

Viscoelastic and Friction Characteristics of Polydiene, and Butadiene–Styrene Copolymer Tread Compounds with Application to Tire Dynamics

JAMES L. WHITE and YIH MING LIN, *Department of Chemical and Metallurgical Engineering, University of Tennessee, Knoxville, Tennessee 37916*

Synopsis

An experimental study of the linear viscoelastic and friction properties of passenger tire tread compounds containing realistic black and oil contents and several different types of elastomers including *cis*-polyisoprene, *cis*-polybutadiene, emulsion polymerized polybutadiene, and three emulsion polymerized butadiene–styrene copolymers (SBR's) has been carried out. $E'(\omega)$ and $\tan \delta$ were determined as a function of frequency and temperature. At any specific frequency and temperature, $\tan \delta$ was an increasing function of T_g or a decreasing function of $T - T_g$. When the $\tan \delta$ -frequency data were plotted at the same $T - T_g$, all of the treads based upon emulsion-polymerized butadiene polymers yielded nearly the same curve. Wet coefficients of friction of the tread compounds correlated with both $\tan \delta$ and $T - T_g$ supporting the idea that lubricated friction is largely due to hysteresis. The correlation among the butadiene–styrene polymers was much better than with the natural rubber, which exhibits a lower $\tan \delta$ and a higher wet coefficient of friction than an SBR of the same T_g . The experimental results are used to investigate the heat buildup and skid properties of tires containing these tread compounds.

INTRODUCTION

Considerable concern exists about tire skid and traction on wet roads where accident rates are more than five times higher than on dry roads.¹⁻³ If we couple this with the rapid changeover in recent years from bias ply to bias-belted to radial ply tires, it indicates a growing need for quantitative tire dynamics supported by experimental data. It is well known that the primary dynamic characteristics of pneumatic tires are due to the cord construction of the so-called tire carcass. Indeed, most papers treating the mechanics of tires are concerned with the inflation and deformation of membranes reinforced with cords.⁴ However, the road performance of tires is greatly modified by the composition of the tread which overlays this construction and contacts the road. This has long been realized with regard to skid resistance and tread abrasion.^{5,6} It is our purpose in this paper to investigate the dynamic mechanical properties of the rubber compounds in tire treads and their interaction with wet and dry pavements. These experimental results will be used in conjunction with theoretical analyses to consider tire behavior.

BACKGROUND

We begin by discussing the character and mechanical properties of tire tread compounds. It must first be noted that these compounds contain only about 50% rubber by weight, and another 50% consists of various fillers, notably finely divided carbon black and mineral oil. The recipe in Table I taken from Kienle et al.⁵ is typical. The rheological properties of these compounds are reasonably represented as being close to isotropic viscoelasticity (though some thixotropic character is often found.⁷ Thus, one may express the stress tensor as an hereditary functional of the deformation history^{8,9} which for small deformations of these materials may be represented by the Boltzmann equation¹⁰:

$$\sigma_{ij} = -p\delta_{ij} + 2 \int_{-\infty}^t G(t-s)d_{ij}(s)ds \quad (1)$$

where δ_{ij} is the Kronecker delta, d_{ij} is the rate of deformation tensor, and $G(t)$ is the relaxation modulus. Most studies of the deformation of elastomers and their compounds have involved the dynamic stress response to sinusoidal strains. Consider a uniaxial sinusoidal extensional strain,

$$\epsilon(t) = \epsilon_0 \sin \omega t. \quad (2)$$

The stress response¹¹ is

$$\sigma(t, \omega) = E'(\omega)\epsilon_0 \sin \omega t + E''(\omega)\epsilon_0 \cos \omega t \quad (3a)$$

with

$$E'(\omega) = \omega \int_0^{\infty} E(z) \sin \omega z dz \quad (3b)$$

$$E''(\omega) = \omega \int_0^{\infty} E(z) \cos \omega z dz \quad (3c)$$

TABLE I
Recipes of Tread Compounds*

Ingredient	Source	Rubber, pph
Rubber	See Table II	100
N-285 (ISAF) carbon black	Cabot Vulcan 5H	70
Aromatic oil	Sundex Aromatic-4120	37.5
Zinc oxide	St Joe No. 20-21	3.0
Stearic acid	—	2.0
Paraffin wax	—	0.5
N-Isopropyl-N-phenyl- <i>p</i> -phenyldiamine	Uniroyal Flexzone 3C	1.0
N-cyclohexylbenzothiazolyl sulfanamide	Uniroyal Delac-S	1.0
Diphenylguanidine	American Cyanamid DPG	0.3
Sulfur	Stauffer Crystex	2.0

* Adapted from Kienle et al.⁵

where ϵ_0 is the amplitude of the strain, $E(t)$ is $3G(t)$ for incompressible materials, and $E'(\omega)$ and $E''(\omega)$ are known as the extensional dynamic and loss moduli. One frequently represents the out-of-phase component of the stress in terms of the phase or loss angle δ between the input $E(t)$ and output $\sigma(t)$:

$$\sigma(t, \omega) = \sigma_0 \sin(\omega t + \delta) = E^* \epsilon_0 \sin(\omega t + \delta). \quad (3d)$$

