Influence of Carbon Black Dispersion on the Thermal Diffusivity of an SBR Vulcanizate

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ABSTRACT: There are few investigations of the influence of filler dispersion on the thermal diffusivity of carbon black rubber compounds. In this article, experimental results of a cured styrene-butadiene rubber (SBR) compound are presented in the range of temperatures between 210 and 350 K at four levels of dispersion obtained in a laboratory mill. The results of thermal diffusivity measurements are discussed in the frame of competitive mechanisms appearing during mixing and involving the breakdown of agglomerates into aggregates and particles in the rubber matrix. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1379–1385, 1999

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INTRODUCTION

In a recent article, we presented an improved method for the determination of the thermal diffusivity of elastomeric compounds. By using this method, the thermal diffusivity can be estimated through the glass transition range.¹

The determination of the degree of cure during vulcanization and of the thermal behavior of a vulcanized sample during its use are important objectives in the design of the material. For this purpose, the general differential equation for the transient conduction of heat, defined as

$$\rho c \frac{\partial \theta}{\partial t} = \nabla (k \nabla \theta) + \frac{dQ}{dt}$$
(1)

must be solved in order to obtain the temperature θ at any time considering the geometry and the

boundary conditions of the sample. In eq. (1), ρ , c, and k are the density, specific heat, and the thermal conductivity of the material, respectively. Q is the reaction heat up to time t. Knowledge of the thermal parameters, k, c, and Q are essential for the correct prediction of the behavior of the material in a given situation.

When a completely cured elastomeric compound is considered (dQ/dt = 0), eq. (1) can be rewritten in the one-dimensional case as

$$\frac{\partial}{\partial x} \left(k \ \frac{\partial \theta}{\partial x} \right) = \rho c \frac{\partial \theta}{\partial t}$$
(2)

$$\frac{\partial^2 \theta}{\partial x^2} + \frac{1}{k} \frac{\partial k}{\partial \theta} \left(\frac{\partial \theta}{\partial x} \right)^2 = \frac{1}{\alpha} \frac{\partial \theta}{\partial t}$$
(3)

where $\alpha = k/c\rho$ is the thermal diffusivity of the material. This parameter relates the energy flux to the energy gradient.

According to the literature, the thermal properties of elastomeric compounds depend on the temperature.²⁻⁶ There is evidence, in respect to

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 Table I
 Compound Composition

Ingredient	phr		
SBR1712	137.5		
Carbon black N339	50.0		
Aromatic oil	5.0		
Zinc oxide	3.0		
Stearic acid	1.5		
Antioxidant	1.5		
Paraffin	3.0		
TBBS	1.0		
Sulfur	2.0		
PVI	0.1		

filled rubber compounds, that α decreases at high temperatures from 125 to 350 K and a step change in diffusivity appears at the glass transition temperature.¹

The mechanical performance of vulcanized samples is very dependent on its process history. In fact, mechanical moduli, fatigue life, and tensile strength are properties of the compound that limit its use. In the case of carbon black-filled rubbers, the dispersion of the filler in the polymer matrix is one of the most important facts to be considered when optimum mechanical properties are desired for the compound. Although there are several investigations dealing with the influence of carbon black dispersion on the mechanical properties of compounds, there is no similar knowledge in the area of the thermal properties.⁷ The aim of this article was to present some experimental evidence of the influence of the dispersion level on the thermal diffusivity of a carbon blackfilled styrene butadiene rubber (SBR) in the range of temperatures between 125 and 350 K.

EXPERIMENTAL

Materials

In this work, an SBR compound was prepared with the composition given in Table I. The compound was mixed in a Farrel mixer of 1.5 L at 296 K, with cold running water, at 77 rpm and a ram pressure of 700 kPa. A masterbatch was prepared without the curatives with the following cycle: 0 min, elastomer; 1 min half of black; 2 min rest of black and rest of ingredients; 3-min sweep; and dump at 478 K.

