



Thermal aging of carbon black filled rubber compounds. I. Experimental evidence for bridging flocculation

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Abstract

An extensive work was performed to analyze how and why electrical properties of carbon black filled rubber compounds change during thermal aging. Several compounds were prepared using different polymer matrices and a broad range of carbon black types. Electrical resistivity of cured and uncured samples was measured, under different conditions, during thermal aging at constant temperature. Other experimental techniques, like transmission electron microscopy, bound rubber measurements and gamma irradiation were also used. Contrary to previous works, it was found that the changes of the electrical resistivity might be explained without any movement of carbon black aggregates during aging. Additionally, a new dependence of the variation of electrical resistivity with carbon black loading is reported and analyzed. This dependence could be the source of the contradictory data and conclusions in previous works. A correlation between the increment of electrical conductivity and the increment of bound rubber during thermal aging was found. This fact suggests that polymer chains and polymer–filler interaction are responsible for the changes during thermal aging instead of aggregate movement.

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1. Introduction

The variations of electrical resistivity of carbon black rubber compounds during thermal aging have been studied for many decades [1–11]. These variations are given by macroscopic expressions that refer to the behavior of the material at the microscopic level and give us information about polymer–filler interaction. These variations are of high relevance not only from a scientific point of view but also for a technological interest since it is very important to get stable compounds for most practical uses. Unfortunately, however, there has been little experimental or theoretical work done on this subject. Furthermore, some of these works show contradictory conclusions about the same phenomena. Some authors describe the variations of electrical resistivity of carbon black rubber compounds

during thermal aging in terms of the carbon black aggregates movement by Brownian diffusion. However, some experimental data seem to be contradictory to this explanation.

This work attempts to present enough experimental evidence to establish what really happens during thermal aging of carbon black rubber compounds. Some old and new results are presented and analyzed. We discuss in this work *how* electrical resistivity varies during thermal aging under different conditions and we leave *why* this occurs for a further paper. So we will focus in this paper on the phenomenological aspects of thermal aging, and we leave the physical discussion and the proposal of a new model for the second part of the work.

1.1. Historical background

The variation of electrical resistivity with time in carbon black rubber compounds is known for long time ago. Already in 1945, Bulgin [1] had observed that electrical resistivity of carbon black natural rubber compounds varies

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with time. However, Bulgin had noted that after a long thermal treatment the compounds kept a constant resistivity value, which did not depend on time. In 1947, Hanson [2] found that the rate of variation of electrical resistivity of carbon black loaded natural rubber compounds decreases with time. He observed that these changes continued during several hours after vulcanization, until reaching an equilibrium value. In 1953 the Anchor chemical company published some results about accelerate aging of carbon black natural rubber compounds in a high oxygen content atmosphere [3]. They found an empirical relationship between the change in the resistivity value and its initial value (ρ_i) given by $\Delta \log \rho = 0.27 \log \rho_i + 0.1$. This means that stability of resistivity decreases when its initial value is higher. In 1962, Berezina et al. [4] found that electrical resistivity of compounds, made of carbon black and different polymers, remained constant after aging the samples for 50 h at 70 °C.

From 1988, Eatah et al. [5–7] have published some papers about how thermal aging affects the electrical properties of carbon black butyl rubber compounds. They explained the variations in electrical resistivity in terms of two processes: (a) the movement of carbon black aggregates to form agglomerates, which decrease electrical resistivity, and (b) the break-up of the carbon black network, which increases compound resistivity. In 1991, Roig and Marzocca [8] analyzed the time dependence of electrical resistivity in carbon black SBR (styrene–butadiene rubber) compounds. They found that the variation of electrical resistivity with time depends on carbon black loading and mixing time. They proposed a phenomenological model to describe the time dependence of the electrical resistivity. One year later, Mattson and Stenberg [9] studied the oxidative degradation process in carbon black EPDM compounds. They observed that the variation of electrical resistivity depends on what atmosphere the samples were aged in. They completed the study with electron microscopy (SEM) of the samples. From this analysis they concluded that the variation of electrical resistivity is not due to carbon black aggregate movement, and another mechanism is necessary to explain this behavior.

In 1995, Bohm and Nguyen [10] published a systematic study about the aging effects of carbon black poly-butadiene rubber compounds on its mechanical properties. In this case they aged uncured samples and then cured them by electron beam irradiation. They analyzed how temperature, type and load of carbon black, molecular weight of the polymer and mixing time affect the kinetic of the variation of mechanical properties. They interpreted the changes of mechanical properties in terms of carbon black aggregate movement through the polymer matrix.

More recently, Jager and McQueen [11] have analyzed the variations of electrical resistivity on carbon black-filled ethylene-butyl acrylate (EBA) compounds. They aged samples with different carbon black loadings at several temperatures and monitored electrical resistivity during

aging. They also explained the changes on electrical resistivity in terms of movement of carbon black aggregates.

Let us briefly describe the flocculation theory and how it could explain the changes of electrical resistivity during thermal aging; then we will introduce some terminology about flocculation for clarity and consistency.

1.2. Flocculation theory

Flocculation occurs generally by one of four mechanisms [17]:

- Double-layer compression or charge neutralization that reduces or eliminates electrostatic repulsion between particles.
- Hydrophobic or electrostatic interactions between monolayer patches on two particles.
- Depletion flocculation by a free polymer is caused by the exclusion of the free polymer from the interparticle regions.
- Bridging flocculation is caused by a polymer adsorbed on the surface of a particle in an extended conformation.

From these four mechanisms, only the last one does not imply movement of particles. In this case the long segments of the polymer protruding into the liquid phase can be adsorbed onto another particle and link both particles together by a polymer bridge. The effectiveness of a bridging flocculant depends strongly on molecular weight and on polymer-particle interaction. Low molecular weight polymers actually function as dispersants.

When flocculation implies particle (carbon black aggregates in our case) movement, the diffusion is produced by Brownian motion. For a given polymer–filler system, diffusion of the filler aggregates in the polymer matrix plays an important role in flocculation kinetics. From the colloid theory, it is known that the diffusion coefficient (Δ) is given by the Einstein–Stokes relation as [18]:

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

where k is Boltzmann constant, T absolute temperature, η medium viscosity and a particle diameter. This equation means that, at constant temperature, flocculation rate depends on polymer viscosity and particle size. On the other hand, for a given compound, the higher the temperature the faster the changes in the physical properties.

It is important to point out here that Eq. (1) was derived for the case of spheres moving in a liquid medium. In the case of carbon black aggregates in a polymer matrix, the interaction between polymer and fillers is very strong and we have to be very careful whether Eq. (1) is valid or not.