The tangent of angle δ and E^* may be shown to be related¹¹ to E' and E'' by

$$\tan \delta = \frac{E''(\omega)}{E'(\omega)} \quad (3e)$$

$$E^* = \sqrt{(E')^2 + (E'')^2} \quad (3f)$$

The monograph by Ferry¹¹ reports experimental studies distinguishing between the linear viscoelastic characteristics of glassy, semicrystalline and vulcanized and raw elastomers. There have also been investigations of the rubber constituents of tire compounds, i.e., natural rubber (*cis*-1,4-polyisoprene),¹²⁻¹⁵ polybutadiene,^{15,16} and butadiene-styrene copolymer^{12,13,16} vulcanizates and their blends¹⁶ have been reported in the literature. Experimental results for the effect of carbon black on the dynamic properties of rubber compounds date to the work of the early 1940's¹⁷ and there have been numerous reports since that time,¹⁸⁻²⁰ with the work of Payne during the last decade being most notable. Generally, the qualitative features of the dynamic mechanical properties of vulcanized gum elastomers are now understood, as are the distinctive differences in response between the major synthetic rubbers. Furthermore, the qualitative variations in properties with addition of compounding ingredients are known. However, there is little in the literature about the mechanical properties of these elastomers in realistic modern trend recipes. The various "tread" data published during the Rubber Reserve Program are based on outmoded recipes, as both the compounding ingredients, in particular the carbon blacks, and the types of elastomers have changed.

The friction characteristics of a tire are determined by the detailed interaction between the tread and the road surface. As such, it varies with the nature of the pavement and the tire construction and tread compound as well as the mode of contact, in particular whether the tire is in motion or sliding and if there are lubricating fluids, such as water, in the region of contact and the quantity of such fluid. Certainly, the place to start any analysis is with the nature of the frictional contact. Generally, the friction force f is characterized through the coefficient of friction μ defined by Amon-ton's law²¹:

$$f = \mu W \text{ or } \mu = f/W \quad (4)$$

where W is the normal load. Generally, μ is considered to be the sum of deformation and adhesion²¹ or abrasion²² components,

$$\mu = \mu_{\text{def}} + \mu_{\text{adh}} + \mu_{\text{abr}} \quad (5)$$

and is a function of temperature and applied pressure. By a deformation component is meant the contribution of hysteresis losses as the vulcanizate is pulled around and over the asperites.

Tabor and his co-workers^{21,23,24} have made a basic study of the mechanisms of friction in rubber vulcanizates in contact with rigid surfaces. In 1952, Tabor²³ was able to show that rolling friction was apparently entirely due to hysteresis induced by deformation. This has found experimental support from various later researchers^{25,26} and several relatively sophisticated stress analyses of this problem²⁷⁻³⁰ based upon the theory of linear viscoelasticity, eq. (1), have appeared. In 1958, Greenwood and Tabor²⁴ argued and presented evidence showing that sliding rubber vulcanizates over surfaces covered with liquid films was also dominated by hysteresis, i.e., μ was simply μ_{def} . While this idea has found support from Bueche and Flom,³¹ Percarpio and Bevilacqua,³² and others, the opinion has not been unanimous (see the discussion of Tabor, Gough, Allbert, and Walker³³). Surface characteristics such as wetting and adhesion have been put forward to explain away experimental results supporting the hysteresis mechanism. However, the majority of evidence certainly supports the Greenwood-Tabor hypothesis. Several papers³⁴⁻³⁶ have also appeared which relate dry sliding friction to viscoelastic behavior. Materials-oriented comprehensive experimental studies of the coefficient of friction or its equivalent for elastomers and rubber compounds and various surfaces have been reported by Grosch,³⁶ Sabey and Lupton,³⁷ Percarpio and Bevilacqua,³² and Baranwal,³⁸ among others. With few exceptions, most investigations have only considered a single sliding velocity. However, some conclusions may be drawn. For butadiene-styrene copolymer tread compounds, it is found that increasing the styrene content increases the coefficient of friction.³⁸

The rubber friction and tire skid literature is in many respects difficult to read and evaluate, for there often seems to be confusion among authors between the coefficient of friction as a basic physical property of relatively ideal geometrics in contact and what actually occurs in a patterned tire tread in contact with a road. First, we note, as indicated by Gough³⁹ among others, the nature of the deformations and stresses between the tread and pavement are complex. Furthermore, as pointed out by Gough and Moore,⁴⁰ Allbert and Walker,¹ and others, the nature of the contact between a tire and a wet road is generally not uniform and the drag force must be represented as a series of terms. For sliding with locked wheels over a wet road,

$$f = \left[\frac{\sum_{i=1}^n \mu_i A_i}{A} \right] W \quad (6)$$

where the summation over i is for the different zones of contact. As one moves from the front of the contact to the back of the region, the thickness of the liquid film on the road surfaces will probably decrease due to water being pushed into the grooves. In the rear of the region of contact, one

may have nearly dry sliding conditions. This will probably result in an increasing coefficient of friction.

