Flocculation in Carbon Black Filled Rubber Compounds[1]

M. Gerspacher, L. Nikiel, H. H. Yang,
and C. P. O'Farrell, Fort Worth, (USA)
G. A. Schwartz, Buenos Aires (Argentina)

Carbon Black · Flocculation · Microdispersion · Bound Rubber

The properties of carbon black filled rubber compounds are greatly influenced by the extent of filler microdispersion. Dispersion takes place during mixing where carbon black pellets are broken up under shear forces into individual aggregates/agglomerates and distributed throughout the polymer matrix. After the mixing process, both the polymer and filler matrices can rearrange, leading to the reaglomeration of the filler network. This process is called flocculation. In this paper, flocculation is evaluated by the variation of the electrical resistivity of rubber samples aged under different conditions. A broad range of carbon black filled compounds were analyzed. Additionally, the correlation between flocculation and bound rubber was studied.

Flokkulation in rußgefüllten Kautschukmischungen

Ruß · Flokkulation · Rußdispersion · Mikrodispersion · Bound-Rubber

Die Eigenschaften von rußgefüllten Mischungen sind stark von der Mikrodispersion beeinflußt. Die Dispersion erfolgt während des Mischens, wenn Pellets unter Scherung in einzelne Aggregate/Agglomerate abgebaut und in der Polymermatrix verteilt werden. Nach dem Mischprozess kann die Polymer-Füllstoffmatrix sich umorganisieren, wodurch eine Reagglomeration des Füllstoffnetzwerks stattfindet. Dieser, auch als Flokkulation bekannter Prozess, wird in diesem Beitrag über die Variation der elektrischen Leitfähigkeit von in verschiedenen Bedingungen gelagerten Proben untersucht. Zudem wird auch eine Korrelation zwischen Flokkulation und Bound-Rubber durchgeführt.

Properties and performance of rubber compounds are dependent on the filler microdispersion. In general, better filler microdispersion leads to better rubber compound performance. This is true regardless of the type of filler used. However, in this paper only carbon black filled rubber compounds are considered.

The dispersion process generally takes place during shear mixing and it is preceded by carbon black incorporation into the polymeric matrices. After shear mixing, the rubber compound remains, from a thermodynamical point of view, in an unstable state. The polymer chains tend to rearrange themselves leading to a new configuration of the interpenetrated filler and polymer networks. During this rearrangement the interpenetrated carbon black/polymer networks densifies, resulting in changes in electrical and mechanical properties of the compound. This phenomena is referred to as flocculation. This process is thermodynamically driven and is strongly dependent on temperature and as such can be greatly accelerated by thermal aging of the rubber.

Since flocculation leads to interpenetrated carbon black/polymer networks densification, the experimental methods to study this phenomena should be sensitive to detect these changes. Low strain dynamic measurements are capable of probing carbon black network density, however during dynamic measurements, the sample is subjected to external strain and the filler network is deformed, greatly reducing the sensitivity and therefore limiting the applicability of this method. On the other hand, electrical measurements seem to be an ideal choice to study this flocculation phenomena. The resistivity of a rubber compound depends largely on the local fluctuation of density of the interpenetrated carbon black/polymer networks. Overall, the resistivity of rubber compounds is a complicated phenomena depending on a large number of parameters (i.e. carbon black type, carbon black micro-dispersion, polymer type, temperature and others).

The changes in electrical resistivity with thermal aging, as well as the changes of mechanical dynamic properties, have been reported previously [1-6]. However, the reports in scientific and trade literature dealing with flocculation are limited and no single source addressed the issue with sufficient depth to fully understand the mechanism of flocculation. The usual approach to this problem assumes that after the mixing process the filler aggregates will slowly reagglomerate (flocculate). In other words, 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 agglomerate. This increases the density of the percolated conductive filler cluster and therefore decreases the electrical resistivity.

When the aggregates are close enough, they can be attracted to each other by Van der Waals forces. Besides the attractive potential between aggregates of the filler, the flocculation process is determined by diffusion of the aggregates due to Brownian motion to form thermodynamically stable agglomerates. For a given polymer-filler system, the diffusion of the filler aggregates in the polymer matrix play an important role in the flocculation kinetics. Some authors [6–8] calculate the diffusion coefficient (δ) given by the Einstein-Stokes relation as [9]:

$$\delta = kT \frac{1}{6\pi\eta a} \qquad (1)$$

where *k* is the Boltzman constant, *T* the absolute temperature, η the medium

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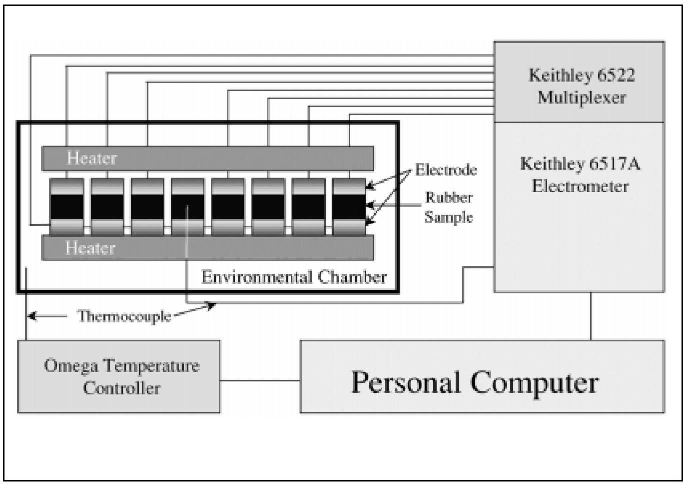


Fig. 1. The experimental setup for electrical measurements

viscosity and *a* the particle diameter. From this equation it can be deduced that at constant temperature, the flocculation rate is controlled by the polymer viscosity and the overall size of the aggregates (radius of gyration, R_g).