Curatives were added to the masterbatch in a two-roll mill with the rolls at 323 K. The mill used in this work has a size of 150×250 mm, with a speed of the slow roll of 24 rpm and a ratio between the slow and fast rolls of 1:14. The compound was banded in the roll mill and three cuts from alternate ends were made allowing 20 s between each cut. The mixing cycle was concluded by passing the rolled batch endwise through the mill six times with a nip gap size of 0.8 mm.

Once this stage was completed, four batches were prepared at several mill-mixing times in order to achieve different levels of carbon black dispersion. Batch a was banded at 0.42 min; batch b, at 1.78 min; batch c, at 3.80 min; and batch d, at 5.23 min. In each case, the batch was finally passed four times through the mill at a setting of 2 mm to give a final sample thickness of about 5 mm.

Rheometer curves were performed in a Monsanto MDR2000 at 433 K. The values obtained for all the samples in minimum and maximum torques are given in Table II. The cure time to achieve the maximum torque of the rheometer curve, $t_{100\%}$, was also determined. The Mooney

Batch	Mixing Time (min)	${ m ML}~1'+4$ ${ m min}^{ m a}$	$\begin{array}{c} \text{Minimum} \\ \text{Torque}^{\text{b}} \\ (\text{N m}) \\ (10^{-1}) \end{array}$	Maximum Torque ^b (N m) (10 ⁻¹)	$\begin{array}{c} \Omega \ (N \ m) \\ (10^{-1}) \end{array}$	$\begin{array}{c} Resistivity^c \\ (k\Omega \ m) \end{array}$	Dispersion Grade ^d
a b	0.42 1 78	38.0 37 5	$1.17 \\ 1.11$	9.11 8 87	$7.94 \\ 7.76$	7.1	5
$c \\ d$	3.80 5.23	36.0 35.5	$1.05 \\ 1.05$	8.22 8.15	7.17 7.10	$14.0 \\ 15.6$	6 7

Table II Characteristic Values of the Different Batches

^a Mooney viscosity at 373 K.

^b Rheometer at 423 K.

^c Resistivity measured at 343 K at 4 min.

^d According to Phillips scale.⁹

viscosity at 373 K was measured at 4 min with a Monsanto MV2000 and the results are also given in Table II.

The aging of uncured compounds alters the filler network and these changes can be verified using resistivity measurements.⁸ To avoid this situation, the samples used in our measurements were cured as soon as possible after the batch achieved room temperature once the mixing was finished.

Sample sheets of $150 \times 150 \times 2$ mm were cured at 433 K up to time $t_{100\%}$. This fact guarantees that all the vulcanization reaction took place and there will not be reaction heat generation during the measurement of the thermal diffusivity. The density of the vulcanized compound was 1.095 g/cm³.

Dispersion Characterization

The dispersion grade was measured in our samples using microscopy techniques. The obtained values are given in Table II, according to the Phillips scale normally used for carbon black in rubber compounds.⁹ The Phillips method is based on a comparative visual analysis of test surface structures in relation to reference pictures.

For evidence of the different levels of carbon black dispersion, resistivity measurements were also performed on uncured samples at 343 K with the device presented in ref. 8. The resistivity cell has a heater and an integral derivative temperature controller in order to maintain the test temperature at ± 0.5 K.

The resistivity cell is assembled in an Instron 4201 in order to apply a pressure of 7.75 MPa over the sample during the resistivity test. A Basic program was use for controlling the pressure applied to the sample by the mechanical device. The mean resistivity and its standard deviation, measured at 4 min of the test, are given for each sample in Table II.

Thermal Diffusivity Device

The apparatus used in our tests was presented in refs. 1 and 6. A schematic diagram is given in Figure 1.

Four samples, 80 mm in diameter and 2 mm in thickness, are cut from each vulcanized sheet. These disks are placed together, and three thermocouples, T_2 , T_3 , and T_4 , are sandwiched between them for monitoring the temperatures in the center and the intermediate positions of the



Rubber compound

Figure 1 Schematic diagram of the thermal diffusivity measurement system. The location of the thermocouples is shown.

device. The overall thickness of 8 mm is maintained by two specially made plates of brass, which are bolted together. Two thermocouples, T_1 and T_{5} , are sandwiched between the brass plates and the samples for monitoring the surface temperature. The five thermocouples are arranged so that their junctions lie as closely as possible to the axis of symmetry of the device. The thermocouple wires were of iron-constantan with a 0.2 mm diameter.