The purpose of this paper is severalfold. First, it is to present a serious study of the linear viscoelastic properties and lubricated and dry sliding friction behavior of tire tread compounds based upon well-characterized polydiene and butadiene-styrene copolymer elastomers. Our compounds resemble those used for passenger automobile tires. Second, we seek to relate the viscoelastic characteristics of the treads to the molecular structure of the base elastomers. We will then investigate the relationship of lubricated friction behavior to the viscoelastic properties of the tread compounds and, in turn, to molecular structure. In the final part of the paper, we look at several specific practical problems related to tire treads (heat buildup, skid distance, lateral force on turning) and try to use the experimental results of this paper to investigate these problems.

EXPERIMENTAL

Polymers

The elastomers included in this study are summarized in Table II. They are six in number, including natural rubber, two polybutadienes, and three butadiene-styrene copolymers. Of these, four were polymerized in emulsion (BR-2, SBR-1, SBR-2, and SBR-3), one is Ziegler polymerized (BR-1), and one is naturally occurring material (NR). The molecular weight distributions of these polymers have been obtained by means of the gel permeation chromatograph using a calibration method essentially the same as that recommended by White and Salladay.⁴¹ Glass transition temperatures of the polymers have been measured using a Perkin Elmer differential scanning calorimeter. These results, together with presumed polydiene microstructures, are summarized in Table II. These results are in good agreement with experimental studies on similar polymers.^{41,42}

Tread Compounds

Tire tread compounds of varying composition have been made by mill mixing elastomers with carbon black, oil, accelerators sulfur, and other compounding ingredients according to the recipe summarized in Table I. This is the same recipe as used by Kienle and his colleagues⁵ in a recently reported extensive tire-testing program related to treadwear. All of the usual problems encountered in mill mixing of these polymers were observed.⁴³ Addition of oil into natural rubber was especially difficult.

The tread compounds were vulcanized at 144°C for various periods so as to obtain the same 300% modulus in an Instron tensile test at 20 in./min and 20°C. This modulus was taken as 690 psi. This vulcanization procedure was carried out in the manner recommended by Kienle et al. with the intention of obtaining tread properties similar to those devised by rubber compounders. The compounds generally contain less than 50 wt-% rubber and contain almost 35 wt-% fine carbon black and 15% aromatic mineral

TABLE II
Molecular Structure and Transition Behavior of Elastomers

Polymer designation	Supplier	Styrene content	Diene microstructure			M_n	M_w/M_n	Branching ^a	T_g , °C
			<i>cis</i> -1,4	<i>trans</i> -1,4	1,2 and 3,4				
NR (polyisoprene)	Uniroyal Tire Co. Smoked Sheet	0	100	0	0	—	—	1	-71
BR-1	American Synthetic Rubber & Chemical Cisdene	0	93	3	4	190,000	3.55	2	(-107) ^b
BR-2	Texas-US Chemical EBR Synpol 18407	0	15	68	17	120,000	7.03	3	-82
SBR-1	Texas-US experimental polymer	15.5	15	68	17	151,000	6.30	3	-66
SBR-2	Texas-US Chemical Synpol 1712	23.5	15	68	17	160,000	6.80	3	-55
SBR-3	Texas-US Chemical Synpol 8227	39.5	15	68	17	185,000	6.08	3	-43

^a Branching values indicate relative levels.

^b Value reported by Kienle et al.⁴

oil. The natural rubber compound is an exception, for it was not possible to incorporate as much oil in it as in the other compounds. It only contains 18.75 parts oil per 100 parts rubber. The modulus of the natural rubber vulcanizate was higher than those of the other compounds.

Pavements

Pavements of varying composition and texture have been used in the friction studies. Specifically, these are a coarse-textured and a fine-textured asphalt and a smooth concrete. The coarse-textured asphalt is representative of a relatively new asphalt road surface. The fine-textured asphalt and concrete are representative of worn pavements. The specific pavements together with their composition and history are summarized in Table III.

TABLE III
Structure of Pavements Used in Friction Experiments

Ingredients	Relative amounts in pavement type, %	
	Concrete	Asphalt
Cement	13.2	—
Asphalt	—	6.5
Mineral filler	—	6.1
Water	7.9	—
Sand gravel		
fine aggregate	31.7	82.7
coarse aggregate	47.2	4.7

Mechanical Measurements

Young's dynamic modulus, $E'(\omega)$, and loss tangent, $\tan \delta$, were measured as a function of frequency and temperature using a commercial Rheovibron viscoelastometer of the type designed by Takayanagi.⁴⁴ Measurements were carried out at frequencies of 11, 35, and 100 Hz and in the temperature range from 25° to 100°C.

Friction Measurements

The coefficients of friction were measured using the British Road Research Laboratory Portable Skid Tester.^{37,45,46} In this apparatus, a pendulum containing a rubber slider is allowed to swing from a predetermined position and come into contact with a pavement surface and then swing up onto a calibrated scale. Thus, if M is the effective mass of the swing arm, W is the average normal load on the pavement, and H and h are the initial and final heights of the swing arm, then the fractional energy loss is

$$Mg(H - h) = f \cdot D = \mu WD \quad (7a)$$

$$\mu = (Mg/WD)(H - h).$$

The magnitude of the upswing gives the coefficient of friction. In practice, the instrument upswing altitude is calibrated in terms of a skid resistance rating which is approximately 100 times the coefficient of friction. Specifically, this is

friction calibration (British Portable Skid Tester Rating)

$$\sim H - h \sim \frac{330\mu}{3 + \mu}. \quad (7b)$$

Using again a simple energetic balance as in the derivation of eq. (7a), we may show that the velocity of initiation of sliding is determined by

$$MgH = \frac{Mv^2}{2} + \Delta E$$

$$v = \sqrt{2gH - (2\Delta E/M)} \quad (7c)$$

where ΔE is the internal friction loss in the instrument during the downswing. Generally, H is 1.33 ft, yielding a value of v of about 9 ft/sec if ΔE is small.