Recently, Bohm and Nguyen [7] have studied the flocculation of carbon black in rubber compounds, using the Payne effect as evidence of flocculation. Also, Jager and MacQueen, [8] 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 aging temperatures. In this paper, flocculation of the carbon black filler in uncured rubber compounds will be investigated. Flocculation occurs to a much larger extent in uncured compounds however this process can also be observed in cured rubber. An important distinction between uncured rubber compounds with and without the incorporation of curatives will be demonstrated. It was found during the course of this study that a correlation between bound rubber and flocculation exist. An explanation of these phenomena will be proposed.

Experimental

Test Procedure – Electrical Measurements

All rubber compounds used in this study were mixed using a Haake Rheocord 90 internal mixer. After mixing, the compounds were mill sheeted to 12 mm thickness and cylindrical samples of about 38 mm in diameter were obtained. Top and bottom faces of the samples were gold sputtered to ensure good electrical contact with the electrodes and eliminate the contact resistance. The samples were prepared using a wide range of elastomers ranging from solution SBRs to Natural Rubber.

Fig. 1 shows the equipment built by the authors that allows conducting the measurements at constant temperature. The samples were placed between chromium plated copper electrodes that are 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 measurement of up to ten samples at a time. The electrometer was controlled by a personal computer through an RS232 port. More detailed description of the equipment and the experimental technique can be found elsewhere [10]. The samples were placed between electrodes at room temperature and the initial volume resistivity measurements were made. This first measurement is the reference point to calculate the extent of the resistivity change. Next, the temperature was increased to 60 °C, 80 °C, and 100 °C respectively. After the temperature reaches the set mark (at a rate of 1 °C/min), the volume resistivity data were collected for 24 hours. Finally, the samples were cooled 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 the resistivity decrease from the slope of the regression line fitted to the volume resistivity data vs. time. The flocculation intensity is calculated as the orders of magnitude change in the volume resistivity value between the corresponding room temperature measurements. The details of temperature sequences and performed measurements are explained in *Figures 2a* and *2b*.

Test procedure – Bound rubber

The bound rubber measurement was conducted at room temperature using toluene as the extracting solvent. Approximately 1 gram of rubber compound was cut into small pieces and placed into a stainless-steel wire-mesh cage of known weight. The cage was then immersed in 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 at 125 °C for another 5 hours. Percentage of the bound rubber was calculated according to the following equation:

$$\text{Bound Rubber }(\%) = \frac{W_B(m_f + m_p) - W_A m_f}{W_A m_p} \tag{2}$$

where W_B and W_A are the mass of the compound after and before extraction, m_f and m_p are the mass of the filler and the polymer in the compound.

Test procedure – Low strain, low frequency dynamic properties

The dynamic measurements were performed on the ARES (Advanced Rheometrics Expansion System) system using the parallel plate geometry [11]. Samples were cured between aluminum plates of 25 mm in diameter. Typical sample thickness was maintained at about 2.5 mm. The test was performed at a frequency of 1 Hz and a strain sweep from 0.1 to 10%. An environmental chamber controlled the temperature at 30 °C.

Test procedure – High frequency dynamic properties

The high frequency dynamic data were collected using the Sid Richardson Carbon Co. developed ultrasonic spectro-

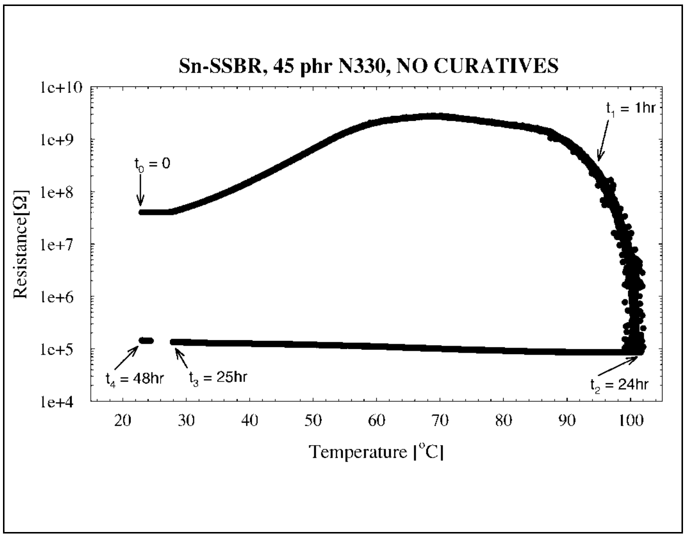


Fig. 2a. The resistance of the rubber compound monitored as a function of time and aging temperature

