

Electrical Properties of Rubber Compounds. Thermal Aging Behavior

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Abstract

In this paper the variation, with time, of the electrical resistivity of carbon black filled rubber compounds was analyzed at constant temperature. Studying this behavior gives information not only about the thermal stability of the compounds but also about the kinetics and dynamics of the filler-polymer interaction. The percolating cluster, dominating the electrical conductivity, modifies itself during the temperature aging process. A broad range of carbon blacks type and loading were analyzed in several polymeric matrices. The degree and rate of change in electrical resistivity were studied as a function of temperature. Additionally, the evolution of the amount of bound rubber in different systems and under different conditions was analyzed.

I. Introduction

The electrical conduction process in carbon black-polymer composites is complicated and dependent on a large number of parameters. i.e.: aggregate size, surface area, surface condition, structure, dispersion, polymer matrix etc.... The electrical properties of carbon black filled rubber compounds are greatly influenced by the state of filler micro-dispersion and depend strongly on the structure of the percolated filler network. It will be shown in this work that the structure of this network changes during temperature and aging and analyze its dependence on carbon black surface area and structure.

The effect of aging on the filler network structure is an interesting subject because not only the electrical properties are influenced but also, the low strain dynamic properties of the rubber compound are strongly dependent on the filler network local density fluctuation. This behavior has been reviewed before in depth in several papers¹⁻⁴. A poor micro-dispersion, characterized by a large filler network local density fluctuation, causes the viscoelastic properties to be more strongly dependent on strain amplitude as well as strain history. The electrical resistivity measurements have shown to be simple and sensitive enough to detect small changes in the filler network. This kind of measurement is much more appropriate than the mechanical one since no strain energy input is applied to the sample which may cause changes in the geometrical structure of the filler network.

The changes in electrical resistivity with aging, as well as the changes of mechanical dynamic properties, have been reported previously⁵⁻⁸. The usual approach to this problem assumes that after the mixing process the filler aggregates will slowly reaggregate

(flocculate). By such a process, the aggregates or agglomerates move randomly by thermal agitation through the polymer matrix and have a given probability to stick together with another carbon black aggregate/agglomerate. This decreases the electrical resistivity and increases the strength of the percolated carbon black network.

In the usual understanding of flocculation, the aggregates being close enough, can be attracted to each other by London-Van der Waals forces. Besides the attractive potential between aggregates of the filler, the flocculation process is determined by diffusion of aggregates due to Brownian motion to form thermodynamically stable network. For a given polymer-filler system, the diffusion of the filler aggregates in the polymer matrix play an important role in the flocculation kinetics. Most authors^{7,8} use to calculate the diffusion coefficient (Δ) using the Einstein-Stokes relation as⁹:

$$\Delta = kT \frac{1}{6\pi\eta a} \quad (1)$$

k being the Boltzman constant, T the absolute temperature, η the medium viscosity and a the particle diameter. This implies that at constant temperature, the polymer viscosity and the size of the aggregates control the flocculation rate. It is important to note that this equation was derived for spherical particles. Furnace carbon black aggregates are, in general, very far from being spherical. However, it is possible to define an effective radius for an aggregate that should depend on its spatial structure, which is partly related to the value of CDBP (ASTM Procedure D-3493).

The evidence of the existence of a filler network in rubber compounds was investigated by many authors after the pioneering work of Payne¹. He observed that the elastic modulus of a carbon black filled rubber compound that is strongly depended on strain, and suggested that the excess storage modulus at low strains can be taken as a measure of carbon black networking. Recently, Bohm and Nguyen⁷ have studied the flocculation of carbon black in rubber compounds, using the Payne effect as evidence of flocculation. More recently, Jager and MacQueen⁸, have used electrical measurements to analyze the kinetics of the flocculation process. They measured the electrical resistivity of EBA(ethylene butylacrylate copolymer) filled with carbon black at different loadings and temperatures.