RESULTS

Linear Viscoelastic Properties

The dynamic modulus $E'(\omega)$ and the loss tangent band were obtained for the six tread compounds as a function of temperature frequency. Figure 1 shows $E'(\omega)$ for the SBR-2 and BR-1 compounds at the various temperatures. Figure 2 contains a similar plot for $\tan \delta$ of these two compounds. These data are typical for all of the compounds. It was found possible to apply the frequency-temperature shift procedure to obtain master curves for $E'(\omega)$ and $\tan \delta$ of each of the compounds. The data for all of the

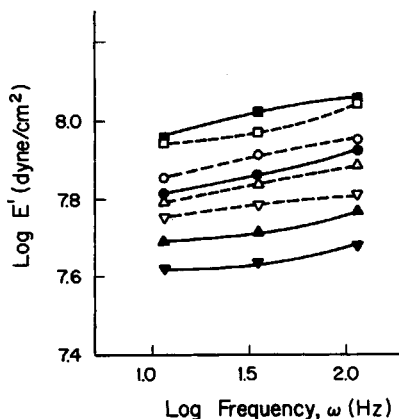


Fig. 1. Plot of $E'(\omega)$ as a function of frequency for SBR-2 (solid symbols) and BR-1 (open symbols) tread compounds at 25°C (\blacksquare); 50°C (\bullet); 75°C (\blacktriangle); 100°C (\blacktriangledown).

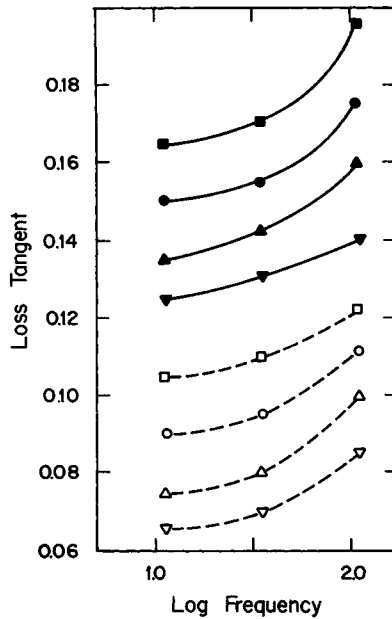


Fig. 2. Plot of loss tangent ($\tan \delta$) as a function of frequency for SBR-2 (solid symbols) and BR-1 (open symbols) at 25°C (■□); 50°C (●○); 75°C (▲△); 100°C (▼▽).

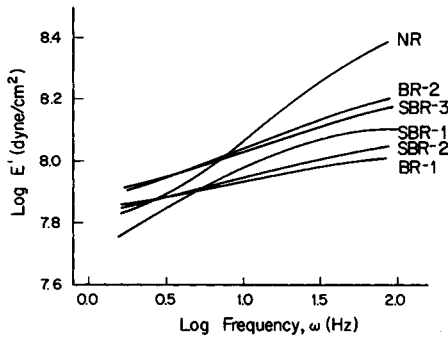


Fig. 3. Master curve of $E'(\omega)$ vs. frequency for the tread compounds studied at the 25°C reference temperature.

compounds is represented in terms of master curves at a 25°C reference in Figures 3 and 4.

Friction

Values of the coefficient of friction determined from the standard British Road Testers procedure under both wet and dry conditions on each of the pavements investigated are summarized in Table IV. The lower values of the coefficients of friction on the wet surfaces are noted, with the concrete values being the lowest. The coarse-textured asphalt has higher μ values than the fine-textured asphalt.

TABLE IV
Coefficients of Friction of Tread Compounds on Different Pavements

Base elastomer of tread compound	$T_g, ^\circ\text{C}$	Coefficient of Friction μ					
		Concrete		Asphalt (coarse texture)		Asphalt (fine texture)	
		wet	dry	wet	dry	wet	dry
NR	-71	0.18	1.06	0.65	>1.5	0.57	1.16
BR-1	-107	0.16	1.29	0.50	>1.5	0.44	1.14
BR-2	-82	0.15	1.11	0.64	>1.5	0.51	1.13
SBR-1	-66	0.18	1.09	0.68	>1.5	0.60	1.12
SBR-2	-55	0.19	1.04	0.73	>1.5	0.63	1.06
SBR-3	-43	0.27	0.98	0.76	>1.5	0.71	1.16