1.3. Terminology

The definition of flocculation is a problematic task. We

will present here a brief review of the existing different meaning of the word ‘floculation’. Then we will define what we call floculation along this work.

When we have particles dispersed in a matrix, dispersion may change because of (1) aggregation (coagulation or floculation), (2) sedimentation, and/or (3) chemical reactions. The differentiation among the terms floculation, coagulation and aggregation is difficult because their ambivalent usage. Heitner [12] defines floculation as the process by which fine particles, suspended in a liquid medium, form stable aggregates called *flocs*. The description of flocs as stable aggregates is inaccurate, however, because flocs may be broken by vigorous agitation. Some authors use aggregation as the generic term and differentiate between floculation and coagulation. According to Smith [13], floculation has been defined as a dynamic process: floculation is a reversible aggregation of particles, which can be redispersed again. In contrast, agglomeration (or coagulation) is a strong (permanent) association of particles. Other authors [14–16] consider floculation and coagulation to be different aggregation processes caused by dissimilar mechanisms. It is easy to note that there is no general agreement yet about what floculation means. A more detailed discussion about the definition of floculation can be read in Kissa [17].

In this work, where we deal with carbon black filled rubber compounds, we will call floculation any change in the carbon black-rubber network structure, regardless of the mechanisms involved. These changes will be reflected as variations of the electrical resistivity of the sample.

2. Experimental

2.1. Materials

Natural rubber (NR) and several styrene–butadiene rubbers (SBR) were used in this work. Table 1 shows the composition of the different SBR; Sn-SSBR (Tin Coupled Solution SBR), Duradene 709 and Duradene 711 (Solution SBR). Fig. 1 shows the monomer units for NR and SBR.

Twelve types of carbon black were selected to cover a broad range of structure and specific surface area values. Relevant analytical data of these carbon blacks are summarized in Table 2. One of these carbon blacks (N299) was graphitized by heating it up to 2500 °C in an

Table 1
Composition of the styrene–butadiene rubbers studied in this work

Polymer	Styrene (%)	Butadiene composition (%)		
		1,2-Vinyl	1,4-trans	1,4-cis
D711	18	10	55	35
D709	35	10	55	35
Sn-SSBR	21	63	20	17

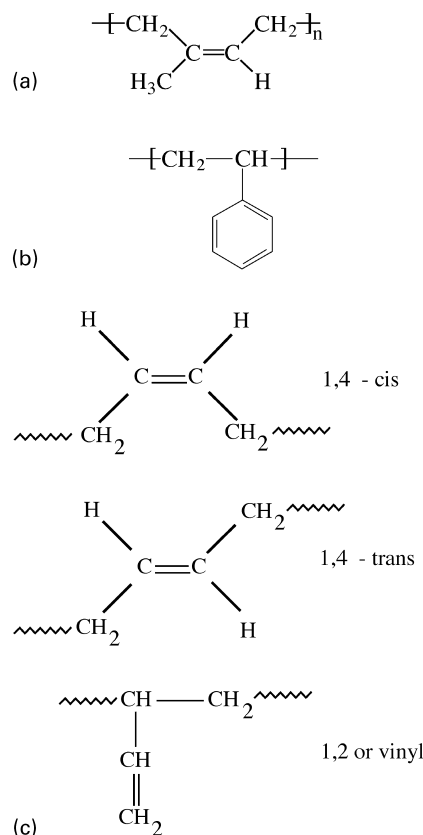


Fig. 1. Monomer units for NR and SBR. (a) NR, (b) styrene and (c) butadiene.

inert atmosphere for 4 h. This process reduces the amount of active sites on carbon black surface diminishing, therefore, filler–polymer interaction, while increasing filler–filler interaction.

2.2. Sample preparation

2.2.1. Cured samples

The cured compounds were prepared according to ASTM 3191 and mixed in a Haake Rheocord 90 internal mixer for 5 min. The mixes were then milled and cylindrical

Table 2
Structure and specific surface area of the carbon blacks used in this work

Carbon black	CDBP (cm ³ /100 g)	N ₂ SA (m ² /g)
N115	94.0	146.4
N134	107.4	144.9
N220	102.4	115.6
N231	86.3	115.8
N299	106.1	102.4
N326	70.1	79.7
N330	91.6	78.6
N358	110.6	79.2
N375	96.5	96.1
N550	89.9	40.9
N660	76.9	35.2
N772	59.8	27.7

samples about 38 mm in diameter were cut and cured at optimum time (t_{90}) + mold lag ($\sim t_{90} + 20\%$) at 160 °C. The type and load of carbon black as well as polymer type of each sample is shown in Table 3.

2.2.2. Uncured samples

Samples with only rubber and carbon black were prepared. For each compound some carbon black loadings were selected around the electrical percolation threshold. Table 4 shows the carbon black type and loadings for the Sn-SSBR compounds. The uncured compounds were also mixed in a Haake Rheocord 90 internal mixer for 5 min. The mixes were milled and cylindrical samples of 38 mm diameter were obtained.

The contact surfaces of samples for electrical measurements were gold sputtered to ensure good electrical contact with the electrodes.

2.3. Techniques

2.3.1. Electrical measurements

An apparatus used to keep the samples at constant temperature during the measurements was built by the authors. The details about this equipment and the measurements were previously reported [19–21] and a brief explanation is given here. Fig. 2 shows a schematic diagram of this equipment. The samples were put between chromium plated cooper electrodes that were in thermal contact with two heaters. The middle sample fitted with a thermocouple was used to control the temperature with a temperature controller. Resistivity was measured with a Keithley Electrometer 6517A equipped with a Keithley 6522 multiplexer card that allows measuring six samples at a time. The Keithley Electrometer was controlled by a personal computer through an RS232 port. A LabWindows/CVI program was developed to record temperature and resistivity both during temperature ramp and at constant temperature, during aging. The samples were put between electrodes at room temperature. The desired temperature was set in the controller and it was reached at a rate of 1 °C/min. The measurements were performed at different temperatures, between 60 and 150 °C, and are indicated in each case.