For measurements at low temperatures, the device is sandwiched between two heat-sink plates, which are air-liquid-cooled using a controlled flow rate. From room temperature upward, the apparatus is immersed in an oil bath, which is heated continuously by electric immersion heaters while the oil is stirred vigorously. No temperature control is needed at either low or high temperature, but we applied a temperature heating rate of around 0.15 K/s. Thermocouple data were recorded by a PC AT286 with a Keithley DAS8/PGA 12 bit A/D conversion board using a customized acquisition program.

With the purpose of improving the procedure, we used the following method¹⁰: If *n* temperature measurements were registered in a time interval Δt , a central value was taken in this interval, and to determine the temperatures corresponding to this value, the following least-square fit was used:

$$E_{j}^{2} = \sum_{i=1}^{n} [f(t_{i}) - \theta_{i}]^{2}$$
(4)

where θ_i is the recorded temperature at time t_i and f is the fit function. A data sampling rate of 100 s⁻¹ and $\Delta t = 10$ s was used, and for simplic-



Figure 2 Variation of the thermal diffusivity with temperature for the different batches.

ity, f was chosen as a second-order polynomial in time.

To obtain the thermal diffusivity, the reduction of eq. (3) to a suitable finite difference equation results in

$$(\theta_{m+1,n} - 2\theta_{m,n} + \theta_{m-1,n}) + \left(\frac{k_{m+1,n}}{k_{m,n}} - 1\right)$$
$$(\theta_{m+1,n} - \theta_{m,n}) = \frac{1}{\alpha_{m,n}} \frac{(\Delta x)^2}{\Delta t} (\theta_{m,n+1} - \theta_{m,n}) \quad (5)$$

where the coordinates of a typical grid point are $x = m\Delta x$ and $t = n\Delta t$, with m and n integers. If the effect of the conductivity term in eq. (3) is not taken into account, then the error in the thermal diffusivity is low.¹ The thermal diffusivity results can be obtained from processing the thermocouple data. The results presented in this article were achieved through off-line processing of the recorded thermocouple data.

From eq. (5), the thermal diffusivity was estimated as

$$\alpha_{m,n} = \frac{(\Delta x)^2}{\Delta t} \left[\frac{\theta_{m,n+1} - \theta_{m,n}}{\theta_{m+1,n} - 2\theta_{m,n} + \theta_{m-1,n}} \right] \quad (6)$$

In our test, we used the temperature values obtained at positions T_2 , T_3 , and T_4 of the cell (Fig. 1) for calculating the thermal diffusivity using eq. (6).

RESULTS

The curves of the thermal diffusivity obtained from the temperature data are shown in Figure 2 for batches a, b, c, and d. In all the cases, the diffusivity decreases with increasing temperature; however, there is a steep decrease around the temperature of 230 ± 2 K which is associated with the glass transition temperature (T_{g}) of the compound. From this figure, it can be appreciated that there is no influence of the compound mixing time on the glass transition temperature.

In comparing the diffusivity values for all the samples analyzed, higher values are obtained at higher mixing times. A comparative graph is given in Figure 3 at four temperatures above and below the T_g . Moreover, it is easy to see that the effect of the dispersion on α is lower at higher temperatures.

Now, we can deduce the error in the diffusivity measurements considering the linear form of eq. (3). If we designated $\tilde{\theta}$ and $\tilde{\alpha}$ as the estimated temperature and diffusivity, we would want to obtain an estimation of the difference of $\alpha - \tilde{\alpha}$. If $\omega = \theta$ minus; $\tilde{\theta}$, we verify that¹¹

$$\frac{\partial w}{\partial t} = \alpha \frac{\partial^2 w}{\partial x^2} + \frac{\alpha - \tilde{\alpha}}{\tilde{\alpha}} \frac{\partial \tilde{\theta}}{\partial t}$$

with $\omega = 0$ for t = 0 and j = 1 and j = 5. Then, using the Fourier series

$$\omega(x, t) = \frac{(\alpha - \tilde{\alpha})}{\tilde{\alpha}} \sum_{n = -\infty}^{\infty} \int_{0}^{t} \times \exp\left[-\frac{n^{2}}{\alpha}(t - s) + i\frac{2\pi n}{L}x\right]\tilde{\theta}_{n}(s) ds$$

where $\tilde{\theta}_n(s)$ are the Fourier coefficients $\tilde{\theta}_t$. Considering *L* the height of the sample and using the Parseval equality, we can write