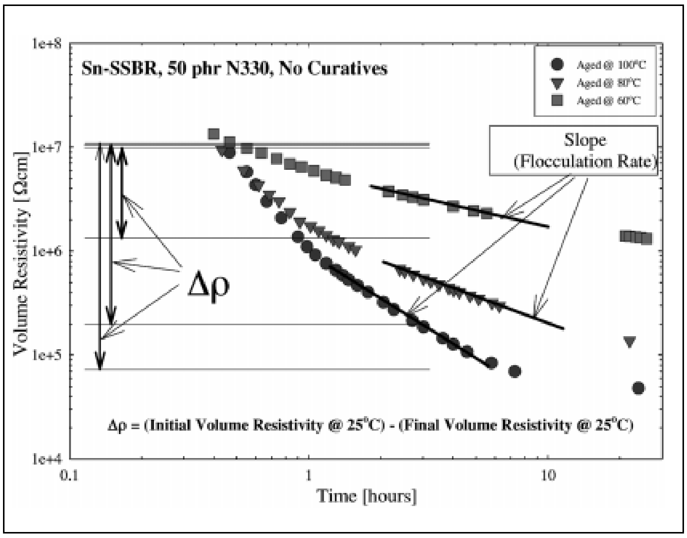


Fig. 2b. The volume resistivity monitored as a function of time at constant aging temperature

meter operating at frequency 1 MHz [12–14]. The instrument is capable of performing an automatic temperature sweep in the range of − 90 °C to + 60 °C. In this measurement, only room temperature data were collected. The details of this method were described previously [14]. A higher attenuation coefficient value indicates more immobilization of polymer chains due to increased polymer/filler interaction in the system after flocculation.

Test procedure – Transmission electron microscopy (TEM)

TEM pictures were collected for samples before and after thermal aging. In addition, the in-situ aging, i.e. heat aging in the TEM chamber, was performed. Samples were prepared using ultra-cryogenic microtome and viewed using Philips 300 TEM [15]. The magnification selected allows us to clearly observe single carbon black aggregates/agglomerates and theirs relative positions.

Experimental results

It was observed during the course of this study that flocculation is evident in the uncured stage and in cured rubber compounds. Flocculation happens also during the curing process. As a consequence of these finding the paper will be divided to cover separately the measurements performed on the uncured and cured rubber compounds. In addition, the different experimental techniques applied will be discussed in separate subsections.

Uncured rubber compounds electrical measurements

Rubber compounds prepared with four different polymers (Natural Rubber, Duradene 711, Duradene 709, and Sn-SSBR) and carbon black (N330) loading ranging from 30 to 60 phr were prepared with no chemical curatives. The volume resistivity was monitored for each sample according to the procedure described above. The data in *Table 1* indicate that there is a strong dependence of flocculation intensity on aging temperature. For the samples with the same composition, higher aging temperature results in larger flocculation intensity. In addition, as it can be observed in Table 1, the flocculation intensity depends on carbon black loading and seems to exhibit a maximum around the percolation threshold. The data in Table 1 demonstrate that the flocculation intensity is also polymer dependent. One of the hypothesis based on Equation 1, suggests that polymer viscosity is responsible for these difference. In *Fig. 3*, the flocculation intensity was plotted as a function of polymer Mooney viscosity for several different carbon black loadings. As expected, the lower polymer viscosity leads to the higher flocculation intensity.

For Natural Rubber, a simple way to reduce the viscosity is to premasticate the polymer. Data obtained for premasticated Natural Rubber indicate larger flocculation intensity as compared to “virgin” polymer. The dependence of flocculation intensity on polymer viscosity and aging temperature confirms the fact that the flocculation is a diffusion-controlled process (Equation 1). In order to further prove this fact the analysis of the flocculation intensity versus carbon black size (grade) was performed. Twelve different grades of carbon black were selected and rubber compounds using Sn-SSBR were prepared. Sn-SSRB was used because it exhibits the highest flocculation intensity. As was shown above, the changes in resistivity values after and before aging increase significantly when loading approaches 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 insignificant effects on resistivity.

Two parameters were extracted from the data obtained for each compound. One is the loading corresponding to the maximum of the flocculation that is equivalent to the percolation threshold

Tab. 1. The flocculation intensity obtained for various rubber compounds

Sample No:	Polymer	Carbon Black Grade	Carbon Black Loading [phr[	Aging Temperature [°C]	Flocculation Intensity
1	Sn-SSBR	N330	40	60	1.898
2	Sn-SSBR	N330	45	60	1.650
3	Sn-SSBR	N330	50	60	1.515
4	Sn-SSBR	N330	60	60	0.786
5	Sn-SSBR	N330	40	80	2.246
6	Sn-SSBR	N330	45	80	1.920
7	Sn-SSBR	N330	50	80	1.664
8	Sn-SSBR	N330	60	80	0.883
9	Sn-SSBR	N330	35	100	3.000
10	Sn-SSBR	N330	40	100	3.542
11	Sn-SSBR	N330	45	100	3.300
12	Sn-SSBR	N330	50	100	2.394
13	Sn-SSBR	N330	60	100	2.055
14	Natural Rubber	N330	30	80	2.249
15	Natural Rubber	N330	35	80	3.193
16	Natural Rubber	N330	40	80	3.952
17	Natural Rubber	N330	45	80	2.282
18	Natural Rubber	N330	50	80	1.924
19	Natural Rubber	N330	30	100	4.282
20	Natural Rubber	N330	35	100	5.265
21	Natural Rubber	N330	40	100	3.930
22	Natural Rubber	N330	45	100	2.597
23	Natural Rubber	N330	50	100	2.168
24	Natural Rubber	N330	60	100	1.516
25	Duradene 711	N330	40	100	0.533
26	Duradene 711	N330	50	100	0.489
27	Duradene 711	N330	60	100	0.012
28	Duradene 709	N330	40	100	1.975
29	Duradene 709	N330	50	100	1.400
30	Duradene 709	N330	60	100	1.163
31	Natural Rubber	N299	30	100	6.507
32	Natural Rubber	N299	35	100	3.061
33	Natural Rubber	N299	40	100	2.285
34	Natural Rubber	N299	45	100	2.068
35	Natural Rubber	Graphitized N299	30	100	4.665
36	Natural Rubber	Graphitized N299	35	100	2.389
37	Natural Rubber	Graphitized N299	40	100	1.409
38	Natural Rubber	Graphitized N299	45	100	0.723