In addition to the change of the electrical resistivity values the evolution of bound rubber was monitored, before and during the aging process. In view of the data presented here, flocculation describe changes of the filler-polymer network not only by small rearrangement of the carbon black agglomerates but also by variations of the bound rubber content implying a change in the polymeric chain configuration.

Both phenomena change the electrical behavior of the compound during aging.

II. Experimental

Sample Preparation

Several carbon black grades were mixed with Sn-SSBR (Tin Coupled Solution SBR). Carbon black loading was varied from 30phr to 60phr. The compounds were mixed in a Haake Rheocord 90 internal mixer with no curatives. The compound was sheeted out using

an open mill to about 12 mm in thickness and cylindrical samples of about 38 mm in diameter were prepared. The top and bottom faces of each cylindrical sample was gold sputtered to ensure good electrical contact with the electrodes and eliminate the contact resistance. Additionally, different solution SBR elastomers, Duradene 709 and Duradene 711 were mixed with different loadings of N330 carbon black.

Test Procedure – Electrical Measurements

Figure 1 shows the equipment built by the authors that allow keeping the samples at constant temperature during the measurements. The samples were put between chromium plated cooper electrodes in thermal contact with two heaters. The middle sample fitted with a thermocouple was used to control the temperature using an Omega temperature controller. The resistivity was measured using a Keithley Electrometer 6517A equipped with a Keithley 6522 multiplexer card that allows one to measure six samples simultaneously. The Keithley was controlled by a personal computer through RS232 port. A LabWindows/CVI program was developed by the authors to measure time, temperature and resistivity during the temperature aging cycle. This first room temperature measurement, at time $t=t_0$, is the reference point to calculate the extent of the resistivity change. Next, the temperature was increased to 60, 80 and 100°C respectively. After the temperature reaches the set marks (60°C, 80°C and 100°C) at a rate of 1C/min, the volume resistivity data were collected for 20 hours at these temperatures. Finally, the samples were allowed to cool down to room temperature (in about 30 minutes) and after another 24 hours the final volume resistivity data were collected. These measurements allow calculating the rate of resistivity change from the slope of the regression line of the volume resistivity data vs. time. The intensity (amplitude) of the change is obtained by the change in the volume resistivity value between the initial and final room temperature measurements. The details of temperature sequences and performed measurements are explained in Figs. 2a and 2b.

Test Procedure – Bound Rubber

The bound rubber measurement was carried out at room temperature using toluene as solvent. For its determination, approximately 1g of compound was cut into small pieces and placed into a stainless-steel wire-mesh cage of a known weight. The cage was then immersed in the solvent for four days. The toluene was replaced every day with fresh solvent. After extraction, the rubber and the cage were dried in a hood for one hour and then in an oven (125C) for 5 additional hours. The percent bound rubber $BR\{\%\}$ was calculated using the following equation:

$$BR(\%) = \frac{W_B(m_f + m_p) - W_A m_f}{W_A m_p} \quad (2)$$

W_B and W_A being the weight of the compound after and before soaking, and m_f and m_p are the weight of the filler and the polymer respectively in the original compound

III. Results

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Carbon Black Loading Dependence

It was shown in previous work⁵ that the changes in resistivity value after and before aging increase significantly when loading approaches the percolation threshold. In this work the focus was set on studying the changes of volume resistivity around percolation. Figure 3 shows an example of the resistivity amplitude change around the percolation threshold. Below, but near, percolation there are no continuous pathways to carry any electrical current. However certain probability exist that some contacts improve or new pathways are created decreasing the electrical resistivity.

On the other hand, above but near percolation, new conductive pathways can be created during aging in addition to the existing ones. In both cases, any small fluctuation of the polymer-filler arrangement substantially modifies the electrical resistivity. Far from percolation, both above and below, small changes in the filler network have negligible effects on resistivity.