A small chamber was built to perform measurements of electrical resistivity during thermal aging in vacuum. A Teflon ring with 80 mm external diameter, 60 mm internal

Table 4

Carbon black type and loading for uncured compounds with Sn-SSBR

Carbon black type	Loading (phr)				
N115	30	35	40	45	39
N134	30	35	40	45	39
N220	35	40	45	50	–
N231	30	35	40	45	47
N299	30	35	40	45	43
N299 graph	30	35	40	45	43
N326	35	40	45	50	58
N330	35	40	45	50	45
N358	35	40	45	50	–
N375	30	35	40	45	40
N550	50	55	60	65	58
N660	50	55	60	65	66

diameter and 25 mm height was used as wall. Two cooper disks were used to close the chamber and make electrical contact with the sample inside it. The chamber was evacuated at 3E-3 mbar before starting the measurement and kept at that pressure during the test. The chamber was kept at constant temperature.

2.3.2. Transmission electron microscopy (TEM)

TEM images were taken for different samples before and after thermal aging. Samples were prepared using ultracryogenic microtome and viewed using Philips 300 TEM. The magnification selected allows us to clearly observe some carbon black aggregates/agglomerates and their relative positions. Uncured samples of natural rubber and 39 phr of carbon black N115 were prepared to be measured by TEM.

2.3.3. Bound rubber

The bound rubber measurement was carried out at room temperature using toluene as solvent, since the used elastomers are easily dissolved in it. For the determination, approximately 1 g 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 solvent in a jar for 4 days. The toluene was replaced every day with fresh solvent. After extraction, the rubber and the cage were dried in a hood for 1 h and then in an oven at 125 °C for 5 h. Bound rubber was calculated according to the following equation [22]:

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

where W_B and W_A are the weight of the compound before and after soaking, and m_f and m_p are the weight of the filler and the polymer in the compound in phr.

Uncured compounds with Sn-SSBR and different types of carbon blacks were mixed to measure the amount of bound rubber and how it evolves with thermal aging. For each compound, the carbon black loading was chosen to observe the maximum change of the electrical resistivity

Table 3

Polymer and carbon black type and loading for the cured compounds

Polymer	Carbon black loading (phr)						
	N134	N326	N330	N358	N550	N660	N772
Sn-SSBR	50	50	50	50	50	60	70
D709	50	50	50	50	50	60	70
D711	50	50	50	50	50	60	70

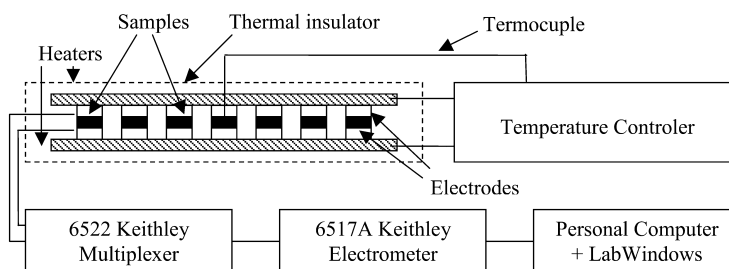


Fig. 2. Schematic diagram of the equipment used to hold the samples at constant temperature and to measure the electrical resistivity.

during aging, i.e. the electrical percolation threshold. The last column in Table 4 shows the loading for each case.

3. Results and discussion

Electrical resistivity of the samples was measured as a function of the time during thermal aging at constant temperature. With varying aging temperature, polymer and carbon black type we were able to analyze how temperature, viscosity and particle size affect the kinetic of flocculation as previously defined. The resistivity values were normalized to their initial values in order to compare all curves at the same scale.

3.1. Is there some aggregates movement?

We will analyze in this section whether Eq. (1) is valid to describe the kinetic of the flocculation process. We will show that no appreciable, if any, carbon black aggregate movement occurs in the polymer matrix during thermal aging. All the samples in this section were cured unless otherwise specified. For the time dependence on uncured compounds the reader is referred to Refs. [19–21].

3.1.1. Aging temperature and time dependence

Fig. 3 shows how electrical resistivity varies with time for several cured compounds aged at different temperatures. Many interesting behaviors can be seen in these four figures. Fig. 3(a) shows the time dependence of electrical resistivity for Sn-SSBR/N330 50 phr cured compound aged at three different temperatures. It is interesting to note that the higher the temperature the slower the resistivity decreases. This behavior does not match Eq. (1). The same dependence was observed for all tread blacks (N134–N358) mixed with Sn-SSBR. However, in the hypothesis of carbon black aggregates movement, the agglomeration process during thermal aging can be understood as the competition between two phenomena. The thermal expansion of the polymer matrix increases the distance among aggregates, while the high temperature activates their motion. The rate of the change in electrical resistivity will depend on which of these processes is the most important. Therefore, the relation: higher temperature \rightarrow higher mobility \rightarrow resistivity decreases faster is not always true. Previous results on

uncured compounds [19–21] showed the opposite behavior, this means faster flocculation rates for the highest temperatures.

For cured Sn-SSBR compounds mixed with carcass blacks (N660–N772) a different behavior was observed as shown in Fig. 3(b). For these compounds electrical resistivity started decreasing for short times (up to 10^4 – 10^5 s) and then increased for longer times, even up to values higher than the initial ones. We will call this behavior *reversion*, which will be the key to understand what is really happening during thermal aging. This reversion has been observed on different compounds and/or at different temperatures and has not been reported previously. Carcass blacks show reversion for all polymer matrices and all measured temperatures. On the other hand, tread blacks show reversion, within our experimental time window, depending on polymer matrix and temperature. Although it seems we have two different behaviors, one for tread blacks and another for carcass blacks, they are actually two expressions of the same phenomenon as we can see in the next figure. Fig. 3(c) shows that for cured D711/N330 50 phr samples there is a gradual transition between the two behaviors previously described. This means that there are not two behaviors but only one, which depends on polymer matrix, carbon black type and temperature. The compounds mixed with Sn-SSBR and tread blacks do not show reversion for temperatures up to 100 °C, at least within our experimental time window. However, when samples are aging at 125 °C a reversion for long time is observed as is shown in Fig. 3(d). It is important to point out here that the reversion appears at higher temperatures (or longer times), depending on polymer matrix, in the following order: NR \Rightarrow D711 \Rightarrow D709 \Rightarrow Sn-SSBR.