Figure 3 Influence of the degree of mixing on the thermal diffusivity above and below $T_{\rm g^{*}}$



Figure 4 Comparison between experimental and numerical data for time-temperature curves in the center of the sample.

$$egin{aligned} &\int_0^T \int_0^L \mid \omega(x,\,t) \mid^2 dx \; dt = \left| rac{lpha - ilde lpha}{ ilde lpha}
ight|^2 \sum\limits_{n = -\infty}^\infty
ight| \; \int_0^t & ilde x & ext{exp} \Bigg[-rac{n^2}{lpha} \left(t - s
ight) + i rac{2 \pi n}{L} \, x \Bigg] ilde heta_n(s) \; ds \;
ight|^2 dt \end{aligned}$$

To deduce the error in the diffusivity measurement, we proceed as in ref. 6, and we obtain that

$$\left|\frac{\alpha - \tilde{\alpha}}{\tilde{\alpha}}\right|^{2} \leq \frac{\int_{0}^{T} \int_{0}^{I} |\omega(x, t)|^{2} dx dt}{\int_{0}^{T} |\int_{0}^{t} \tilde{\theta}_{0}(s) ds|^{2} dt}$$
(7)

Using the estimated diffusivity, we recalculate the temperatures in the center of the specimen, considering variable boundary conditions from the variation of temperatures T_1 and T_5 with time.

As an example, Figure 4 shows excellent agreement between the measured and recalculated temperatures for batch a. By using these curves and the relationship given by eq. (7), one finds that the relative error of the diffusivity was approximately 10^{-3} .

DISCUSSION

Thermal transport in materials is due to electronic transport and the frequency of the atomic vibrations. These quanta of the thermal vibration energy are called phonons. In ordinary organic polymers, as opposed to metals and alloys, heat transfer takes place mainly by atomic vibrations. For this reason, thermal diffusivities are much lower in polymers.

Since electronic effects are virtually absent in most polymers, the thermal conductivity of these materials could be approached by using the Debye equation

$$k = \frac{1}{3} C \nu \lambda \tag{8}$$

where *C* is the specific heat capacity per unit volume; ν , the average phonon velocity; and λ , the phonon mean free path. According to Debye, the phonons or the elastic waves are scattered at the inhomogeneities of solid bodies and they are attenuated along their paths. The quantity λ is related to the length where the intensity falls by $1/e.^4$

In amorphous polymers, the mean free path length is in the range of atomic distances and, then, the phonons are scattered by each lattice point.⁴ Considering the definition of thermal diffusivity and eq. (8), it is easy to obtain

$$\alpha \cong \nu \lambda \tag{9}$$

where $c\rho$ is considered to be related to *C* in eq. (8).¹²

The addition of fillers in the amorphous polymer introduces another scattering mechanism in the compound. In the case of black dispersion in rubber compounds, some authors speculated that there would be a measurable effect on thermal properties.^{5,15}

Let us consider the mixing process in rubber compounds. First, the carbon black agglomerates enter the rubber and then the black is dispersed. In this stage, some breakdown of the agglomerates into aggregates, and these into particles, takes place as a result of the high shear stress attained during the mixing. A continuous network of carbon exists and is formed with many interaggregate contacts, leading to an increase in electrical conductivity.

Ramani and Vaidyanathan,¹⁵ using the finite element method (FEM), performed simulations of this stage. They developed a method to predict macroscopic effective thermal conductivity of a filled compound. They concluded that, from the agglomerate to network formation, thermal conductivity increases.