Similar curves were obtained for the different carbon black and two parameters were extracted from the data obtained for each compound. The loading corresponding to the maximum corresponds to the percolation threshold. The peak height is the maximum change in resistivity at room temperature calculated by dividing the initial resistivity measurements by the final value. Figure 4 shows the dependence of the peak height with the specific surface area (N_2SA) for each carbon black under investigation. It is easy to note that for the same value of N_2SA different peak heights is observed, which depends on the structure (CDBP) of the carbon black. Using statistical tools, a relationship between the peak height and N_2SA and CDBP values was found, giving rise to the following regression:

$$H = 3.6784 - 0.0624CDBP + 0.0472N_2SA \quad (3)$$

CDBP is given in $cm^3/100g$ and N_2SA in m^2/g . Figure 5 shows the corresponding contour plot.

Looking at the coefficients of each term, it can be noted that the higher the surface area and the lower the structure result in greater changes in resistivity. This tendency agrees with the changes of bound rubber content that will be discussed later.

Temperature Dependence

Figure 6 shows the temperature dependence of the resistivity variation with time. As expected, the higher the temperature the higher the rate of flocculation. Figure 7 shows that the flocculation rate is linear, in a first approximation, with temperature in the temperature range under consideration.

Around the percolation threshold the maximum resistivity change occur as well as the highest temperature dependence. In Figure 8 the rate of flocculation for Sn-SSBR/N330 compound as a function of loading at different temperatures is plotted. The data shows that for high and low loading, compared to the percolation threshold loading, the rate decreases and becomes less temperature dependent.

Bound Rubber

In order to elucidate the mechanism responsible for the variation of the electrical resistivity, the change in the quantity of bound rubber in the different systems under different conditions was evaluated. Figure 9 shows the increment of the amount of bound rubber in a Sn-SSBR/N330 50phr sample aged at 80C and 100C. A significant increase can be observed after 20 hours of aging. It is also interesting to note how the increment of bound rubber change depends on temperature. Similar to resistivity measurements the higher the aging temperature the higher the rate of formation and amount of bound rubber. Additionally, the evolution of bound rubber in different polymer matrices were analyzed. Figure 10 shows the evolution of bound rubber in Sn-SSBR, D709 and D711 filled with 40phr of N330. Again, the higher the quantity of bound rubber the higher the resistivity change.

IV. Discussion

It was shown that the variation of the electrical resistivity observed during aging depends on carbon black, type and loading, polymer matrix and aging temperature. Experiments performed in this work allow postulating that two processes could contribute to the observed changes in the volume resistivity. First, a very small change in the carbon black network density and second, the contribution from the polymer rearrangement as measured by bound rubber concentration. It is well known that tunneling effects largely contribute to electrical conductivity. This process is described by an exponential dependency of the current to the distance between aggregates. Therefore tunneling is only possible when the aggregates are at very close proximity to each other. Because of the exponential character of the tunneling process any small changes in the inter-aggregate distance cause significant changes in the macroscopic resistivity. Transmission Electron Microscope (TEM) experiments were performed in order to observe the movement of carbon black aggregates during aging. No measurable changes were detected suggesting that the rearrangement of carbon black network, if it occurs, is in the order of a few percent of carbon black particle diameter. Such small changes would be significantly below the resolution of the available equipment.

The bound rubber analysis shows a parallel evolution between the amount of bound rubber in the percolating cluster and the increase of the electrical conductivity of the compound. This behavior suggests a possible relationship between the electrical resistivity changes and the increase of bound rubber. The mechanism is still not clear but two hypotheses could be taken into account. First, the polymer chain movement can contribute to the rearrangement of the filler/polymer network improving the electrical conduction as was discussed above. Second, the bound rubber improves the electrical conduction whether increasing the tunneling probability or conducting electrical current between aggregates attached to the same polymer chain. Previously, Abo-Hashem¹⁰ suggested that the strong interaction between carbon black and rubber led to band-like conduction. More studies are necessary to resolve this question.