Table 2. The flocculation intensity vs. mixing time obtained for Duradene 709 loaded with 30 phr N115. Aging at 100 °C for 24 hours

Sample No.	Mixing Time [min.]	Flocculation Intensity
1	1	0.884
2	2	2.215
3	3	3.264
4	5	6.021
5	10	7.209

and the other is the maximum flocculation intensity. As it can be seen from *Fig. 4* the flocculation intensity is larger for smaller tread grade carbon black and is lowest for larger carbon blacks (carcass grades). The case of N326, N330, and N358 suggests that the structure (CDBP defined by ASTM D3493) of carbon black also plays an important role. These three grades of carbon black have essentially the same specific surface area but significantly different structure. The statistical analysis presented in *Fig. 5* indicates that the flocculation intensity increases with increasing N_2SA and decreasing CDBP. In general, the radius of gyration, R_g, is decreasing with increasing N_2SA and with decreasing CDBP. For the three carbon blacks mentioned above, the flocculation was minimal for rubber compounds prepared with N358 (high structure), and was largest for compounds prepared with N326 (low structure).

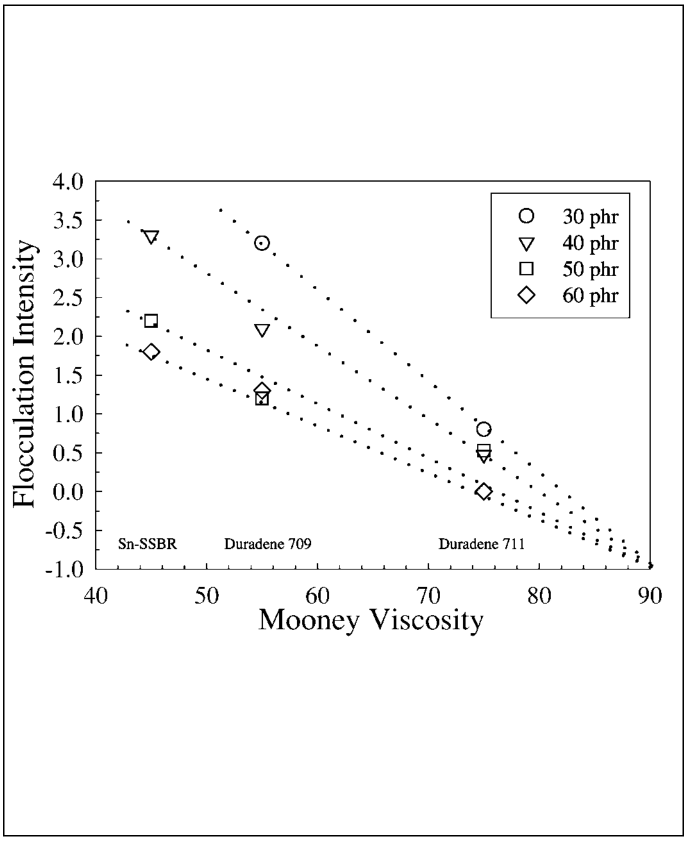


Fig. 3. The flocculation intensity plotted as a function of polymer viscosity. Aging at 100 °C for 24 hours

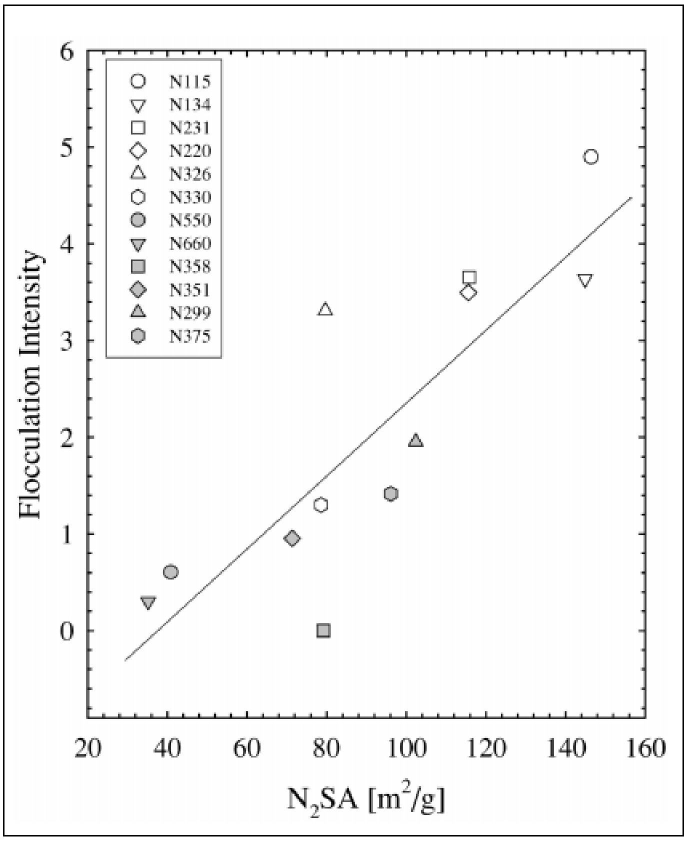


Fig. 4. The flocculation intensity vs. nitrogen surface area for different grades of carbon black compounded with Sn-SSBR. Aging at 100 °C for 24 hours

Flocculation, as defined above, depends on the initial carbon black network density (microdispersion). This network density could be altered by different level of carbon black dispersion. The simple way to alter filler dispersion is to change the mixing time. In the experiments presented in *Table 2*, the mixing time ranged from 30 sec. to 10 minutes. The carbon black loading was chosen around the percolation threshold to maximize the effect. The measured flocculation intensity as can be seen in Table 2, increases with increasing mixing time. With improved dispersion, more carbon black surface is exposed for interactions with polymer chains. This in turn leads to increased flocculation. This is a very important observation and supports a model of flocculation based on simultaneous rearrangements of polymer and carbon black networks.

