

Evaluation of the Thermal Diffusivity of Rubber Compounds Through the Glass Transition Range

ESTEBAN CAMAÑO, NATALIA MARTIRE, SILVIA N. GOYANES, ANGEL J. MARZOCCA,
and GERARDO H. RUBIOLLO*

Laboratorio de Propiedades Mecánicas de Polímeros y Mat. Compuestos, Dpto Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón I, Ciudad Universitaria, 1428 Buenos Aires, Argentina

SYNOPSIS

The thermal diffusivity of several natural and synthetic rubber compounds was measured in the temperature range from 125 to 350 K with an automatic device. In every case, a step change has been found in the thermal diffusivity at the glass transition range. In partially crystalline elastomers, the thermal diffusivity shows a minimum, which agrees very well with the melting temperature of crystallites. Also, new estimations of thermal diffusivity of some elastomeric compounds are given at above and below the glass transition temperature. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Values of thermal diffusivity α and thermal conductivity k are needed for heat flow calculations, the determination of structure-property relationships, and material selection and comparison.

Conductivity is conceptually easier to understand than diffusivity, and it has received more attention. However, diffusivity is the essential parameter for transient heat flow calculations.

As already documented,¹⁻³ a moderate peak or break in the curve of k as a function of temperature is expected at the glass transition in any plastic or rubberlike material. Thermal conductivity measurements can therefore also be used, in principle, to determine the glass transition temperature T_g .

However, actual temperature variation of k is rather small. For natural rubber,¹ k increases from about 3.64×10^{-4} cal/s cm K at 93 K to about 3.87×10^{-4} cal/s cm K near T_g , where there is a break in the curve and it starts to fall, reaching 3.40×10^{-4} cal/s cm K at 363 K. Hence, the

sensitivity of this technique for detecting T_g is poor.

Since $\alpha = k/\rho c$, where ρ is the density and c is the specific heat, diffusivity is often regarded merely as a mathematical parameter than as a material property. However, diffusivity is the parameter relating energy flux to energy gradient.

Not much research work has been done on the thermal diffusivity of amorphous polymers as on conductivity. The diffusivity decreases gradually with increasing temperature up to T_g . Where measurements have been made through T_g , some workers reported a change in the slope, and others a slight step decrease in diffusivity.⁴

As far as we are aware, no diffusivity measurements have been done on rubber compounds below 273 K, apparently due to the fact that heating and cooling cycles in the production of rubber articles are always above ambient temperature.

In this paper, thermal diffusivity results are reported for a series of natural and synthetic rubber compounds from 125 to 350 K. The data were obtained from each experiment as a curve by a continuous heating method. A description of the apparatus is given. In all cases, the dependence of α with temperature looks like a thermogram obtained with a differential thermal analyzer (DTA) for an amorphous polymer going through

* To whom correspondence should be addressed.

T_g . An estimate of T_g was made from the transition region, and they were compared against the available experimental data obtained by means of more conventional methods.

EXPERIMENTAL

The equation of the conduction of heat, in the absence of heat generation and convection, for heat in one direction is given by the following:

$$\frac{\partial^2 T}{\partial x^2} + \frac{1}{k} \frac{\partial k}{\partial T} \frac{\partial T}{\partial x} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad (1)$$

where T is the temperature, and t is the time.

The reduction of the eq. (1) to a suitable finite difference equation results in

$$\begin{aligned} & (T_{m+1,n} - 2T_{m,n} + T_{m-1,n}) + \left(\frac{k_{m+1,n}}{k_{m,n}} - 1 \right) \\ & \times (T_{m+1,n} - T_{m,n}) = \frac{1}{\alpha_{m,n}} \frac{(\Delta x)^2}{\Delta t} (T_{m,n+1} - T_{m,n}) \end{aligned} \quad (2)$$

where the coordinates of a typical grid point are $x = m\Delta x$, and $t = n\Delta t$, with m and n integers. Now, suppose that the experimental conditions are matched in such a way that $T_{m-1,n} \cong T_{m+1,n}$, then eq. (2) becomes

$$\begin{aligned} & \left(\frac{k_{m+1,n}}{k_{m,n}} + 1 \right) (T_{m+1,n} - T_{m,n}) \\ & \cong \frac{1}{\alpha_{m,n}} \frac{(\Delta x)^2}{\Delta t} (T_{m,n+1} - T_{m,n}) \end{aligned} \quad (3)$$

If the effect of the conductivity term in eq. (1) is not taken into account, then the error in the calculated diffusivity resulting from the same mathematical procedure and experimental conditions will be as follows:

$$\frac{\Delta \alpha_{m,n}}{\alpha_{m,n}} = \frac{k_{m+1,n} - k_{m,n}}{k_{m+1,n} + k_{m,n}}$$

