusion coefficient were calculated. Figure 4(a) shows the relation between the concentration of paraffin wax and the penetration rate. The relation is a straight line and can be described by the equation

$$P = P_0(1 - aC) \qquad (5)$$

where P_0 is the penetration rate at zero wax concentration $= 6.32 \times 10^{-3}$ cm/min$^{1/2}$, C is the concentration of wax, and $a = 2.6 \times 10^{-5}$. According to eq. (2), the average diffusion coefficient, D, would have the same behavior for all studied samples as shown in Figure 4(b).

In a previous work,[13] the Young's modulus of these samples was calculated and found to decrease with the addition of wax. The relation between the Young's modulus and the average diffusion coefficient is shown in Figure 5. A direct relation between them can be described by the equation

$$E = bD - E' \qquad (6)$$

where E' is a constant. The parameter b is the slope and has the units of Pa s m^{-2}. It is noticed that by multiplying the ratio between the elastic modulus, E, and the diffusion coefficient, D, with the surface area, A, of the sample, each concentration of paraffin wax gives a new parameter, b' ($= EA/D$), which has the dimensions of the coefficient of viscosity. On the other hand, the coefficient of viscosity is related to the characteristic time, τ, according to $\eta_\tau = E \ \tau$.[14] The calculated values of both b' and η_τ for all vulcanizates are listed in Table II. It is noted from the table that the values of η decrease (in general) with the addition of wax. Also, in comparing the values of η and b', one notices an approximately constant difference between them. So one may consider that b' resembles the coefficient of viscosity and η_τ is the coefficient of viscosity after a time τ, that is, after a time at which the swelling of the samples reaches 67% of its maximum degree of swelling.

Electrical Behavior

Conduction Through the Vulcanizates

To determine the conduction mechanism prevailing in the composite, the current–voltage characteristics of the studied vulcanizates are plotted in Figure 6. Straight-line relations with two slopes are clear except for that which contains 40 phr of wax. The slopes of these lines (named S_1 at low voltage and S_2 at high voltage) are listed in Table III.

Table III   Calculated Values of S_1 and S_2

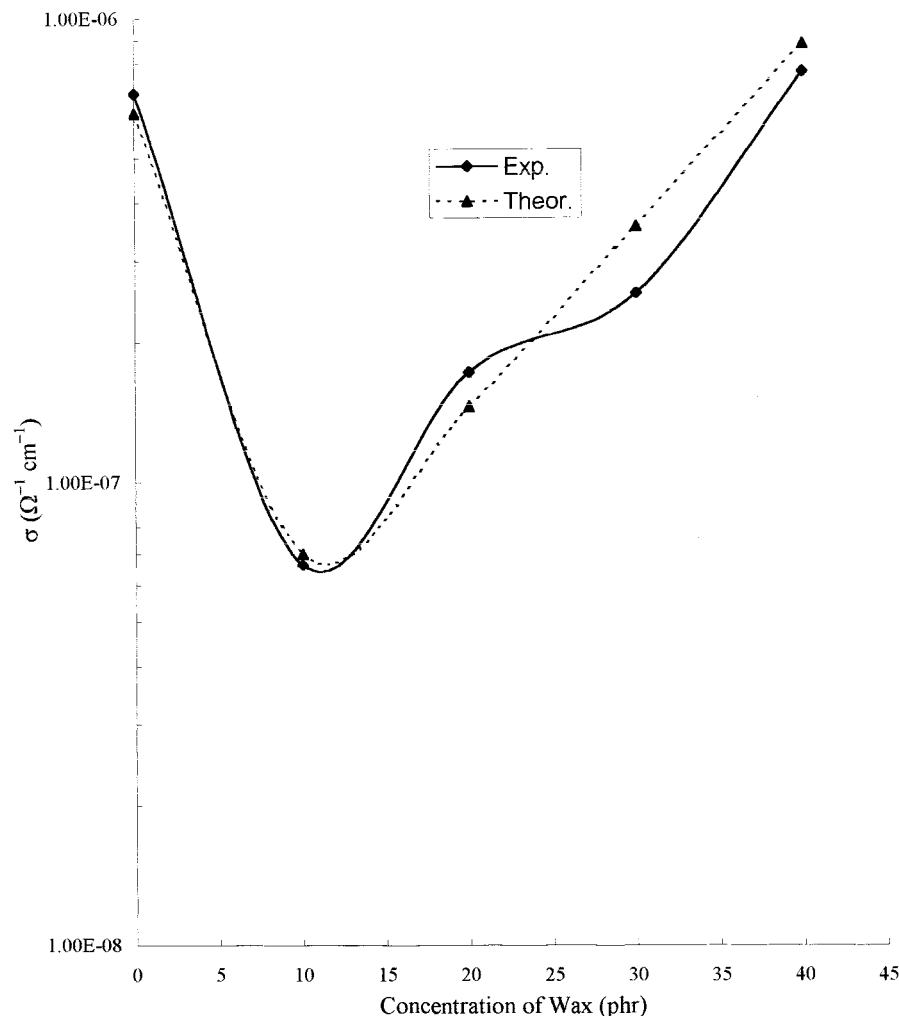| Concentration of Wax (phr)	S_1	S_2
0	1.25	1.89
10	1.3	2.48
20	0.98	1.71
30	0.77	1.3
40	—	1.27