To test the proposed model, the flocculation intensity was measured in rubber compounds containing an untreated N299 and graphitized N299 (at 2500 °C) carbon black. Graphitization of carbon black increases the filler-filler interaction, reduces the filler-polymer interactions [14] and adversely affects microdispersion. As is shown in Table 1, the flocculation intensity is lower for the compounds with graphitized carbon black for a wide range of carbon black loadings.

Typical rubber compound contains significant amount of processing oil. Oil improves processibility but reduces the shear forces during mixing leading to a poorer dispersion. The competition between flocculation intensity increasing with better dispersion and decreasing with decreasing compound viscosity is presented in *Table 3*. The maximum of the flocculation intensity observed for an oil loading of 10 phr indicate that below this loading the oil content does not hinder the effective dispersion process. Above 10 phr of oil, the compound viscosity decreases and reduces filler dispersion, which in turn decreases the flocculation intensity.

Table 3. The flocculation intensity obtained for compounds with different oil loading. Compounds were prepared with Sn-SSBR and 40 phr N115. Aging at 100 °C for 24 hours

Sample No.	Oil Loading [phr]	Polymer Loading [phr]	Flocculation Intensity
1	0	100	2.365
2	5	95	4.546
3	10	90	4.892
4	15	85	4.431
5	20	80	3.513
6	25	75	2.362

Uncured rubber compounds high frequency measurements

One of the methods to measure the amount of polymer filler interactions is to apply high frequency dynamic measurements. The samples for this experiment were prepared as disks of 38 mm

Table 4. High frequency viscoelasticity data obtained for rubber compounds before and after 24 hours aging at 80 °C. Compounds were prepared with Sn-SSBR and 50 phr N330

Sample No.	Sample Treatment	Longitudinal Attenuation Coefficient, α_L [mm^{-1}]
1	Before Aging	0.214
2	After 24 hours aging at 80 °C	0.246

in diameter and variable thickness in order to apply the Beer law to calculate the attenuation coefficient. The measurements presented in Table 4 indicate that the attenuation coefficient increases for aged rubber samples. Thermal aging leads to increased polymer/filler interactions and increased flocculation. The aggregates that don't belong originally to percolated cluster will contribute the most to this effect.

Increased polymer/filler interactions should also be manifested by an increased amount of bound rubber. Based on the previous work [5], it was expected that the amount of bound rubber would increase with increasing mixing time and increasing aging temperature. The experimental results will be presented in the following paragraph.

Uncured rubber compounds bound rubber

It was discovered during the course of this study that the amount of bound rubber correlates well with the flocculation intensity. The data presented in *Figs. 6* and *7* show that the higher the amount of bound rubber, observed for the compounds prepared with Sn-SSBR, the higher the flocculation intensity. In addition, the bound rubber increases with increasing aging temperature, similarly to the flocculation intensity. Bound rubber measurements can provide very useful informations about the filler network density. As can be seen from *Fig. 8*, the toluene extract is clear or black depending on the carbon black loading and the thermal aging history. From the TEM picture of the unaged rubber compound loaded with carbon black around percolation level one could easily identify the "loose" aggregates that will be extracted by toluene from the compound causing the dark color of the extract. These aggregates participate in polymer-filler interactions, however, they are not a part of a large conducting cluster. The aging densifies the interpenetrated carbon black/polymer networks in such a way that previously "loose" aggregates becomes a part of the network as manifested in *Fig. 9* where the transparency of the toluene extract was evaluated. Before the aging process, the "loose" aggregates can be identified even for the compounds above percolation threshold. The aging practically eliminates "loose" aggregates. This also could be observed for the compound around percolation threshold. Also very interesting is the mixing time dependence for compounds loaded with 50 phr N115. At the beginning, when the dispersion is very poor, the carbon black network is very dense. Later, with increasing mixing time the color of toluene extract become darker indicating that some aggregates are extracted by the solvent. Further mixing, minimize the amount of "loose" aggregates as indicated by the lighter color of the extract. These results are consistent with the resistivity and dynamic properties measurements.

Uncured rubber compounds low strain, low frequency dynamic measurements

Dynamic measurements are relatively difficult to perform on uncured compounds. During the course of these experiments, the samples were aged in the uncured stage. Next, the compounds were cured using electron beam radiation at the Bridgestone/Firestone research facility in Akron, Ohio. This is a low temperature process so the samples remain at room temperature all the time. In order to be cured by the electron beam procedure, the sample does not have to contain the conventional sulfur-curing package. An example of the data obtained during these measurements is presented in *Fig. 10*. The storage shear modulus G'_{MAX} increases after thermal aging for each sample under investigation indicating that the additional connections between carbon black aggregates were created during the aging process.