Simultaneously, the aggregates and particles are dispersed throughout the rubber. This process involves the fracture of pellets and of the rubber-filled pellet fragments or agglomerates and successive peeling away of the outer layers of the aggregates. Continuous mixing decreases the number of contacts and increases the average separation of aggregates and particles from each other.¹⁵ During these processes, the average diameter of the aggregates decreases with a logical increase in the number of particles and smaller aggregates.

The effect of the reduced particle diameter on thermal conductivity was analyzed by Nakai et al.¹⁶ They presented experimental results and FEM and Monte Carlo (MC) simulations of the thermal conductivity in a compound of Ag particles in epoxy resin. They found that at a constant filler content thermal conductivity increases at a lower particle diameter.

A consequence of the mixing is an increase in the interfacial area associated with the second phase present in the compound. The interfacial area can be thought as of a defect in the compound that causes diffusive scattering of the phonons. These interfaces are known to decrease the phonon mean free path λ and thus a decrease of α according to eq. (9).^{12,17}

Eiremann⁴ asserted that crosslinking affects the thermal conductivity of polymers. This fact was measured by Überreiter and Nens¹⁸ in crosslinked polystyrene. Heat transfer would have two important mechanisms in amorphous polymers: first, throughout the network of primary valences along the chains and, second, due to van der Waals bonds between chains. The first process has very little heat resistance compared with the second one. With every crosslink step, a new primary valence bond is added and the thermal conductivity and diffusivity increases.⁴ Following these ideas, fillers in the rubber compounds would behave in the same way as do crosslinks from the point of view of the thermal properties and an increase in the quantity of the filler attached to the polymer chains would increase the paths of thermal transfer. In this way, it is expected that during mixing, as the level of dispersion is enhanced and the total level of particle bonding molecular chains is higher, an increase in thermal conductivity and diffusivity would be expected.

One of the models used to describe the thermal conductivity of filled polymers was introduced by Nielsen¹⁹ who proposed the following relationship:

$$\frac{k_c}{k_p} = \frac{1 + AB\phi}{1 - B\psi\phi} \tag{10}$$

where

$$B=rac{k_{f}/k_{p}-1}{k_{f}/k_{p}+A}\qquad\Psi=1+igg(rac{1-\phi_{m}}{\phi_{m}^{2}}igg)\phi$$

where the subscripts p, f, and c mean the polymer, filler, and compound, respectively. A is a factor which depends on the geometry of the particles and θ_m is the maximum filler content possible while still maintaining a continuous matrix phase. This parameter is known as the maximum packing fraction. Values of A and θ_m can be obtained from ref. 20 where it was shown that θ_m ranges between 0.524 and 0.7405 considering the spherical particles and single cubic and hexagonal close packing order, respectively. $\theta_m = 0.637$ in the case of a random close packing order and 0.601 for a random loose packing order. A = 1.5for a spherical filler type.

Considering that during the mixing there is an improvement in the filler dispersion, followed by a more homogeneous distribution of the particles in the matrix, where the gap between the filler increases, it is easy to view from eq. (10) that k_c is higher at lower values of θ_m . The same effect is expected for thermal diffusivity.

Then, from our point of view, competitive mechanisms would be present in the behavior of the thermal properties of carbon black-filled rubber compounds when the dispersion is enhanced during mixing. These mechanisms would be the quantity of new interfaces following the breakdown of agglomerates and aggregates, the new bonds appearing between fillers and the polymer and the change in the packing order in the compound.

If we observe Figures 2 and 3, the thermal diffusivities increase from sample a to d at the same time that dispersion improves. We believe that sample a has a mixing level that produces a structure where the early agglomerate network is broken down. In this stage, the isolated aggregates are spread apart and the change in the diffusivity at higher dispersion levels follow the ideas mentioned above. This behavior is rein-

forced by the other mechanical and electrical parameters that we measured.

The effects of the mixing time on the rheometer curve at 433 K can be observed in the value of Ω = $\tau_{max} - \tau_{min}$, where τ_{max} and τ_{min} are the maximum and minimum torques, respectively. As given in Table II, Ω decreases while the mixing time increases. A similar behavior was reported by Coran and Donnet²¹ in their studies of NR with N-330 carbon black. They observed that the value of G', the real part of the complex shear modulus, decreases once the mixing time of the compound increases. This fact was associated with the presence of a network of agglomerates, which exists when the quality of the dispersion is poor.