Finally, it is possible to explain the flocculation intensity dependence with loading from the percolation theory. It is known from percolation theory¹¹ that only a subset of all aggregates present in the sample belong to the percolating cluster, and only a subset of the aggregates that belong to the percolating cluster contributes to the electrical conductivity. This last structure is called the "backbone". At very low loading of carbon black, percolating cluster does not exist, and the agglomeration of aggregates cannot modify the macroscopic electrical behavior of the compound. At very high concentration, the electrical conduction

takes place through the percolated carbon black network and small changes on this network do not affect significantly the macroscopic behavior. Near but below the percolation threshold the flocculation can induce the formation of the percolating cluster. Near but above the percolation threshold any rearrangement of the filler/polymer network could densify the backbone of the percolating cluster.

V. Conclusions

Carbon black flocculation in uncured rubber compounds was investigated. Various experiments to study the influence of carbon black loading, polymer type and aging temperature on flocculation rate and intensity have been carried out. It was found that flocculation can change significantly the electrical properties of uncured compounds and that near the percolation threshold the flocculation effects are at maximum.

Besides the possible movement or rearrangement of the carbon black aggregates in the filler/polymer network, an incremental increase in the amount of bound rubber with aging time was found and investigated. This increment of bound rubber with aging time is well known from previous literature reports, however, to the knowledge of the authors, there is no reference about its effect on electrical behavior of aged samples.

Currently, new studies are being carried out to analyze the structure of the percolating cluster and its evolution during aging. These studies will give more information about the exact mechanism of flocculation as well as about the mechanism of interaction between polymer and carbon black.

