

NOTES

The Thermal Diffusivity of Natural Rubber

A convenient and effective method of measuring the thermal diffusivity of elastomers was introduced by Rehner;¹ in his method a two-inch sphere of the elastomer with a thermocouple embedded in its center is first equilibrated at one temperature and then suddenly plunged into a bath at another temperature. The thermal diffusivity k can be calculated from the change with time of the temperature at the center of the sphere by means of the equation:²

$$u_c = \frac{T_1 - T_c}{T_1 - T_0} = 2 \sum_{m=1}^{\infty} (-1)^{m+1} \exp\{-m^2\pi^2 kt/a^2\} \quad (1)$$

where T_c is the center temperature, T_0 the initial uniform temperature, T_1 the final surface temperature, t the time, and a the radius of the sphere. Rehner, using an initial temperature of 25°C. and a final one of 100°C., found that k decreased in a linear manner with increasing "diffusivity-average" temperature¹ of the sphere.

Recently Gengrinovich and Fogel³ have reported measurements carried out in a similar manner. However, these authors treat their data by making use of the fact that, for long times, eq. (1) reduces to:

$$u_c = 2 \exp\{-\pi^2 kt/a^2\} \quad (2)$$

Accordingly, they plot the logarithm of u_c versus t and calculate k from the slope of the straight-line portion of this plot. They criticize Rehner's method of calculation on the basis that it assumes immediate equilibration of the surface temperature of the sphere and could lead to a serious error. It is the purpose of this note to demonstrate that failure of instantaneous surface-temperature equilibration leads to errors much smaller than those introduced by heat conduction along the thermocouple wires.

In doing similar measurements on natural rubber samples with 0.010-in. copper-Constantan thermocouples, we have indeed found that unreasonably high k values were obtained at the beginning of each run. Moreover, the results of heating runs (30° water bath to boiling water bath) were quite inconsistent with those of cooling runs (100 to 30°C.), as shown in Figure 1a. It was our hypothesis that this discrepancy was caused primarily by heat conduction along the thermocouple wires. To test this assumption, the 0.010-in. copper wire, which conducts about 20 times more heat than the Constantan wire, was replaced by 0.0035-in. copper, and the portion of the thermocouple embedded in the sphere was lengthened from 1 to 4 in. As shown in Figure 1b, this thermocouple gave far better results.

A further, but not as great, improvement could be made by plotting the results semilogarithmically according to eq. (2) and extrapolating the straight-line portion back to $u_c = 2$. This intersection was usually at slightly negative times (0 to 1.5 min.), apparently because of a lag in surface temperature equilibration, as suggested by Gengrinovich and Fogel.³ Diffusivities were then calculated with eq. (1) and the extrapolated, rather than the actual, zero time. This is essentially equivalent to finding a better fit of the data to eq. (1) by shifting the time axis and results in k values which decrease only slightly with temperature (Fig. 1c).

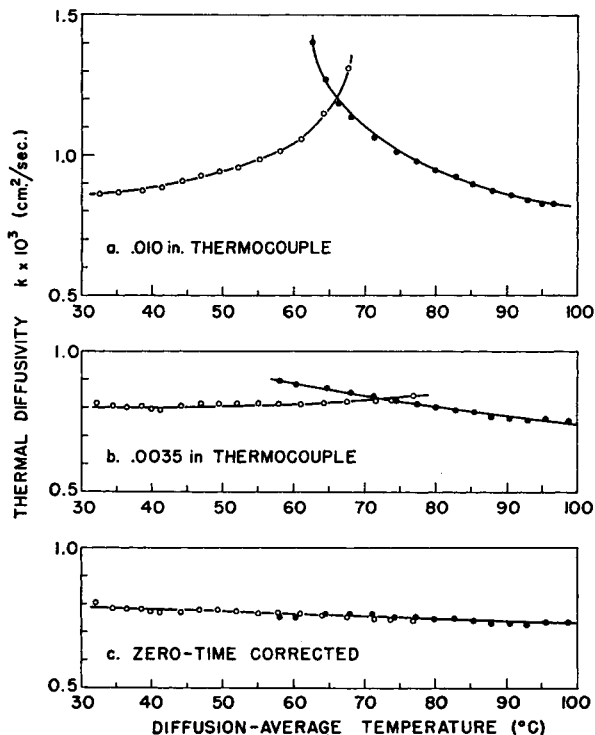


Fig. 1. Thermal diffusivity of gum natural rubber calculated by eq. (1) as a function of diffusivity-average temperature: (●) heating runs 30°C. to 100°C.; (○) cooling runs 100° to 30°C.

The results thus obtained for gum and black-loaded natural-rubber stocks are compared in Table I with those of Rehner¹ and of Gengrinovich and Fogel.³ Both the thermal diffusivity and its temperature coefficient were found to be appreciably lower than those reported by the first author, who used 0.010-in. copper-Constantan thermocouples. Gengrinovich and Fogel's method of treating the data, that of focussing attention on the later stages of the run, minimizes the effect of heat conduction, although it gives no information on the temperature coefficient of k . Thus, though they used even thicker thermocouples (0.016-in. copper, 0.008-in. Constantan), their results are in quite good agreement with those of this note.

In summary, it has been shown that heat conduction along the thermocouple wires can be a serious source of error in thermal diffusivity measurements made according to Rehner's sound and convenient method. The previously reported thermal diffusivities and temperature coefficients are too high, primarily for this reason and not, as suggested by Gengrinovich and Fogel, because of a time lag in surface-temperature equilibration.