During curing behavior electrical measurements

All the above examples used rubber compounds prepared without curatives; in the following examples the compounds with curatives will be considered. Usually, mixed rubber sample will contain the curative package and will be vulcanized at elevated temperatures in order to form the final product. During the vulcanization process, the temperature induced motions of both polymer and carbon black networks lead to a new configuration resulting in reduction of the rubber compound resistivity. Data presented in *Table 5* show that indeed the volume resistivity decreases with increasing degree of vulcanization.

Cured compounds electrical measurements

Flocculation could be also observed in cured rubber compounds. However, the effect is significantly smaller than in uncured compounds. The crosslinking reduces significantly the mobility of polymer chains and blocks carbon black aggregates in position. A simple experiment was conducted, where the polymer crosslinking density was controlled by different sulfur content in the sample. The flocculation intensity and the flocculation rate decrease with increasing sulfur content (see *Fig. 11*). The changes observed in this experiments are small, however significant. It is important to note that

Table 5. Volume resistivity obtained for the rubber compounds at different cross-link densities. Compound: Duradene 706, 30 phr N220. Curing temperature: 138 °C. $t_{90} = 65$ min

Sample No.	Curing Time [min.]	Volume Resistivity [Ωcm]
1	0	2.71×10^9
2	15	2.10×10^9
3	30	6.82×10^7
4	35	3.40×10^6
5	40	6.87×10^5
6	45	5.24×10^4
7	50	4.51×10^4
8	55	4.20×10^4
9	60	2.67×10^4
10	65	2.37×10^4
11	80	2.49×10^4
12	110	2.64×10^4

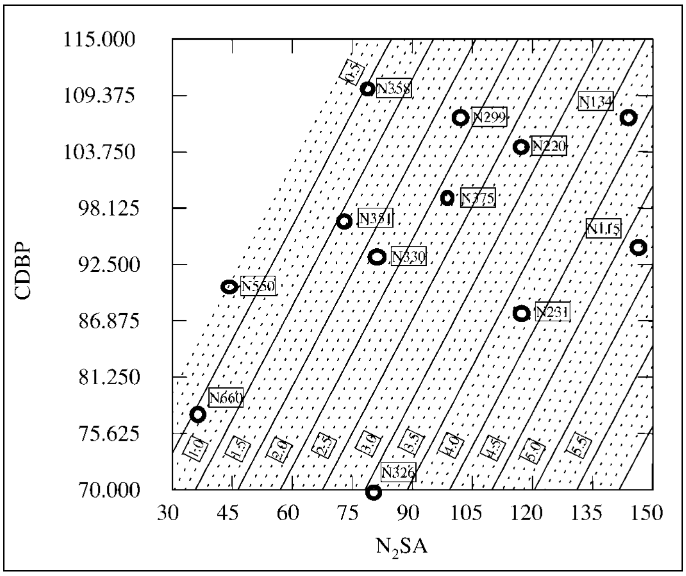


Fig. 5. Contour plot of the flocculation intensity derived from statistical model

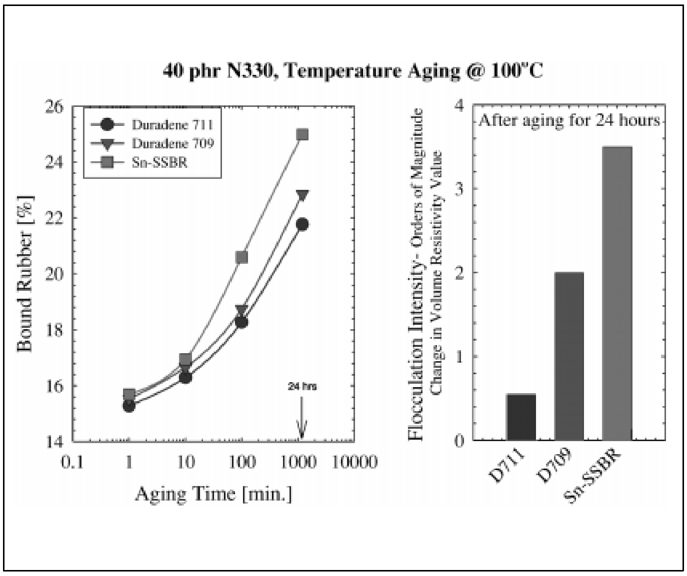


Fig. 6. Correlation between the bound rubber and the flocculation intensity obtained for different polymers and aging times

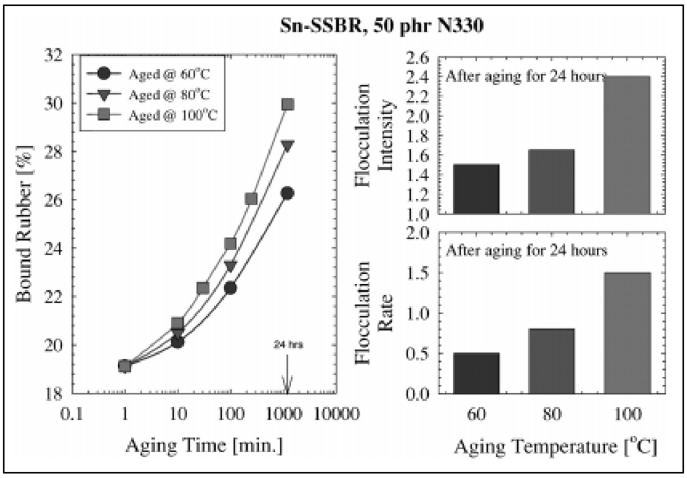


Fig. 7. Correlation between the bound rubber and the flocculation intensity obtained for Sn-SSBR loaded with 40 phr N330 and aged at different temperatures