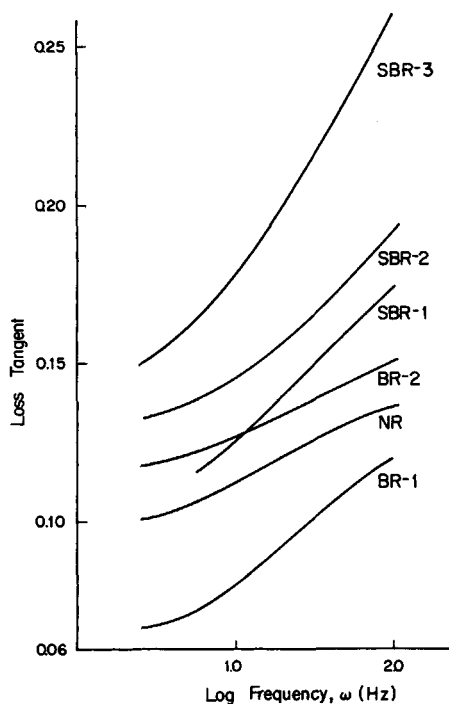


Fig. 4. Master curve of loss tangent ($\tan \delta$) vs. frequency for the tread compounds studied at the 25°C reference temperature.

DISCUSSION

Linear Viscoelastic Properties

Certain trends in the experimental data are clear in Figures 1 through 4. From Table II and Figure 4, the loss tangent may be seen to be an increasing function of styrene content among the SBR's. However, the three zero-styrene polydiene compounds each have rather different values of \tan

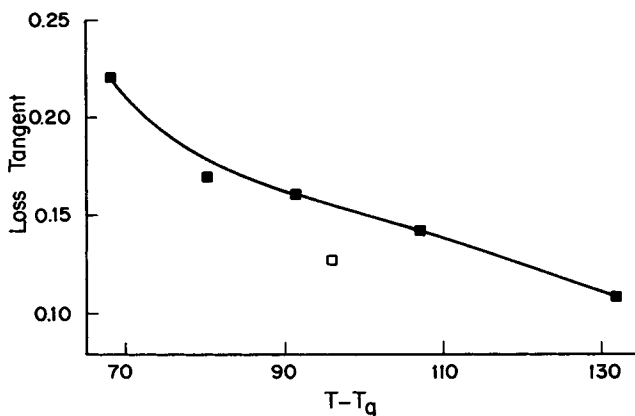


Fig. 5. $\tan \delta$ (25°C, 35 Hz) as a function of $T - T_g$. Solid points are for the polybutadienes and the butadiene-styrene copolymers. Open point is for natural rubber.

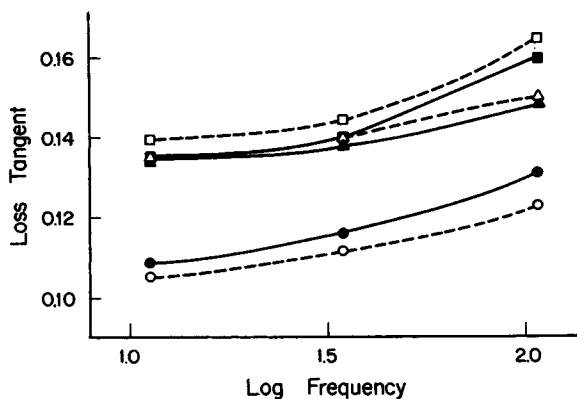


Fig. 6. Plot of $\tan \delta$ vs. frequency for tread compounds at the same $T - T_g$: tie points BR-1 (O); NR (●); BR-2 (▲); SBR-3 (▽); SBR-2 (■); SBR-1 (□).

δ , with the BR-1 and NR compounds having lower values than the BR-2. These results are pretty much in qualitative agreement with experimental studies on gum vulcanizates by Fujimoto and Yoshimura.¹⁵ It must be realized that the loss tangent curves of Figure 4 involve, relatively, low frequencies. At higher frequencies, the curves will exhibit a maximum and then decrease. In this very high frequency region, the order of the curves will be reversed.

If one thinks in terms of chain flexibility rather than styrene content, it would seem obvious to make a plot using a coordinate of the difference between the temperature of measurement and the glass transition temperature. Figure 5 plots $\tan \delta$ measured at 25°C and 35 Hz versus $T - T_g$. A rather good correlation is obtained except for the natural rubber where the value of $\tan \delta$ is somewhat too low. It probably may be concluded that the $\tan \delta - (T - T_g)$ relationship only has a quantitative meaning within a family polymers such as the butadiene-styrene system.

Another interesting way of replotting loss tangent data is to consider whether the $\tan \delta$ function itself may be uniquely dependent upon $T - T_g$. For this purpose, we have plotted $\tan \delta$ -frequency data in Figure 6, with all of the curves being evaluated at the same $T - T_g = 130^\circ\text{C}$. Thus, we have the BR-1 tread compound data at 25°C , the NR at 60°C , and the SBR-3 at 87°C . It is clear from Figure 6 that the data seem to separate into two distinct ranges, one for the BR-2 and the three SBR's and the second for the BR-1 and the NR. This would seem to suggest that the tread compound based on emulsion polybutadiene microstructures and styrene behave as a family and so do the high *cis*-1,4 polydiene tread compounds.

Friction

The most striking result from the friction experiments is, of course, the well-known phenomenon of wet friction giving lower values of μ than dry friction experiments. The value of μ increases with the coarseness of the pavement. Such experimental results are well known.