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Figures

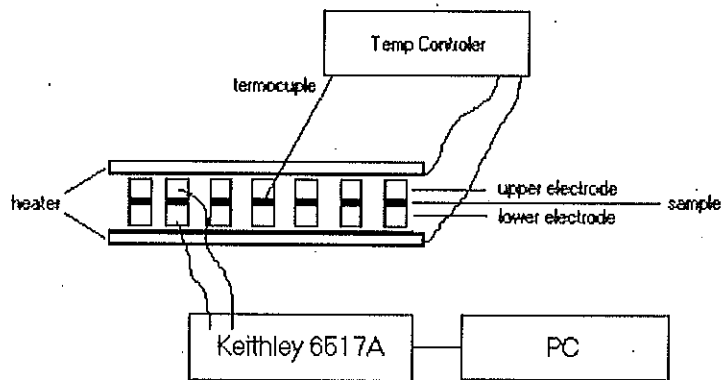


Figure 1

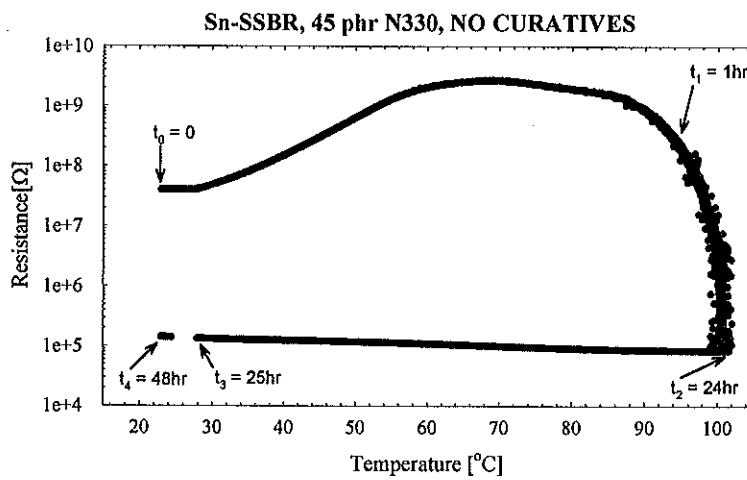


Figure 2a

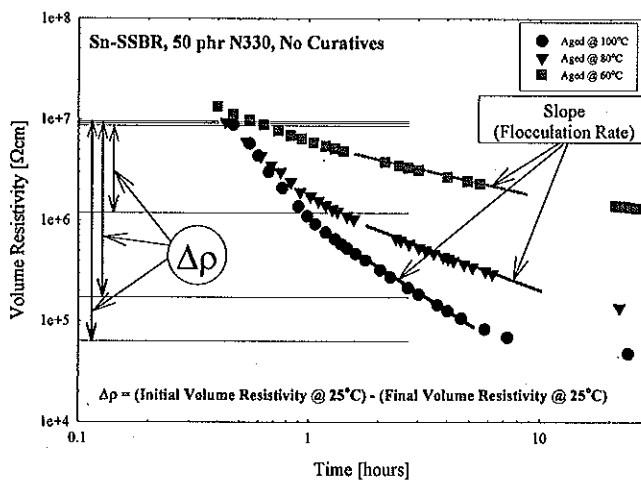


Figure 2b

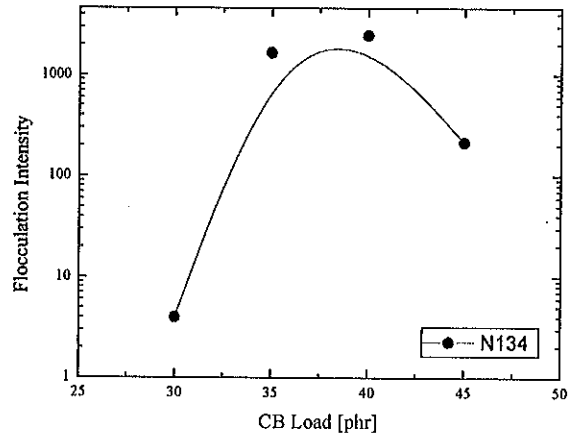


Figure 3

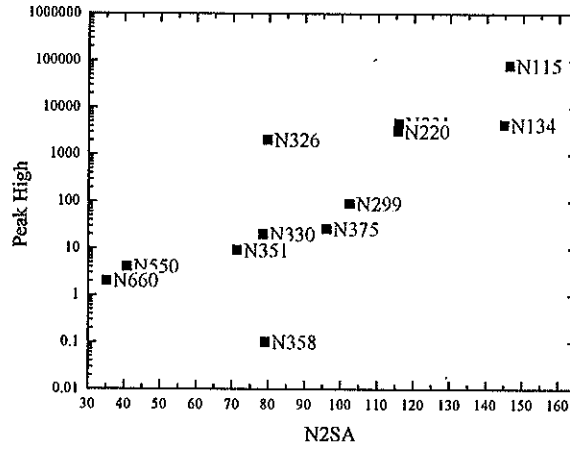