The consequence of improved dispersion is also reflected in the electrical properties of the compound. The electrical resistivity of the uncured compound increases as can be observed in Table II. Following Medalia,²² a macroscopic specimen of a compound contains a large number of aggregates separated by gaps of different width and potential barriers. As mixing increases, two effects would be present: the breaking of aggregates in thinner particles and the dispersion of these in the matrix. As these agglomerates become dispersed as isolated aggregates, the network disappears and the electrical pathways are more difficult because of the increase in the gap between individual aggregates. This process gives higher values of electrical resistivity.²¹

CONCLUSIONS

The effect of the dispersion level on the thermal diffusivity was measured in a carbon black SBR compound. No effect of the dispersion on the glass transition of the compound was detected.

Higher values of α were obtained as the mixing time increased in the range of temperatures evaluated. This behavior was associated with different competitive mechanisms that appear in filled polymers. Some of these are the increase in the interfacial area between fillers and the polymer matrix, the increase in the new bonds created between the filler and the molecular chains, and the gradual development of the packing order of the filler in the polymer. To elucidate the contribution of each mechanism, more investigation will be done in the near future. Finally, the electrical resistivity and rheometer measurements made in the compound point to the suggestion that the structure of the compound develops an increase in the gap between aggregates or particles as is mentioned in the literature.

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REFERENCES

- Camaño, E.; Martire, N.; Goyanes, S. N.; Marzocca, A. J.; Rubiolo, G. H. J Appl Polym Sci 1997, 63, 157.
- 2. Eiermann, K. Kunststoffe 1961, 51, 512.
- Eiermann, K.; Hellwege, K. H. J Polym Sci 1962, 57, 99.
- 4. Eiermann, K. Rubb Chem Technol 1966, 39, 841.
- 5. Hands, D. Rubb Chem Technol 1977, 50, 480.
- Mariani, M. C.; Beccar Varela, M. P.; Marzocca, A. J. Kaut Gummi Kunstst 1997, 50, 39.
- Coran, A. Y.; Donnet, J. B. Rubb Chem Technol 1992, 65, 973.
- Roig Fernandez, D.; Marzocca, A. J. Rubb Chem Technol 1991, 64, 501.
- Stumpe, N. A., Jr.; Railback, H. E. Rubb World 1964, 151(3), 41.
- Feng, L.; Ottmann, M. C.; Thauvin, G. Rev Metal 1993, Jan, 115.
- Beccar Varela, M. P.; Mariani, M. C.; Marzocca, A. J.; Rial, D. F. Proceedings of the First Latin American Workshop of Applied Mathematics in Industry and Medicine, Buenos Aires, 1995.
- Agari, Y.; Ueda, A.; Omura, Y.; Nagai, S. Polymer 1997, 28, 801.
- 13. Gehman, S. D. Rubb Chem Technol 1967, 40, 36.
- Medalia, A. I.; Kraus, G. In Science and Technology of Rubber; Mark, J. E. Erman, B.; Eirich, F.R., Eds.; Academic: San Diego, CA, 1994; pp 387–418.
- Ramani, K.; Vaidyanathan, A. J Compos Mater 1995, 13, 1725.
- Nakai, T.; Tanaka, M.; Shimoji, T.; Nakajima, K.; Kohinata, S. High Temp-High Press 1995, 27/28, 665.
- 17. Choy, C. L. Polymer 1977, 18, 984.
- 18. Überreiter, K.; Nens, S. Kolloid Z 1951, 123, 92.
- Nielsen, L. E. Mechanical Properties of Polymers and Composites; Marcel Dekker: New York, 1974; Vol. 2.
- 20. Biggs, D. M. Polym Compos 1986, 7, 125.
- 21. Coran, A. Y.; Donnet, J. B. Rubb Chem Technol 1992, 65, 1016.
- 22. Medalia, A. I. Rubb Chem Technol 1986, 59, 432.