Following experimental data of natural rubber,¹ taken a spatial temperature difference around 10 K and the lower value of k , the error is 0,7%. Hence, the simpler equation is adequate

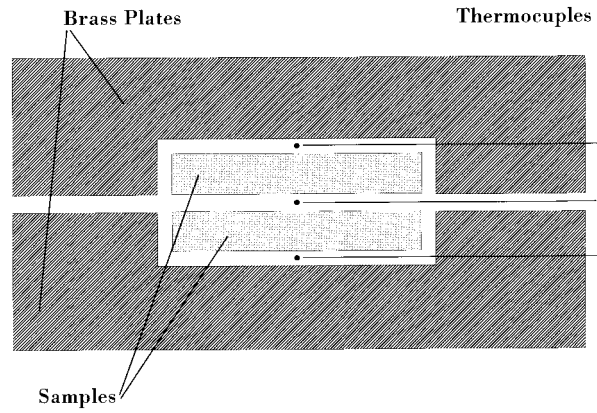


Figure 1 Schematic diagram of diffusivity apparatus.

in order to obtain the temperature dependence of the diffusivity, even through the glass transition temperature.

A continuous heating method for measuring the diffusivity of rubber based on this type of boundary condition has been developed by Hands and Horsfall.⁵ Our apparatus is similar to their own and is shown schematically in Figure 1. Two disk-shaped samples, 80 mm diameter and 4 mm thick, are placed together, and a Iron–Constantan thermocouple is sandwiched between them for monitoring the center temperature. The overall thickness of 8 mm is maintained by two specially made plates of brass, which are bolted together. Two other thermocouples are sealed into grooves in the plates with epoxy resin. The thermocouples are arranged so that the three junctions lie as closely as possible to the axis of symmetry. The diameters of the thermocouples wire is 0.2 mm.

For measurements at low temperature, the apparatus is sandwiched between two heat sink plates, which are air-liquid-cooled using a controlled flow rate. In order to avoid condensation, the complete assembly is then sealed in a plastic bag, and a continuous flow of argon is injected into the envelope.

From room temperature upwards, 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 both high and low ranges, but we apply a temperature rate around 0.15 K/s. The temperature difference between the surface and center is about 5 to 10 K, depending on the diffusivity of the sample.

Thermocouple data were taken by a PC AT286

Table I Compound Recipes

Sample	NR	SBR 1502	SBR 1712	CR	1.4- <i>cis</i> -BR	Carbon Black	Condition
A	100	—	—	—	—	45	a
B	—	100	—	—	—	—	b
C	—	—	100	—	—	—	b
D	—	—	—	100	—	—	b
E	—	—	—	—	100	—	a
F	50	50	—	—	—	50	a
G	—	29	98	—	—	85	a

^a Vulcanized with sulfur and accelerator at 160°C and time of 100% of maximum torque of the rheometer curve.

^b Unvulcanized; molded at 100°C.

with a Keithley DAS8/PGA 12 bit A/D conversion board. Each datum was the average of 50 readings sampled at a rate of 12 kHz, and the data were taken at four seconds intervals.

The thermal diffusivity results can be obtained from processing the thermocouple data in real time; however, the results presented in this paper were obtained through off-line processing of the recorded thermocouple data. The temperature data were used for calculating the thermal diffusivity with the following equation:

$$\alpha_{m,n} = \frac{(\Delta x)^2}{\Delta t} \left[\frac{T_{m,n+1} - T_{m,n}}{T_{m+1,n} - 2T_{m,n} + T_{m-1,n}} \right] \quad (4)$$

Measurements of thermal diffusivity, by the method described here, have been performed in a series of natural and synthetic rubber compounds in the range of temperatures between 125 and 350 K. The composition of elastomers used in the present work are given in Table I.

RESULTS AND DISCUSSION

The effect of temperature on thermal diffusivity of the NR compound (sample A) can be seen in Figure 2. The diffusivity decreases with increasing temperature; however, there is a step decrease around the reported value of the glass transition temperature for a similar compound.⁶

In interpreting this kind of diagram, three regression lines are applied to the curve: R_1 , R_2 , and R_3 . And three temperatures are defined: T_i , T_f , and T_g , as is shown in Figure 2. The value of T_g corresponds, in this analysis, to the middle point $(T_i + T_f)/2$.

This behavior holds quite well for samples in

Table I, as can be seen from Figures 2 to 5. In average, the height of the step decrease is 40% of the α value in T_i . The estimated values of T_i , T_f , and T_g for the elastomers of Table I are given in Table II, together with the reported values of glass transition temperatures previously reported in literature. Comparing the values, a reasonable agreement is noticed.