Figure 4

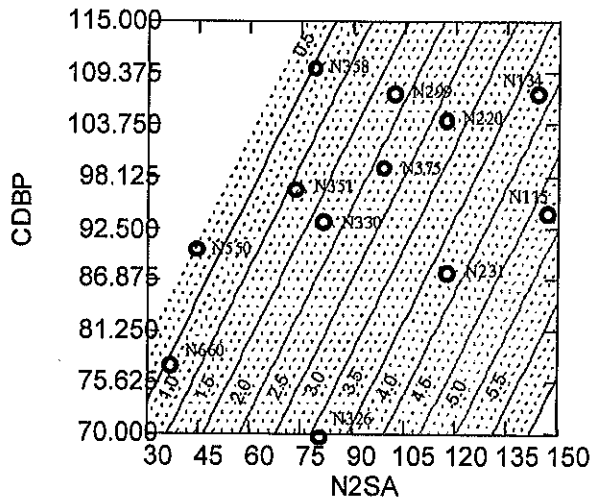


Figure 5

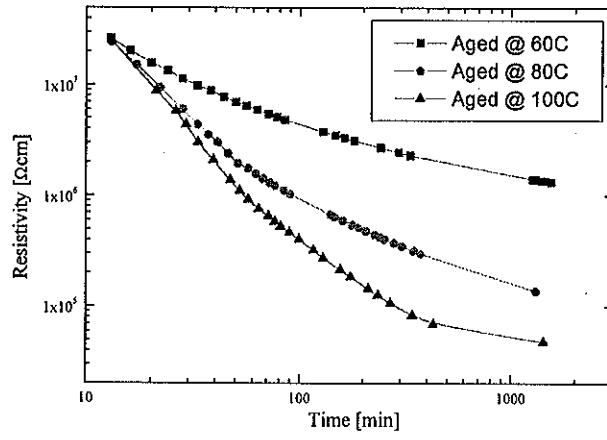


Figure 6

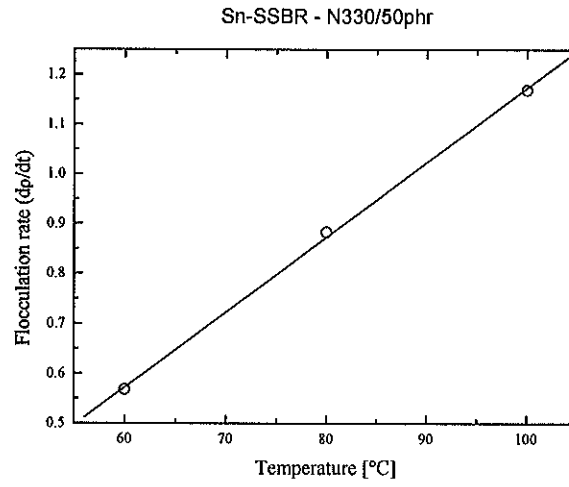


Figure 7

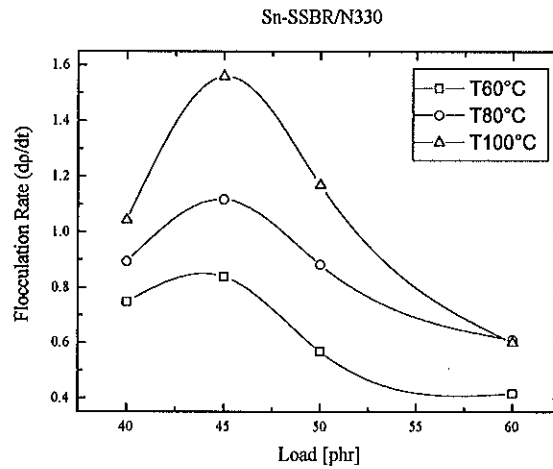


Figure 8

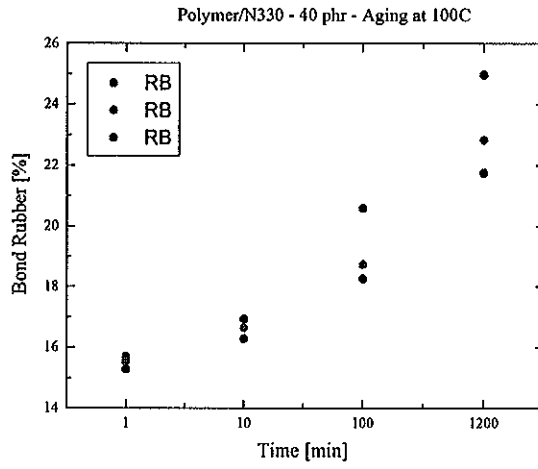


Figure 9

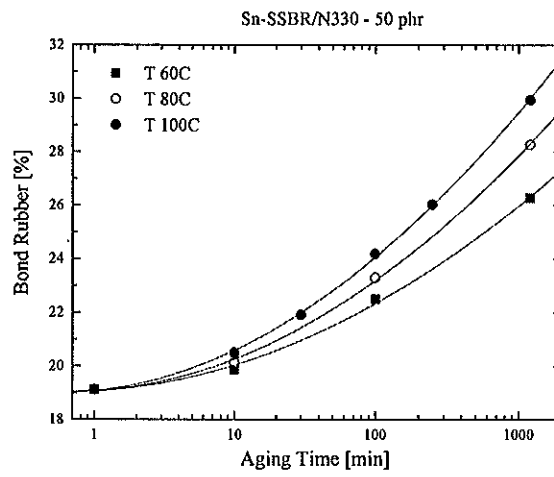


Figure 10