Some authors explain the increment of electrical resistivity in terms of break-up of the carbon black network. This means that carbon black aggregates, which were together can be separated by thermal agitation. However, this mechanism cannot explain why the reversion of electrical resistivity depends on oxygen content of the aging atmosphere as was reported previously [9] and also was observed by us (see Fig. 3(d)). In this figure it is possible to note how the atmosphere in which the sample is aged affects its electrical behavior during thermal aging. For all the studied samples the reversion appears before at room conditions than in vacuum. Another interesting thing from

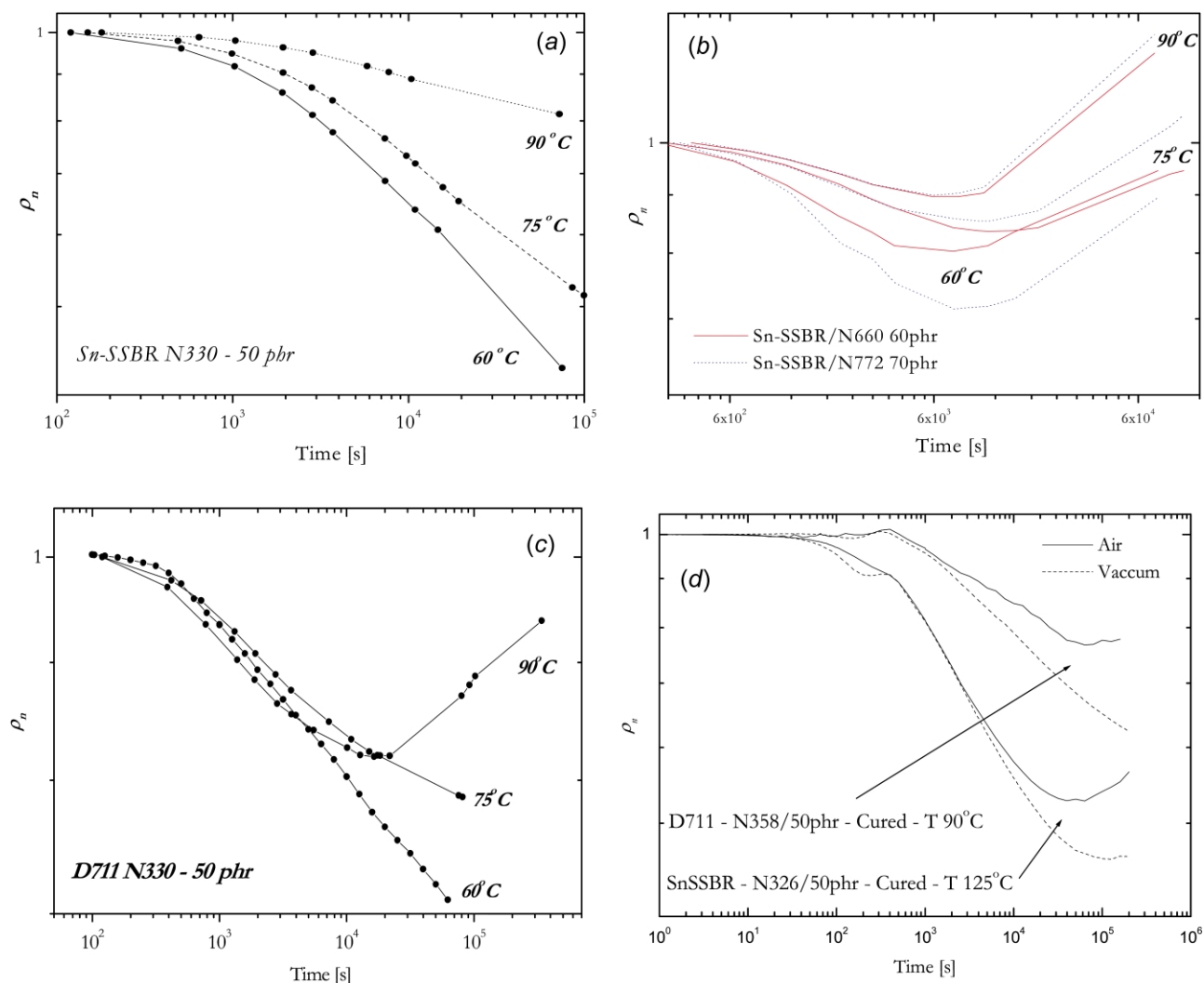


Fig. 3. Normalized resistivity vs. time for several compounds aged at different temperatures.

Fig. 3(d) is that resistivity decrease faster in vacuum than in air. Clearly, it is very difficult to explain this behavior from aggregate movement and break-up of the carbon black network. New mechanism(s) are necessary to take into account this behavior.

3.1.2. Viscosity dependence

Eq. (1) establishes that higher the viscosity the lower the diffusion coefficient and, therefore, slower the rate of flocculation. However, it is not clear, for carbon black rubber compounds, whether pure polymer or compound viscosity should be used. Irrespective of these uncertainties no clear correlation was found neither between pure polymers viscosity nor between compound viscosity and the rate of flocculation for several cured compounds and/or experimental conditions. Although a correlation between pure polymer viscosity and flocculation rate was found in previous works [10,19–21] the latter was not measured at the percolation threshold and comparison among different compounds could be wrong (see Section 3.2.1). As we will

show later, an important point that affects the flocculation rate is the chains mobility, which is actually related to the polymer viscosity.

3.1.3. Particle size dependence

According to Eq. (1) the smaller the particle diameter the higher the diffusion coefficient and, therefore, higher the flocculation rate. This fact has been used for several authors as experimental evidence for the validation of flocculation kinetics through Eq. (1). However, we have found several cases where carbon black with smaller particle size (and the same polymer matrix and carbon black loading) shows slower flocculation rates. Fig. 4 shows how electrical resistivity varies for cured Sn-SSBR compounds loaded with 50 phr and different carbon blacks. As we will show in Section 3.2.1, this fact does not mean necessarily that Eq. (1) is not appropriate to describe the flocculation behavior. The problem is related with the loading dependence of the flocculation rate and whether is valid or not to compare

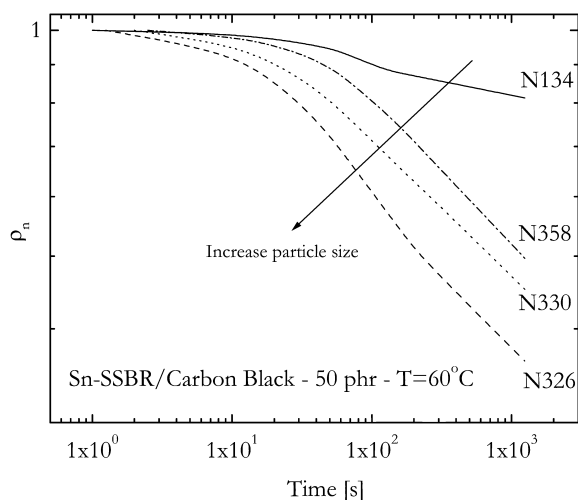


Fig. 4. Variation of electrical resistivity with time, at 60 °C, for compounds with different carbon black type.