It is of interest to contrast the wet coefficients of friction with the composition and properties of the tread compounds. If we restrict ourselves to the butadiene copolymers, it is clear that μ increases with styrene content. This is in agreement with an experimental study of Baranwal³⁸ using similar compounds. According to the Greenwood-Tabor hypothesis,¹⁷ the lubricated coefficient of friction depends upon the level of hysteresis in the rubber compound. In Figure 7, we plot μ against $\tan \delta$, which measures the ration of dissipated to recovered energy in a vibration experiment. The frequency for $\tan \delta$ is taken arbitrarily to be 35 Hz; μ is a monotonically increasing function of $\tan \delta$ for all of the butadiene polymers. The value of μ for the polyisoprene is too high. A correlation between the wet coefficient of friction and the rebound R of a steel ball off a tread specimen has been found by Percarpio and Bevilacqua.³² Rebound is not a fundamental property,

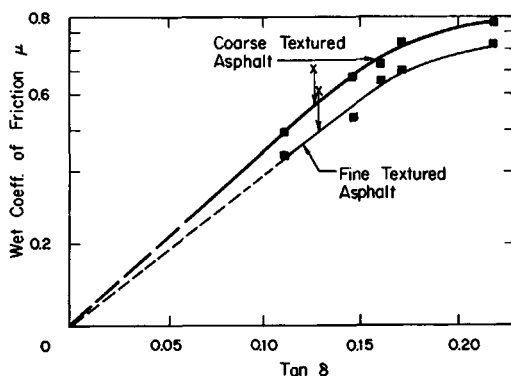


Fig. 7. Plot of wet coefficient of friction vs. $\tan \delta$ at 125°C , 35 Hz. Solid points are for BR's and SBR tread compounds; (x) for natural rubber (NR).

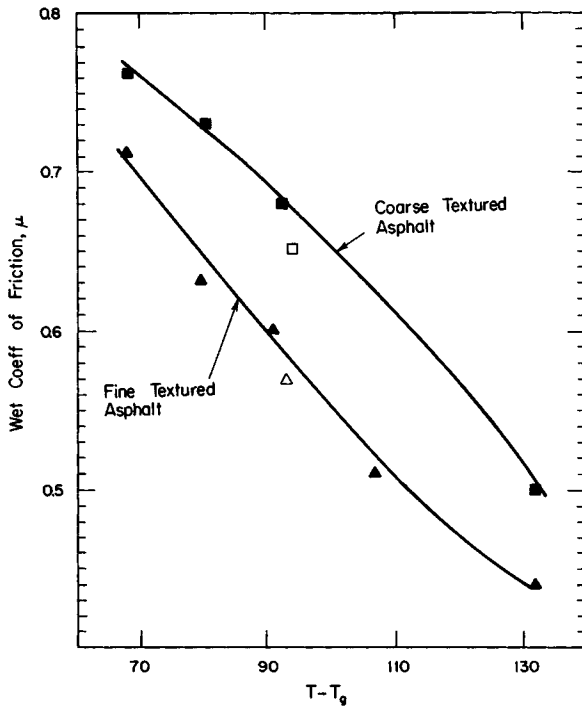


Fig. 8. Plot of wet coefficient of friction vs. $T - T_g$. Solid points are for BR and SBR tread compounds. Open points are for the natural rubber compound.

so this is not a basic correlation. Marvin⁴⁷ has however shown that, approximately,

$$R \sim e^{-\tau \tan \delta} \quad (8)$$

which suggests at least qualitative agreement between their work and ours.

If we realize that hysteresis is related to chain flexibility, a second possible correlation is between the lubricated coefficient of friction and the glass temperature T_g . In Figure 8, we plot μ versus $T - T_g$ a good correlation is obtained though the value of μ for natural rubber seems somewhat too low.

APPLICATIONS

General

The experimental results of the previous section of this paper may be used to make calculations of interest to tire response. This is especially the case for heat buildup which relates directly to the rheological properties of the vulcanizate and to the skid resistance of treads. However, it must be borne in mind that such calculations are only of qualitative value.

Heat Buildup in Tires

If we represent the rheological properties of a tread vulcanizate as a linear viscoelastic material whose response is represented by Boltzmann's equation, then the energy equation may be expressed as follows:⁴⁸

$$\rho c \frac{\partial T}{\partial t} = -\nabla \cdot \mathbf{q} + \Phi \quad (9a)$$

$$\text{dissipation function} = \Phi = \sigma_{ij} d_{ij} = 2d_{ij}(t) \int_{-\infty}^t G(t-s) d_{ij}(s) ds \quad (9b)$$

where T is temperature, ρ is density, c is heat capacity, and \mathbf{q} is the heat flux vector due to heat conduction. Remembering that tires are subjected to periodic deformations as they roll down a road, we may represent applied deformation as a Fourier series in time. In the rolling of tires along a surface, the effective friction on the road surface is due to hysteresis, implying that the deformation in the tread is primarily extensional rather than shearing. We may thus approximately represent the deformation at a position in a tread as a sum of tensile sinusoidal deformations with different frequencies. If we choose only the major component which has frequency ω , the extensional stress may be represented by eq. (3). Substituting eq. (3) into eq. (9), it may be shown that of the two terms in eq. (3), the term involving $E'(\omega) \sin \omega t$ does not contribute permanently to the dissipation function, but rather produces heating and cooling action which cancel out for each cycle. We may thus write eq. (9) as

$$\rho c \frac{\partial T}{\partial t} = -\nabla \cdot \mathbf{q} + E''(\omega) \omega^2 \epsilon_0^2 \cos^2 \omega t. \quad (10)$$