Figure 7 Dependence of the electrical conductivity of 40HAF/(SBR–NR) vulcanizates on the concentration of wax at room temperature.

The table shows a slight increase of S_1 and S_2 at 10 phr followed by a regular decrease in them. The presence of a sublinear slope in the I–V characteristics is not often reported in single-phase systems. However, it has been reported in complex systems with two or more materials.[15,16] In the present studied system, there is a definite presence of sublinear I–V variation, when the slope itself decreases with an increasing paraffin wax content. Part of this sublinearity can be attributed to the possibility of the contacts being quasi-ohmic and requiring a small voltage to be expended at the electrode to break through the contact resistance.[17] The sublinearity may be understood as follows: The relation between the current density J of a semiconductor to the applied electric field E is

$$J = nev = (ne\mu)E \qquad (7)$$

where n is the concentration of charge carriers; e, the electronic charge; v, the speed of charges; and μ, the mobility. The relation shows that Ohm's law is obeyed and J increases linearly with the electric field E when the conductivity $(ne\mu)$ does not vary with the applied field. Thus, the sublinear dependence of the current on the applied voltage seems to indicate that there is a decrease in n (due to the presence of the traps) or μ. The slopes at high fields are supralinear. The mechanism for this could be a release of charge carriers from traps via field-assisted lowering of the trap depth.[17]