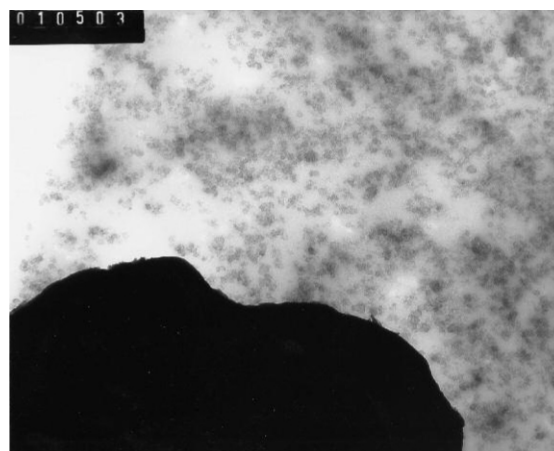
compounds with different carbon black type at the same loading.

We have presented experimental evidence to show that Eq. (1) is not the appropriate model to explain all the observed behaviors about flocculation kinetics. Does it mean there is no aggregate movement in the carbon black filled rubber compounds during thermal aging? not necessarily. Eq. (1) is based on macroscopic hydrodynamics that treats the liquid as a continuum. This picture must clearly break down in rubber compounds, which are composed of polymer chains and, therefore, are heterogeneous. The inadequacy of the Einstein–Stokes equation is one of the characteristics of flocculation kinetics.

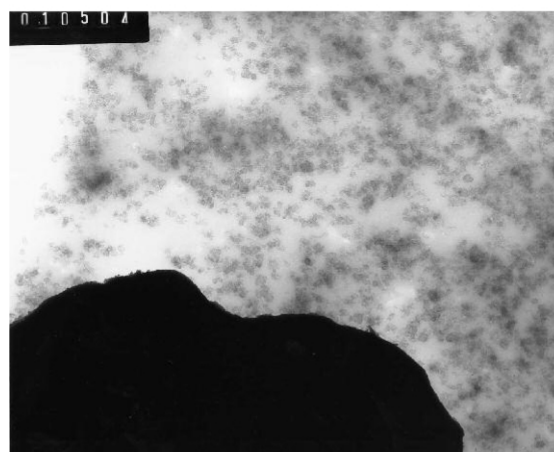
3.1.4. Transmission electron microscopy (TEM)

Cured and uncured compounds with different polymer matrices, different carbon black types at different loading were examined using TEM techniques and no movement could be detected within the resolution range [23]. The samples were aged in situ and out of microscope at different temperatures and times. Based on previous work [19], uncured samples with NR and N115 were selected since they had shown the highest resistivity ratio before and after aging. For this compound changes of seven orders of magnitude were observed in electrical resistivity for loading around percolation threshold. Fig. 5 shows TEM images, before and after aging, for this compound. No measurable changes were detected suggesting that rearrangement of the carbon black aggregates, if it occurs, would be 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 and the image analysis software capabilities.

We have to be careful here and to remember that most of electrical conduction in carbon black filled rubber compounds occurs through tunneling and not by direct contact between neighboring aggregates (depending on carbon



(a)



(b)

Fig. 5. TEM images for NR/N115 30 phr aged at 70 °C for 2 h. (a) Before aging and (b) after aging. The big black area on the corner was taken as reference to localize exactly the same region after aging.

black loading) [26]. The tunneling current depends exponentially on the distance between aggregates; therefore, even small changes in order of the Angstroms or the change in dielectric constant between pairs of aggregates will lead to changes in resistivity. These small changes could be detected only by electrical measurements and not by TEM techniques.

Another difficulty using TEM techniques is that the movement of carbon black aggregates, if it exists, could be restricted in the very thin TEM sample. To avoid this problem studies on different compounds aged before cutting the TEM samples with the microtome were performed showing no appreciable changes on the local density of carbon black aggregates before and after aging. Moreover, Mattson and Stemberg [9] analyzed samples of EPDM filled with carbon black after aging them at 200 °C for 5 days. They observed by SEM analysis that the agglomeration of aggregates did not take place but the agglomerates break-up in smaller aggregates giving a less dense carbon black

network. They conclude from this analysis that the variation of electrical resistivity is not due to carbon black aggregate movement and that another mechanism is necessary to explain this behavior. Anyhow, the important point here is that the flocculation does not involve significant, if any, movements of carbon black aggregates as reported elsewhere [10].

3.2. Experimental evidence for bridging flocculation

From our own results as well as from some published ones [9] we concluded that we had to look for other mechanisms in order to explain the variations of electrical resistivity of carbon black filled rubber compounds during thermal aging. We had some experimental evidence that polymer–filler interaction was playing an important role in this process and we decided to study this interaction by means of bound rubber analysis. Before to do that, and to ensure a valid comparison among different compounds, we analyzed the loading dependence of the variation of electrical resistivity and how the treatment of carbon black surface affects flocculation. With exception of the samples for gamma irradiation, all the samples in this section were uncured in order to maximize the changes on electrical conductivity and to avoid the uncertainties introduced during the vulcanization process.

3.2.1. Carbon black loading dependence

We have observed an interesting load dependence for the variation of electrical resistivity, of carbon black filled rubber compounds during thermal aging, not previously reported. In order to analyze it we defined a new quantity: $I(T, t)$. This is the amplitude of the variation of electrical resistivity, measured at room temperature, before and after aging the sample for t hours at a temperature T . This means the ratio ρ_b/ρ_a (where ρ_b and ρ_a are the resistivity values before and after aging, respectively). It was observed, for these uncured compounds, that $I(T, t)$ depends on carbon black loading and reaches a maximum around the percola-

tion threshold. Fig. 6 shows a typical dependence of $I(100, 20)$ with loading for an uncured compound of Sn-SSBR and N134.

The fact that $I(T, t)$ strongly depends on carbon black loading means that comparisons among compounds with different carbon black loading or different polymer matrix could not be valid. Imagine two compounds with different carbon black types whose $I(T, t)$ loading dependences curves are those shown in Fig. 7. If we compare both $I(T, t)$ at 40 phr we will conclude that the compound A varies its resistivity two orders of magnitude more than compound B, this means compound A flocculates more and faster than compound B. But if we compare both $I(T, t)$ at 60 phr we will obtain exactly the opposite behavior. The same effect is observed if we compare compounds with the same carbon black type but with different polymer matrix. This is reasonable since the percolation threshold depends also on polymer matrix. This load dependence was not previously analyzed and could be the source of contradictory analysis and conclusions about experimental data if it is not taken into account.