The maximum amount of heat buildup during a period of time t equal to one cycle is found by neglecting the heat conduction term and integrating to yield

$$T(t) - T(0) = \Delta T = \frac{E''(\omega) \omega^2 \epsilon_0^2}{\rho c} t \quad (11a)$$

Let us compare the various tread stocks that we have been considering on the same carcass. If we presume equivalent density and heat capacity and equivalent strain cycles under similar rolling conditions, the ratio of T for one of these tread stocks to, say, the SBR-2 (23.5% styrene) compound would be

$$\frac{\Delta T}{\Delta T(\text{SBR-2})} = \frac{E''(\omega)}{E''(\omega)(\text{SBR-2})}. \quad (12a)$$

A detailed comparison is carried out in Table V. However, these results are suspect, for they imply the tread responds in the same manner irrespective of its modulus or the applied forces. If we normalize eqs. (11a) and

TABLE V
Predicted Relative Heat Buildup in Tread Compounds Relative to That
of Compound Based on 23.5% Styrene SBR*

Compound	$E'(\omega) \times 10^{-7}$, dynes/cm ²	$\frac{E''(\omega)}{E''(\omega)(\text{SBR-2})}$	$\frac{\tan \delta}{\tan \delta(\text{SBR-2})}$	$\frac{J''(\omega)}{J''(\omega)(\text{SBR-2})}$
NR	29.1	1.74	0.70	0.28
BR-1	11.2	0.61	0.63	0.65
BR-2	16.2	1.10	0.78	0.56
SBR-1	12.3	0.96	0.90	0.77
SBR-2	11.5	1.00	1.00	1.00
SBR-3	14.5	1.77	1.40	1.12

* Based on eq. (12); $\omega = 110$ Hz, $T = 25^\circ\text{C}$.

(12a) so as to compare compounds with the same value of $E'(\omega)$, we obtain instead

$$\frac{\Delta T}{\Delta T(\text{SBR-2})} = \frac{\tan \delta}{\tan \delta(\text{SBR-2})}. \quad (12b)$$

Detailed calculations based upon eq. (12) are also contained in Table V.

To compare heat buildup at the same stress, we note that the stress response out of phase with a sinusoidally oscillating strain is given by eq. (3d) from which it follows that $E^* \epsilon_0$ is the stress amplitude σ_0 , and one may write the temperature rise in eq. (11a) in the equivalent form

$$\Delta T = \frac{E''(\omega)\omega^2\sigma_0^2}{E^{*2}\rho c}. \quad (11b)$$

Comparison of the temperature rise at constant stress with the (SBR-2) tread yields

$$\frac{\Delta T}{\Delta T(\text{SBR-2})} = \frac{J''(\omega)}{J''(\omega)(\text{SBR-2})}, \quad (12c)$$

where $J''(\omega)$ is the loss compliance

$$J''(\omega) = \frac{E''}{E^{*2}} = \frac{E''}{(E')^2 + (E'')^2} = \frac{\tan \delta}{E'(\omega)[1 + \tan^2 \delta]}. \quad (13)$$

A detailed comparison based upon eq. (12c) for the tread compounds studied in this paper is given in Table V.

The relative heat buildup results are of considerable interest if only to indicate that when the dynamic modulus varies, from stock to stock one must be careful to specify the mode of application of the deformation to obtain a realistic comparison. Thus, the high-dynamic-modulus natural rubber compound exhibits a more than 70% higher heat buildup than the SBR-2 compound when the comparison is made at constant kinematics and a 70% lower value when the comparison is made at constant stress. The question, of course, arises as to which column is most appropriate. The answer may perhaps be found in the studies of Kainradl and Kauf-

mann,⁴⁹ who have shown experimentally that heat buildup in truck tire treads is related to the dynamic properties and may be expressed in the form

$$\Delta T = C_1 + C_2 J''(\omega) \Big|_{\text{crown}}^{\text{tread}} + C_3 \tan \delta \Big|_{\text{base}}^{\text{tread}} + C_4 \tan \delta \Big|_{\text{carcass}} \quad (14)$$

If the tread crown compound is the only variable in question, then $J''(\omega)$ will be the determining factor. If both the tread crown and tread base compounds are in question, then $\tan \delta$ needs to be considered. A not too dissimilar conclusion would seem to be reached by Collins, Jackson, and Oubridge,⁵⁰ who find that energy losses in passenger tire treads may be represented as a sum of a term proportional to $J''(\omega)$ and containing $E''(\omega)$. Thus, one is led to expect after studying Table V to conclude that heat buildup will be least in NR and BR-1 treads and will increase with styrene content in the emulsion polymer treads.