Dc Electrical Conductivity

The electrical conductivity is one of the essential electrical characteristics of a substance and the elucidation of the conductivity mechanism is of primary importance in determining its practical
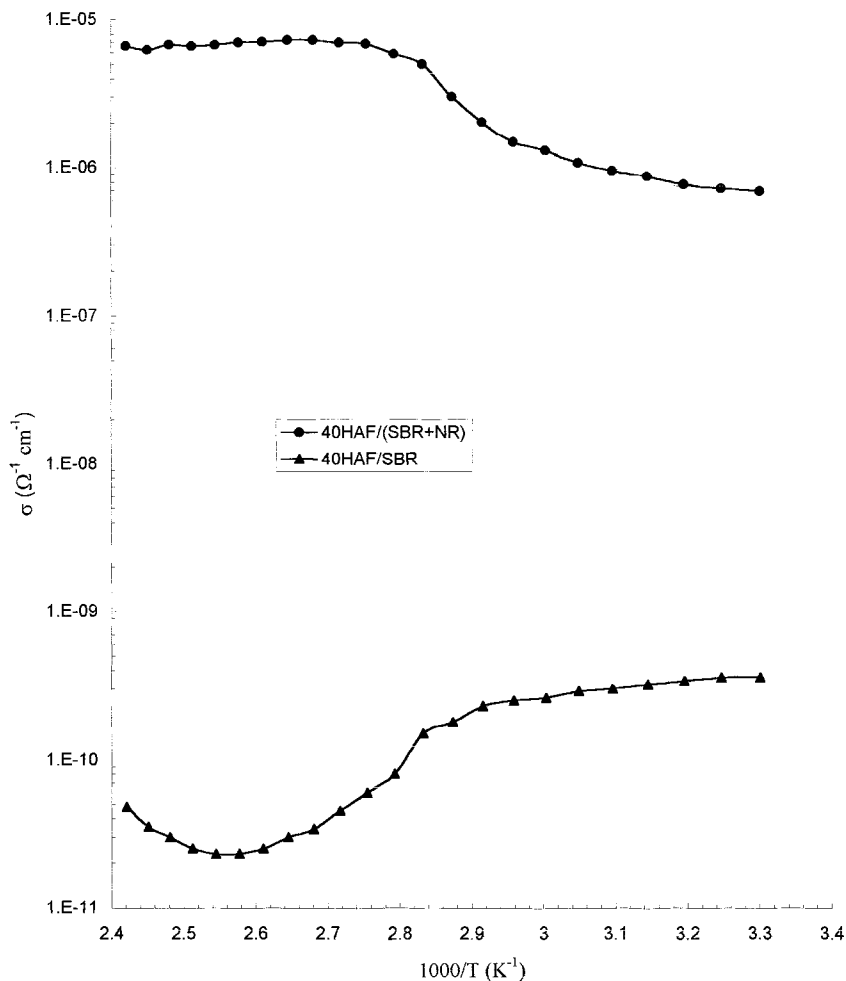
Figure 8 Temperature dependence of both 40HAF/(SBR–NR) and 40HAF/SBR.

applications. The influence of the concentration of paraffin wax on the dc electrical conductivity, σ, of 40HAF/(SBR–NR) vulcanizates at room temperature (30°C) is shown in Figure 7. The addition of 10 phr of wax decreases the conductivity by about one order of magnitude, which may refer to the isolation of the conducting charge carriers by the paraffin wax and/or due to the presence of traps as discussed before. Concentration of wax beyond 10–40 phr increases the conductivity, gradually owing to a new configuration of conducting aggregates or the release of charge carriers from the traps. The whole dependence is fitted fairly well with an empirical equation of the form

$$\sigma = \sigma_0[\exp(-\alpha C) + B \exp(\beta C)] \qquad (8)$$

where $\sigma_0 = 6 \times 10^{-7} \ \Omega^{-1} \ cm^{-1}$ is the electrical conductivity at zero loading of wax; C, the concen-

tration of wax; and α, β, and B, constants with values 0.4, 0.1, and 0.04, respectively.

Figure 8 shows a comparison between the temperature dependence of σ or both 40HAF/(SBR–NR) and 40HAF/SBR at an applied field of 50 V/cm (with data achieved from a previous work[18]). One may find that

- The addition of 50% of NR increases the conductivity by about three orders of magnitude at room temperature, indicating the liberation of excess charge carriers.