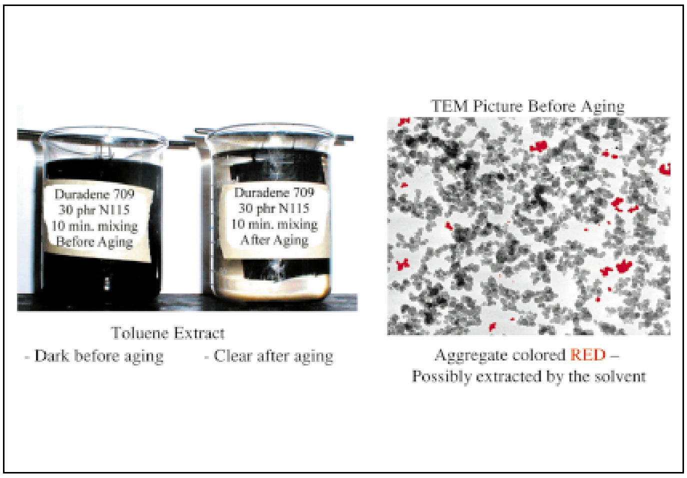


Fig. 8. TEM picture of rubber compounds loaded with carbon black around percolation threshold. Color comparison of the toluene extract from the compounds before and after aging

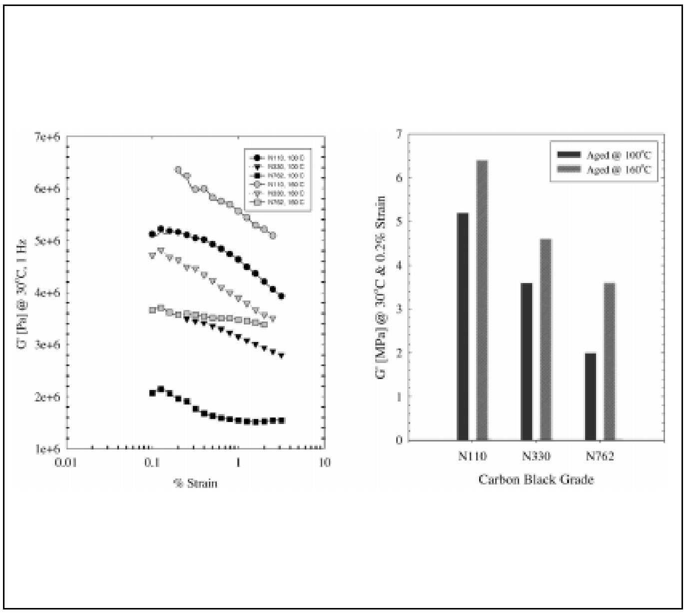
the thermal aging for these samples was performed on cured samples.

Cured rubber compounds low strain, low frequency dynamic measurements

The following data were obtained for samples with curatives aged in the uncured stage and then cured before performing dynamic measurements. The samples were prepared using three different polymers (Sn-SSBR, Duradene 706, and Duradene 709) and N234 with loading ranging from 35 to 50 phr. One set of samples was cured after short storage (about 2 hours) at room temperature, and the other sets were cured after aging for 24 hours at 60 °C, 80 °C, and 100 °C. In every single case the storage and loss shear modulus (G'_{MAX} and G''_{MAX}) were reduced as compared to unaged samples. The data are presented in *Table 6*. The rheometer measurements performed on aged samples suggests that partial curing occurs during aging. M_L was higher, M_H was lower, and the t_{90} was reduced. The extent of the partial curing was proportional to aging temperature. In addition, the electrical measurements (not shown here) indicate that the flocculation is reduced significantly for samples containing the curatives.

Discussion

It was shown that the variation of the electrical resistivity observed during aging depends on the carbon black type and loading, the polymer matrix, the aging temperature, and presence of curatives. 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 caused by Brownian motion of carbon black aggregates and second, the contribution from the polymer rearrangement as manifested by increased polymer/filler interactions.



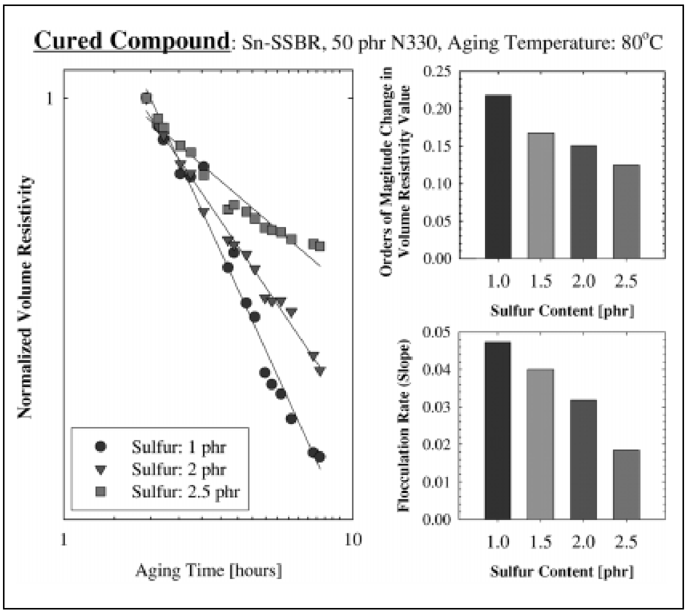


Fig. 9. Color of the toluene extract rating and bound rubber content obtained for the rubber compounds around and above percolation