Since it is well known that there is no step change in the density-temperature and conductivity-temperature curves for an amorphous polymer going through the glass transition range, the step change in the specific heat appears to be the dominating factor in our results around T_g .

Hands and Horsfall⁵ have studied the thermal diffusivity of vulcanized filled natural rubber compounds in the range between room temperature and 473 K. Those results are therefore suitable for comparison purpose. They reported α ranging from 0.086 to 0.11 mm²/s at 323 K. The addition of carbon black increases the diffusivity when

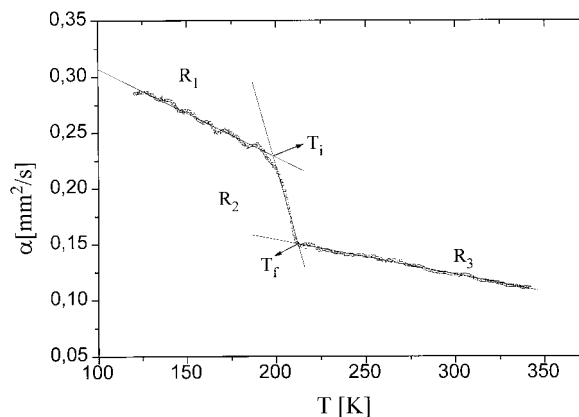


Figure 2 Thermal diffusivity of natural rubber with 45 phr black loading. Glass transition evaluation in which three regression lines are applied to the curve.

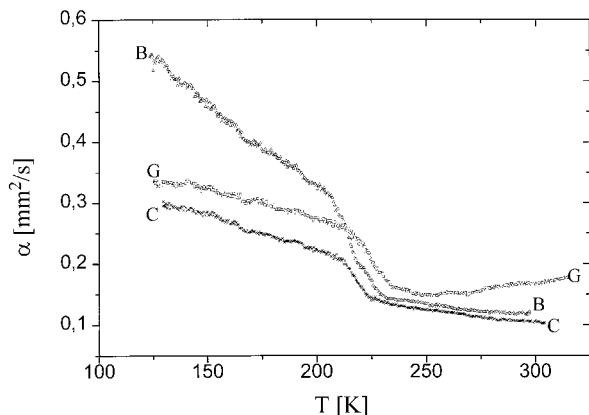


Figure 3 Thermal diffusivity of SBR 1502 (sample B), SBR1712 (sample C), and a vulcanized blend of SBR 1502/SBR 1712 with carbon black (sample G).

comparing with the unfilled compound. They also noticed that α decreases with temperature in all the compounds analyzed. A similar behavior was observed in our results, and a value of $0.114 \text{ mm}^2/\text{s}$ was obtained at 323 K .

The effect of oil extension on the thermal diffusivity of SBR can be seen in Figure 3. Comparing SBR 1502 with SBR 1712, the last one is a cold oil masterbatch with 37.5 phr of high aromatic oil in its composition. The addition of oil decreases considerably the diffusivity below T_g , but the effect disappears above T_g . Extended oils have almost the same values of thermal transport properties and density than SBR elastomers at room temperature;⁷ therefore, no significant effect might be expected for the addition of oils from

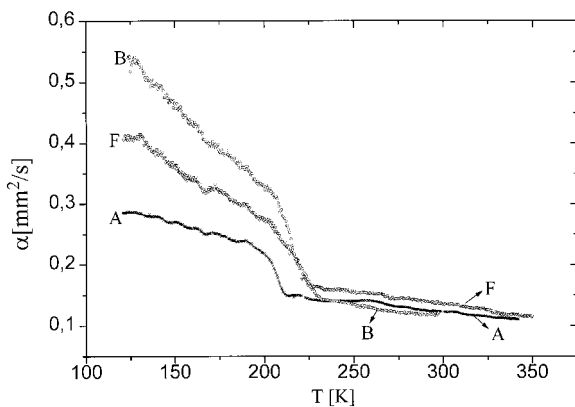


Figure 4 Thermal diffusivity of NR/SBR 1502 vulcanized blend with 50 phr black loading. Thermal diffusivity of its components (samples A and B) are shown for comparison purposes.

room temperature upwards. Since specific heat of liquids can be taken as constants over the full temperature range, and the conductivity exhibits a small decrease with temperature, the decrease in thermal diffusivity of the elastomer for addition of oils below T_g would reflect the increase in the density of it with increasing temperature.