The loading dependence of $I(100, 20)$ was measured for the compounds listed in Table 4 and some results are shown in Fig. 8. From these results the maximum value of $I(T, t)$ ($I_{\text{Max}}(T, t)$) was determined for each compound as well as the load (L_{Max}) at which the maximum occurs. Although the general tendency for ($I_{\text{Max}}(T, t)$) is to increase with the specific surface area of carbon black as shown in Fig. 9, it is interesting to note that for similar values of $N_2\text{SA}$ differences of two or three orders of magnitude are found for ($I_{\text{Max}}(T, t)$). A similar tendency is observed if the size of aggregates is considered. This means that the dependence of $I(T, t)$ with carbon black loading cannot be explained only from purely geometric factors. We will see below that a better correlation is obtained by considering the increment of bound rubber which is related with the carbon black surface activity and the filler–polymer interaction. No

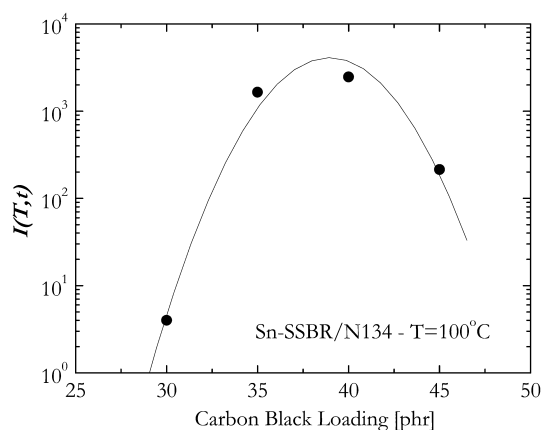


Fig. 6. Load dependence of $I(T, t)$. The line is the best quadratic fit to the experimental data.

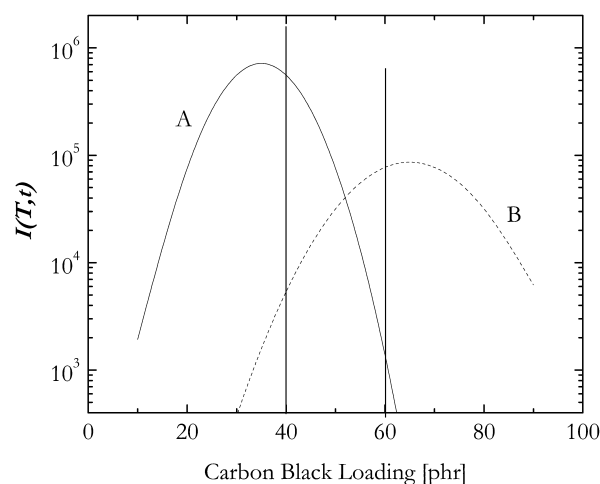


Fig. 7. Load dependence of $I(T, t)$ for hypothetical compounds A and B.

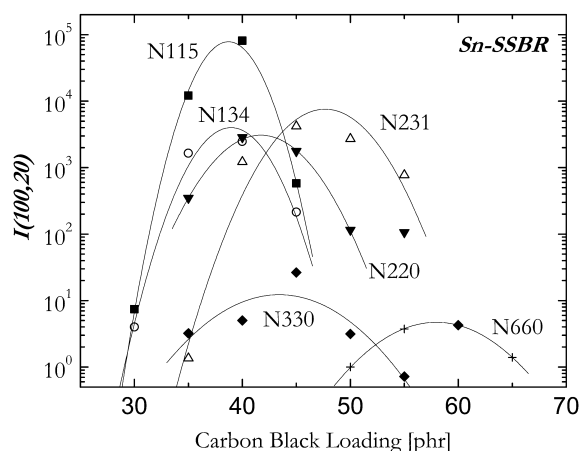


Fig. 8. Load dependence of $I(100,20)$ for Sn-SSBR uncured compounds with different carbon black types. (For clarity, only some curves are shown).

correlation was found between $(I_{\text{Max}}(T, t))$ and the structure parameter of carbon black (CDBP).

3.2.2. Graphitized carbon black

In order to analyze how the carbon black–polymer interaction affects flocculation, uncured compounds were prepared using NR with standard and graphitized N299 carbon black. The graphitization process consists in heating carbon black up to 2500 °C in an inert atmosphere. This process reduces the amount of active sites on carbon black surface diminishing, therefore, filler–polymer interaction. Table 5 shows the carbon black loading and the $I(100,20)$ values for each compound. It is interesting to note that for all analyzed loading the values of $I(100,20)$ for the compounds with standard carbon black are one or two orders of magnitude above the corresponding values for compounds with graphitized carbon black.

This experiment shows the importance of the carbon black–polymer interaction in the variation of electrical

Table 5

Resistivity ratio for graphitized and non-graphitized carbon black/NR compounds at different loading, aged at 100 °C for 20 h

Resistivity ratio	Carbon black loading (phr)			
	30	35	40	45
N299	3.2×10^6	1.15×10^3	1.17×10^2	1.93×10^2
N299/2500 °C	4.6×10^4	2.45×10^2	2.60×10^1	5.30×10^0

resistivity during thermal aging. The only change between each pair of compounds is the treatment of the carbon black surface. Moreover, if carbon black aggregates really move, the graphitized ones should move easier and faster than the standard ones due to the diminished interaction with the polymer chains. Actually, since filler–filler interaction is very strong with graphitized carbon black, those aggregates which do not belong to the percolating cluster before thermal aging, should have a very high trend to join it very fast. This is not what we observe.

The strength of the carbon black–polymer interaction, and how it changes with thermal aging, can be measured through the amount of bound rubber. It was observed that not only the initial amount of bound rubber diminishes for the graphitized carbon black compared to the standard one, but also the increment of the amount of bound rubber during thermal aging was severely restricted as shown in Table 6 (see Section 3.2.3). A more detailed analysis of the relation between the increase of bound rubber and the increase of electrical conductivity is discussed in Section 3.2.3.

3.2.3. Bound rubber measurements

Several uncured compounds were prepared mixing Sn-SSBR and different types of carbon blacks at L_{Max} . Table 6 shows carbon black loading and properties for each compound. The samples were aged in air at 100 °C for 20 h. The amount (percentage) of bound rubber, before and after aging, was determined as it was previously described. For these samples the value of $I_{\text{Max}}(100,20)$ was also calculated. The results are shown in Table 6.