Rubber stocks 1. Gum stock: Smoked sheet, 100; Neozone D, 1; ZnO, 5; stearic acid, 4; sulfur, 3; MBT, 1. Cured 30 min. at 150°C.

2. Black stock: As above, plus EPC black, 54; Nujol mineral oil, 20.

TABLE I
Thermal Diffusivity of Natural Rubber at 60°C.

	This work	Ref. 1	Ref. 3
Gum			
$k \times 10^3, \text{cm.}^2/\text{sec.}$	0.76	1.06	0.72
$-\frac{dk}{dT} \times 10^6, \text{cm.}^2/\text{sec.} \cdot ^\circ\text{C.}$	0.9	5.9	—
Black			
$k \times 10^3, \text{cm.}^2/\text{sec.}$	1.14	1.49	1.11
$-\frac{dk}{dT} \times 10^6, \text{cm.}^2/\text{sec.} \cdot ^\circ\text{C.}$	1.2	7.1	—

References

1. Rehner, J., Jr., *J. Polymer Sci.*, **2**, 263 (1947).
2. Carslaw, H. S., and J. C. Jaeger, *Conduction of Heat in Solids*, 2nd ed., Oxford, 1959, p. 233 ff.
3. Gengrinovich, V. I., and V. O. Fogel, *Kauchuk i Rezina*, **16**, 27 (1957); *Rubber Chem & Technol.*, **32**, 444 (1959).

H. K. FRENSDORFF

Elastomer Chemicals Department
Experimental Station
E. I. du Pont de Nemours & Company, Inc.
Wilmington, Delaware

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Dependence of Activation Energy for Viscous Flow of Polyhydrocarbons on Bulk of Substituents

The temperature coefficient of the steady-state viscosity η of molten polymers is of importance in processing. It is usually represented by an apparent energy of activation for viscous flow E^* and defined by the Arrhenius equation

$$\eta = A \exp \{E^*/RT\} \quad (1)$$

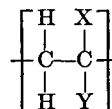
The higher value of E^* for low-density polyethylene, compared with that of high-density polyethylene, has been tentatively explained in terms of the hole theory¹ as being due to short-chain branches.^{2,3} The size of the segment of a polymer chain moving as a single unit in viscous flow may be increased by branches or substituents in two ways. First, their bulk hinders rotation around carbon-carbon bonds in the backbone, thereby rendering the chain stiffer. The influence of chain flexibility on the size of the flow unit is confirmed by the fact that a completely rigid chain can move only as a single unit. Second, branches and substituents increase the volume of the chain for any given length. According to the theory that E^* represents the energy required for hole formation,¹ substituents should increase the size of the flow unit in proportion to their volume and to their frequency of recurrence, thereby augmenting the size of the hole required for flow and consequently increasing E^* .

The purpose of this note is to correlate empirically the value of E^* of different polymers with the bulkiness of the substituents. Bulkiness is expressed as molar volume of the

substituents at the boiling point. This is simpler than detailed geometrical analysis. Concerning atomic models, their use can be misleading. For instance, the polyisobutylene molecule cannot be constructed with Taylor-Hirschfelder models because of the overcrowding of methyl groups and secondary hydrogen atoms, yet the properties of the polymer are indicative of a flexible chain.

Another factor likely to affect the magnitude of E^* is the attraction between chains by secondary valence forces. By limiting the considerations to polyhydrocarbons, the variation in interchain attraction from polymer to polymer is minimized. Below certain levels of molecular weight and temperature, increasing molecular weight and decreasing temperature usually cause increases in E^* . The values selected here were obtained with samples of molecular weight high enough and at temperatures high enough to fall in the range where E^* is practically independent of these factors. Where temperature is concerned, this means raising it to 100°C. or more above the glass transition. The activation energies for viscous flow either refer to zero shear or to fixed shear stress. It has been observed that the two are equal, i.e., that E^* at fixed shear stress is independent of shear stress.^{3,4}

For a series of polyhydrocarbons of the type



the sums of the molar volumes at the boiling point of the two substituents X and Y on the second carbon atom, V_{X+Y} , are listed in Table I together with the apparent energies of activation for viscous flow. Volume equivalents are those of Le Bas,⁵ namely, 3.7 ml. for the hydrogen atom, 14.8 ml. for the carbon atom, and 15.0 ml. subtracted for a benzene ring. The values of V_{X+Y} plotted against E^* give rise to a smooth curve which can be used as a guide for estimating the E^* values of unknown polyhydrocarbons. On a semi-logarithmic scale the relation is linear and can be expressed by

$$\log E^* = 0.784 + 0.0060 V_{X+Y} \quad (2)$$

Extrapolations can be made only if X and Y are smaller than the flow unit.

TABLE I
Energy of Activation for Viscous Flow of Molten Polyhydrocarbons as a Function of Molar Volume of the Substituents

Polymer	V_{X+Y} , ml.	E^* , kcal./mole	Ref.
Polyethylene	7.4	6.5	2
		7.0	3 ^a
Polypropylene	29.6	9.0 ± 1.0	6
		9.6	7
		12.0	4
Polyisobutylene	51.8	15.5	8 ^a
		16.2	9
		22.6	10 ^a
Polystyrene	96.0	22.6	10 ^a
Poly(α-methylstyrene)	118.2	32.0	11

^a Contains additional references listing similar values of E^* .