Fig. 10. Low strain dynamic properties obtained for samples aged at various temperatures and then cured by electron beam

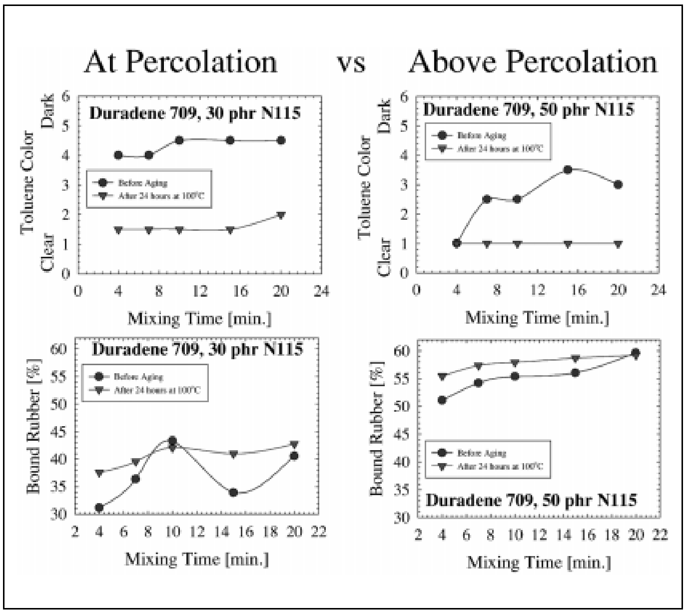


Fig. 11. The flocculation intensity obtained for cured rubber compounds prepared with various amount of curatives. Compounds were prepared with Sn-SSBR and 50 phr N330. Aging at 80 °C for 24 hours

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 [16]. Therefore, the 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. Two separate sets of the Transmission Electron Microscope (TEM) experiments were performed in order to try to observe the movement of carbon black aggregates during aging. In one group, the samples were prepared using compounds before and after aging. In the second set of samples, the aging was performed in-situ in TEM chamber. 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 and the image analysis software capabilities. However, at the same time the measurements performed during this study support the fact that diffusion process as described by Equation 1 can describe most of the obtained data. However, some anomalies are observed for cured compounds. These cases are currently under investigation and will be reported in a separate paper.

The bound rubber analysis shows a parallel evolution between the amount of bound rubber in the percolating cluster and the increase of the flocculation intensity as measured by electrical resistivity. 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. When polymer/filler interactions play a significant role, thermodynamically driven movement of polymer chains is rearranging in space the attached carbon black aggregates. 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-Hashem [17] suggested that the strong interaction between carbon black and rubber led to band-like conduction. More studies are in progress to verify these hypotheses.

Table 6. Low strain dynamic properties (G'_{MAX} and G''_{MAX}) obtained for samples aged at 80 °C and then conventionally cured

Sample No.	Polymer	Carbon Black Loading [phr]	Aging at 80 °C	G'_{MAX} [MPa]	G''_{MAX} [MPa]
1	Duradene 706	35	NO	2.48	0.335
2	Duradene 706	40	NO	3.11	0.439
3	Duradene 706	45	NO	4.26	0.601
4	Duradene 706	50	NO	5.48	0.794
5	Duradene 706	35	YES	2.09	0.331
6	Duradene 706	40	YES	2.54	0.423
7	Duradene 706	45	YES	3.54	0.572
8	Duradene 706	50	YES	4.64	0.764
9	Duradene 709	35	NO	2.77	0.399
10	Duradene 709	40	NO	3.60	0.551
11	Duradene 709	45	NO	4.72	0.749
12	Duradene 709	50	NO	6.35	1.04
13	Duradene 709	35	YES	2.31	0.351
14	Duradene 709	40	YES	3.17	0.497
15	Duradene 709	45	YES	4.30	0.698
16	Duradene 709	50	YES	5.69	0.957
17	Sn-SSBR	35	NO	1.79	0.192
18	Sn-SSBR	40	NO	2.62	0.325
19	Sn-SSBR	45	NO	3.70	0.492
20	Sn-SSBR	50	NO	5.25	0.756
21	Sn-SSBR	35	YES	1.70	0.170
22	Sn-SSBR	40	YES	2.35	0.279
23	Sn-SSBR	45	YES	3.24	0.434
24	Sn-SSBR	50	YES	4.83	0.694

Finally, it is possible to explain the flocculation intensity dependence with loading from the percolation theory. It is known from the percolation theory [18] 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, the 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 conductivity takes place through the percolated carbon black network and small changes on this network does 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.

Conclusions

Carbon black flocculation in uncured rubber compounds was investigated. Various experiments to study the influence of the carbon black grade and loading, the polymer type, and the aging temperature on the flocculation rate and intensity have been conducted. It was found that the flocculation could 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 increase in the amount of bound rubber with aging time was found and investigated. This increase of the 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 the flocculation as well as about the mechanism of the interaction between polymer and carbon black.

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The authors

Dr. M. Gerspacher is Director of Basic Research, Dr. L. Nikiel is Research Physicist, Dr. H. H. Yang is Senior Research Engineer, and Dr. C. P. O’Farrell is the Vice President of Research and Development at Sid Richardson Carbon Company in Forth Worth, Texas. Dr. G. A. Schwartz is affiliated with the Physics Department at the University of Buenos Aires in Argentina.

Corresponding author
Dr. Michael Gerspacher
Sid Richardson Carbon Co.
4825 North Freeway
Forth Worth, Texas USA