A good correlation between the increment of the amount of bound rubber and the logarithmic increment of $I_{\text{Max}}(100,20)$ was observed. Fig. 10 shows this correlation with the best linear fit to the experimental data. Furthermore, temperature and polymer type dependences (not shown here) of both electrical conductivity and the amount of bound rubber are similar. In all cases the higher the increment of the amount of bound rubber the higher the increment of electrical conductivity ($I(T, t)$). Although correlation does not imply causality, this fact seems to suggest that the increment of the electrical conductivity could be due to the increment of the number of polymer bridges among aggregates instead of aggregates movement, assuming electrical conduction through polymer chains. If this is true a completely different model is needed to explain the variations of electrical resistivity during thermal aging.

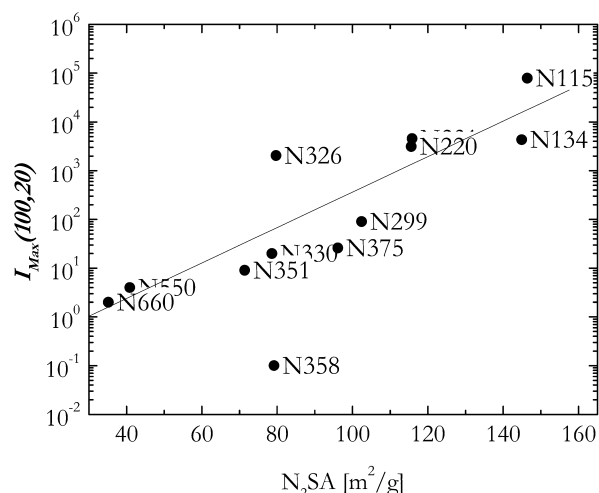


Fig. 9. Correlation between $I_{\text{Max}}(100,20)$ and specific surface area (N_2SA) for all carbon blacks.

Table 6
Bound rubber (BR[%]) and resistivity ratio ($I(100, 20)$) for different uncured compounds

Carbon black	CB loading	CDBP (cm ³ /100 g)	N ₂ SA (m ² /g)	Bound rubber (%), aging time (h)		Resistivity ratio $I(100, 20)$
				0	20	
N115	39	94.0	146.4	24.72	42.90	79000
N134	39	107.4	144.9	32.11	49.59	4330
N231	47	86.3	115.8	20.24	39.13	3130
N299	43	106.1	102.4	27.87	43.97	90
N299(g)	43	106.1	102.4	3.54	5.16	5
N326	58	70.1	79.7	28.00	43.06	2034
N330	45	91.6	78.6	25.44	35.60	20
N375	40	96.5	96.1	25.26	37.21	26
N550	58	89.9	40.9	28.02	33.05	4
N660	66	76.9	35.2	18.72	26.80	2

Let us analyze here two important points: (a) the formation of carbon black-polymer network, and (b) the possibility of electrical conduction through polymer chains.

The formation of carbon black-polymer network. The idea of polymer chains mediating among filler aggregates to form a network is not completely new. Recently, Yurekli et al. [24] showed how the percolation threshold in carbon black filled rubbers is lowered due to the polymer mediation of the filler structure, allowing for long loops and tails that can either bridge filler particles or entangle with one another. In this way, the filler aggregates do not need to be in direct contact to form a network that span the whole material. We assume that something similar happens after thermal aging, even above the percolation threshold. This means that the carbon black-polymer network becomes stronger and bigger due to the increment of polymer bridges between neighbor aggregates instead of carbon black aggregate movement. The carbon black-polymer network becomes stronger due to the increment of the number of polymer bridges between neighbor aggregates, which already had polymer bridges among them before aging; and becomes bigger due to new polymer bridges between carbon black

aggregates, which were disconnected from the percolating cluster before aging. In this way the percolating cluster increases its size. Fig. 11 shows a schematic representation of this idea. The fact that the physical network in carbon black filled rubbers is largely formed by bridging chains between the neighboring aggregates was also shown by using low-resolution proton NMR [25].

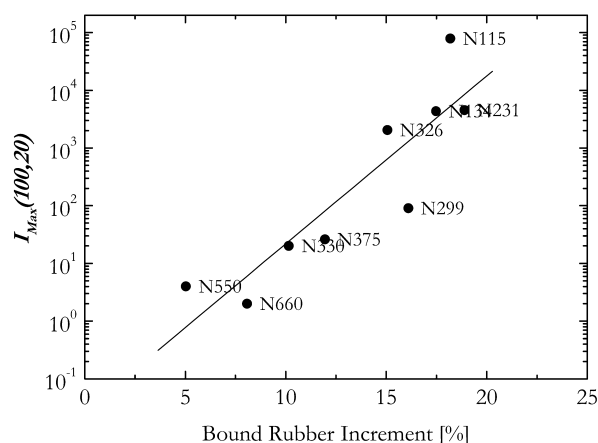


Fig. 10. Correlation between the logarithmic increment of electrical conductivity and the increment of the amount of bound rubber.

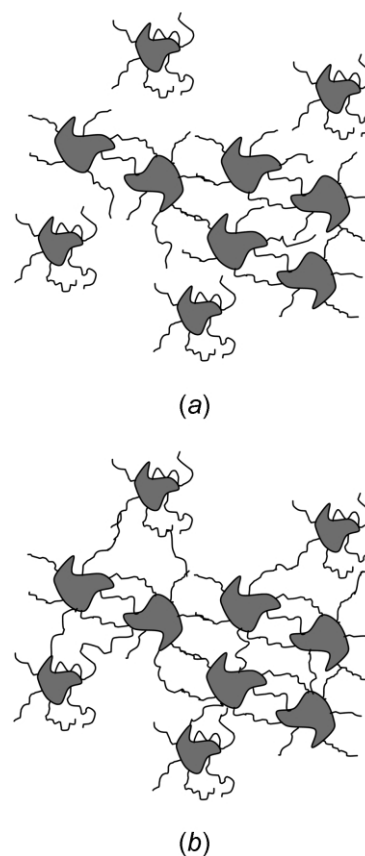


Fig. 11. Schematic representation of bridging flocculation and its evolution during thermal aging. (a) Before aging and (b) after aging. Note how aggregates which do not belong to the percolating cluster before aging are incorporated through polymer chains.