From the point of view of the glass transition temperature, Table II shows that T_g of SBR 1712 is higher than that of SBR 1502. The increase of the value of T_g in elastomers with the addition of large amount of aromatic oil was previously reported by Corish.⁸ Following Bueche,⁹ the effect of diluent on the glass transition temperature can be estimated by

$$T_g = \frac{\beta_p v_p T_{gp} + \beta_d v_d T_{gd}}{\beta_p v_p + \beta_d v_d} \quad (5)$$

where T_g is the glass transition of the polymer-diluent system, v is the volume fraction, and β is the volume coefficient of expansion. The subscripts p and d refer to the polymer and diluent, respectively. Then, considering $\beta_p = 8.2 \times 10^{-4} \text{ K}^{-1,10}$ and $\beta_d = 1 \times 10^{-3} \text{ K}^{-1,9}$, $v_p = 0.74$, $v_d = 0.26$, and, using the values of $T_{gp} = 215 \text{ K}$ and $T_g = 219.5 \text{ K}$ (given in Table II), a value of $T_{gd} = 228.6 \text{ K}$ can be obtained. This value lies in the range of glass transition temperatures reported in literature for normal rubber process oils.⁸

Measurements were made on two rubber blends (samples F and G). The results are shown in Figures 3 and 4, together with those of their respective elastomers. Any additive rule for calcu-

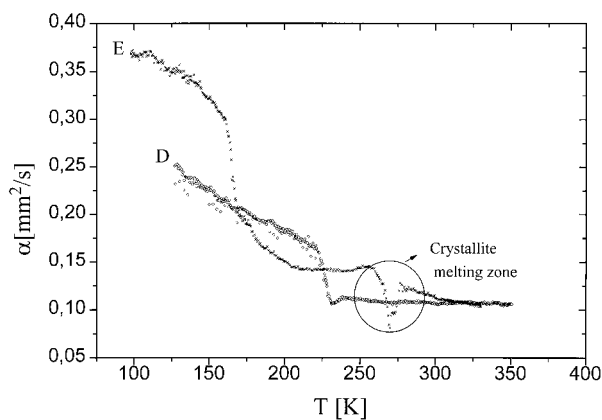


Figure 5 Thermal diffusivity of 1,4-*cis*-polybutadiene (sample E) and polychloroprene (sample D) showing the glass transition. In sample E, the melting temperature of the crystallites is noticed.

Table II T_g Values Obtained From Thermal Diffusivity Diagrams

Sample	T_i (K)	T_f (K)	$T_f - T_i$ (K)	T_g (K)	T_g^* (K)
A	200	213	13	206.5	208
B	206	224	18	215	209–214
C	212	227	15	219.5	209–214
D	221	230	9	225.5	228
E	162	171	9	166.5	167
F	205	231	26	218	—
G	216	242	26	229	—

T_g^* = glass transition temperatures reported in Wodd.⁶

lating thermal diffusivity of components might be expected to have serious limitations. However, for a blend of two components, the curve which one certainly expects falls between those of their components. The trend can be seen in the figures below T_g , but it does not follow above T_g . In our opinion, there is at least one possible explanation for this effect. The addition of carbon black and vulcanization of the blends increase the value of α over the full temperature range, then the blends have higher diffusivity than the primary elastomer components, where the later have close diffusivity values. From Figure 3, another fact can be appreciated: the sample G has a shift of T_g to higher values than that of the constituent elastomers. This behavior could be explained considering the cross-linking reaction. It is known that side reactions with the cross-linking agent, in our case, by sulfur, modify the chemical nature of the polymer with a substantial change in the monomeric friction coefficient produced by a decrease in the free volume.^{10,11} Then, an increase in the value of the glass transition temperature is associated with an increase in the combined sulfur.^{10,12}

The effect of temperature on the thermal diffusivity of a crystalline polymer (sample E) can be seen in Figure 5. The diffusivity decreases with the temperature showing a first transition at T_g . Then a second transition appears in the diagram as a minimum in the curve. The temperature of this minimum agrees very well with the melting temperature of crystallites of 1,4-*cis*-polybutadiene measured by differential scanning calorimetry (DSC).¹³

Other remarkable fact can be observed in Figures 2 to 5 and Table II: the effect of blending of rubbers in the widening of the T_g range can be appreciated. In fact, pure elastomers such as NR, CR, and 1,4-*cis*-BR (samples A, D, and E) have

the lower values of $(T_f - T_i)$. This value increases in the case of copolymers as SBR (samples B and C) and presents the highest values in considering rubber blends as samples F and G.

CONCLUSIONS

A continuous heating method for measuring thermal diffusivity of elastomeric compounds from 125 to 350 K has been developed. Two disk-shaped samples, 80 mm diameter and 4 mm thick, are used. The method presented in this paper is simple to use, the whole temperature range is covered in about half an hour, and the data acquisition system can give the temperature dependence of the thermal diffusivity on-line.

This work has shown that the method gives excellent qualitative and quantitative results of the glass transition temperature and melting point of crystalline phases in rubber compounds.

Finally, new estimations of the thermal diffusivity of some elastomeric compound are given at above and below the glass transition temperature.

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