The behavior of the temperature dependence of the two vulcanizates is nearly opposite in nature. For the vulcanizate 40HAF/SBR, there is a competition between two mechanisms. One of them acts to increase the electrical conductivity with the temperature by increasing the mobility of car-
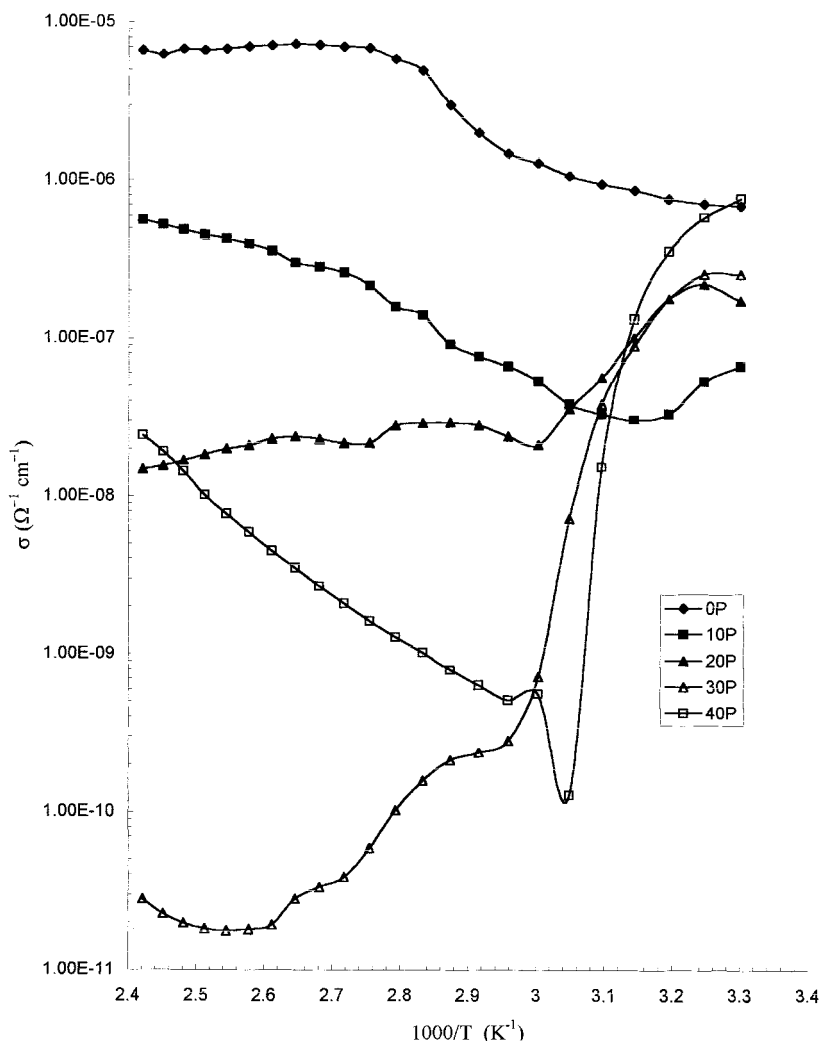
Figure 9 Temperature dependence of 40HAF/(SBR–NR) at different concentrations of paraffin wax.

riers inside the matrix, while the other decreases the conductivity with the temperature due to the thermal expansion of the rubber matrix with respect to the carbon black particles, which increases the distance between the carbon particles.[19–22] For 40HAF/(SBR–NR) vulcanizates, the same competition exists but the increase in mobility (thermally activated mechanism) is predominant. At high temperatures, the nearly constant conductivity may be due to the existence of a space charge at the boundary between two rubber phases which prevents a decrease in the electrical conductivity.

The addition of paraffin wax highly affects the temperature dependence of σ for 40HAF/(SBR–NR) composites as seen from Figure 9, from which one can point out that

(a) As the value of added paraffin wax increases, the values of the calculated maximum temperature coefficient of conductivity, TCC ($= 1/\sigma \, d\sigma/dT$) is increased, as shown in Table IV.

(b) The thermally activated mechanism decreases gradually and completely disappears for samples containing 30 phr of wax.

(c) Samples containing 40 phr of wax show a minimum conductivity behavior at 55°C and behave like those with low concentrations of carbon black. The excess paraffin wax begins to melt above that temperature, resulting in easy motion of charged carbon particles and, hence, enhancement of the conductivity.

Table IV   Maximum Calculated Values of TCC for 40HAF/(SBR–NR) Loaded with Different Concentrations of Paraffin Wax

Concentration of Paraffin Wax (phr)	TCC (deg^{-1})
0	—
10	0.025
20	0.029
30	0.069
40	0.20

CONCLUSIONS

One may conclude from this study that the penetration rate, the average diffusion coefficient of kerosene, and the coefficient of viscosity decrease with the addition of paraffin wax. The addition of NR to SBR in equal proportions increases the dc electrical conductivity of the matrix and converts the temperature dependence of conductivity into a thermally activated one. The addition of 10 phr of wax decreases the dc electrical conductivity more than do other concentrations. The minimum conductivity behavior for the temperature dependence of the dc electrical conductivity appears with the addition of paraffin wax.

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