Electrical conduction through polymer chains. If the increment of the amount of bound rubber is the responsible of the increment of electrical conductivity, we should assume that polymer chains take part in the electric conduction process between close aggregates. According to Medalia [26] and Jachym [27] it is possible that polymer chains, grafted to carbon black aggregates, act like conductive hairs or like insulated wires with bare ends. In 1982 Jachym [27] has pointed out that the polymer chains appear as conductors well insulated on all sides, which are bound together by weak van der Waals forces or by mutual entanglement and indentation. He said that the long-chain polymers containing covalent bonds in the carbon skeleton, sufficiently strong to form wide bands, should have conductivity characteristics typical of semiconductors. As a consequence of the slight intermolecular orbital overlapping, the electrons and holes are forced to move in close proximity to the chain. This explains the small electrical conductivity of raw polymers. The presence of conducting powders, like carbon black aggregates, does not change the structure of the polymer chains, and the overlap integral between the conducting particles and the polymer chains is still too small to allow the macromolecules to participate in the transport of charge. The only method of incorporating the polymer into the conduction process is to remove the potential barrier at the ends of the polymer chains. This may be achieved by formation of a chemical bond with another chain or by chemical coupling of macromolecules with conducting particles. The presence of free radicals in the form of unpaired spins on the carbon black surface leads to the formation of chemical bonds between polymer chains and carbon black particles (bound rubber). In such conditions, the carbon black particles are a source of charge carriers, which may move freely through the polymer chains.

In this frame, the increment of bound rubber, which implies an increment of the number of polymer bridges among neighbor aggregates, increases the number of paths between aggregates, and therefore, the electrical conductivity. The gamma irradiation (as we will show below) or the thermal oxidation (see vacuum measurements) decreases the number of chain connections between aggregates and, therefore, increases the electrical resistivity.

The last experiment in the present work, gamma irradiation of carbon black filled rubber samples, was done to support the idea of the electrical conduction through polymer chains.

3.2.4. Gamma irradiation

The irradiation of carbon black filled rubbers modifies polymer structure without any movement or rearrangement of carbon black network. Therefore, any change in the electrical properties before and after irradiation must be attributed exclusively to polymer chains. In order to analyze how electrical conductivity is affected by these changes three samples (Sn-SSBR/N330 50 phr cured) were irradiated

at the Ezeiza Atomic Center Irradiation Plant (Argentina) using Co60, which produces gamma rays at 1.17 and 1.33 MeV. The samples were irradiated at room temperature and at different doses between 50 and 150 kGy.

The resistivity ratios between values before and after irradiation were calculated and plotted vs. irradiation dose. Fig. 12 shows these results together with the best linear fit to the experimental data. A linear increment of the electrical resistivity with irradiation dose can be observed from this figure.

The interaction of high-energy radiation with molecular substances usually involves the following sequence of events [28]. The molecules are first excited and ionized. Secondary electrons are emitted with relatively low speeds and produce many more ions along their tracks. Within 10^{-12} s or so, molecular rearrangements take place in the ions and excited molecules, accompanied by thermal deactivation or the dissociation of valence bonds. As far as subsequent reactions are concerned, bond dissociation is the more important. It leads to the production of ions or radicals whose lifetimes depend on diffusion rates and may be weeks or months in solids at low temperatures. The major effects in polymers arise from the dissociation of primary valence bonds into radicals, whose existence can be demonstrated by chemical methods or by EPR spectroscopy. The dissociation of C–C and C–H bonds leads to different results, degradation and crosslinking, which may occur simultaneously. Anyhow, regardless the kind of process, the irradiation at these doses affects only the polymer structure and not the carbon black one.

During the days after the irradiation it was observed that electrical conductivity increased slowly. Since a recombination of free radicals is produced, as was mentioned before, this fact contributes to support the idea that polymer chains play an active role in the electrical conduction process. This result shows that, at least part of, the electrical conduction takes place through polymer chains.

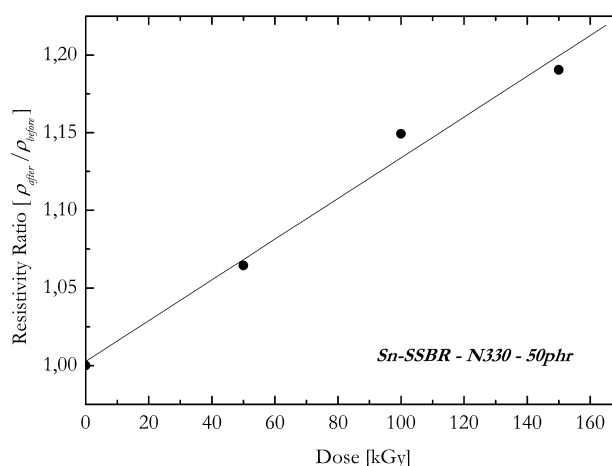


Fig. 12. Resistivity ratio, after and before gamma irradiation, vs. irradiation doses for a cured sample of Sn-SSBR with 50 phr of N330.

3.3. A new model

The detailed discussion about the proposed model is out of the scope of this work. However, we can say in advance that all the observed behaviors can be explained in terms of the competition of two mechanisms. The first one is related to the increment of the amount of bound rubber during thermal aging, which means the increment of polymer bridges among close aggregates. This mechanism increases electrical conductivity and depends on molecular weight of the polymer, aging temperature, carbon black loading and surface activity, and the presence of free radicals due to chain scission during mixing. The second mechanism is related to debonding of polymer chains from carbon black surface or scission of polymer chains by means of oxidization or irradiation. This mechanism decreases the electrical conductivity and depends, mainly, on the polymer microstructure. This model will be treated in depth in the second part of the work.

4. Conclusions

An extensive work was performed to analyze the changes in the electrical properties of cured and uncured carbon black filled rubber compounds under several different aging conditions. Various experiments have been carried out in order to study the influence of carbon black type, loading and surface treatment, polymer type, aging temperature and environment conditions on the electrical properties of these compounds. It was found that no aggregate movement is present during thermal aging and that the flocculation theory, as it was used in previous works, is not a good frame to explain most of the observed behaviors.

A new dependence of the variation of electrical resistivity with carbon black loading during thermal aging was found and a new quantity to analyze this dependence was introduced ($I(T, t)$). It was shown that $I(T, t)$ has a maximum around the percolation threshold. This dependence with carbon black loading, which is different for each carbon black type, can be the source of contradictory data in the literature. We have shown what kind of contradictory conclusions can arise by comparing different compounds at the same loading.

A correlation between the increment of the amount of bound rubber and the logarithmic increment of electrical conductivity was found. This correlation was not previously reported and is the key to understand what is really happens during thermal aging. This fact suggests that the polymer chains take part in the conduction process. In order to support this idea gamma irradiation of the samples was performed and an increment of electrical resistivity was observed. In the second part of this work we will present more experimental evidence to support this hypothesis.

Additionally a simple model, based on creation and destruction of polymer bridges among aggregates, will be presented to give account of all observed behaviors.

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