Skid Distance and Time

If a moving vehicle locks its brakes and skids to a stop, the initial kinetic energy of the moving vehicle may be related to the frictional dissipation by

$$\frac{Mv^2}{2} = \int_0^L f ds = \left[\int_0^L \sum_i \mu_i(s) A_i(s) ds \right] \frac{M}{A} \quad (15)$$

where we have introduced eq. (6). It follows that the skidding distance L is

$$L = \frac{v^2}{2\bar{\mu}} \quad (16a)$$

where

$$\bar{\mu} = \int_0^1 \left(\sum_i \mu_i(s) \frac{A_i(s)}{A} \right) ds \quad (16b)$$

Generally, $A_i(s)$ will change during the skid and $\mu_i(s)$, with the increasing temperature. Using the SBR-2 compound (23.5% styrene) again as a standard, we may contrast the relative skidding distances for the various treads studied (if placed on the same type of tires and the same automobile) through the expression

$$\frac{L}{L(\text{SBR-2})} = \frac{\bar{\mu}(\text{SBR-2})}{\bar{\mu}} \quad (17)$$

The problem with eq. (17) is that we do not know $A_i(s)$ or $\mu_i(s)$. Table VI summarizes the results of calculations based on eq. (17) where we have considered a single zone to exist. Our reason for believing that these results have some meaning is the correlation of Percarpio and Bevilacqua.⁴⁶ The longest skid distances involve wet smooth roads with *cis*-polybutadiene treads. High-styrene SBR and dry, coarse aggregate roads leads to small values of L .

TABLE VI
Relative Skid Distances and Lateral Forces for Cornering Tires Upon
British Portable Skid Resistance Tester Values

Base elastomer of tread compound	Road conditions	L^* and $\frac{F(\text{SBR-2})}{F}$	
		$\frac{L^*}{L(\text{SBR-2})}$	
SBR-2	fine-textured asphalt, wet		1.00
SBR-2	fine-textured asphalt, dry		0.60
SBR-2	coarse-textured asphalt, wet		0.86
NR	fine-textured asphalt, wet		1.10
BR-1	fine-textured asphalt, wet		1.34
BR-2	fine-textured asphalt, wet		1.24
SBR-1	fine-textured asphalt, wet		1.05
SBR-3	fine-textured asphalt, wet		0.90

* On wet, fine-textured asphalt pavement studied.

Lateral Force in a Cornering Tire

Consider a tire with a circumferential velocity \mathbf{V} which is turning around a corner which results in a net traveling velocity \mathbf{v} . A tire must be slipping if its circumferential velocity is different from its traveling velocity. This slip velocity is

$$\Delta \mathbf{v} = \mathbf{v} - \mathbf{V}. \quad (18)$$

Schellamach and Turner⁵¹ and Livingston and Brown⁵² have analyzed the lateral force \mathbf{F} of the tire due to this slip. The lateral force counteracts centrifugal forces and high values improve driving stability. Inspecting the contact region, they point out that there will be at first an elastic lateral deflection of the tread increasing along its length until a point is reached, say, at distance a at which slipping begins. Thus,

$$F = F_{\text{def}} + f = b \int_0^a ky(x)dx + b \int_a^l \mu p(x)dx \quad (19)$$

where F_{def} is the elastic deflection force, f is the slip friction force, b is the contact width, k is the lateral stiffness, $y(x)$ is the lateral deflection, and $p(x)$ is the pressure distribution. The distance a is determined by the equality at the point of contact between the two regions:

$$ky(a) = \mu p(a) \quad (20)$$

and eq. (19a) is equivalent to

$$F = \mu(a)W'\alpha \quad (21a)$$

with

$$\alpha = \left[\int_0^{a/l} \frac{y(x)}{y(a)} d\left(\frac{x}{l}\right) + \int_{a/l}^1 \frac{\mu(x)}{\mu(a)} \frac{p(x)}{p(l)} d\left(\frac{x}{l}\right) \right] \quad (21b)$$

$$W' = p(a)bl. \quad (21c)$$

Let us compute the ratio of lateral forces exhibited by two tires of equivalent carcass construction and tread design on the same vehicle; we obtain

$$\frac{F}{F(\text{SBR-2})} = \frac{\mu(a)\alpha}{\mu(a)\alpha(\text{SBR-2})} \quad (22a)$$

where we have again used the SBR-2 compound as a standard. It should be noted that the value of W' is not exactly for force bearing down on the contact area, and there may be errors in eq. (22a) in comparing tread compounds with very different moduli. If we are comparing tread compounds with similar moduli, the α factors will also be equal and eq. (22a) is

$$\frac{F}{F(\text{SBR-2})} = \frac{\mu(a)}{\mu(a)(\text{SBR-2})} \quad (22b)$$

Table VI summarizes values computed from eq. (22b) using the coefficient of friction values determined in this paper. In our calculations, eq. (22b) is the reciprocal of eq. (17). High lateral forces go together with short relative skid distances.

CONCLUSIONS

An experimental study of the linear viscoelastic and sliding friction properties of tread compounds with modern black oil, etc., recipes containing a variety of well-characterized polydiene and butadiene-styrene copolymers has been carried out. Specifically,

1. Dynamic modulus $E'(\omega)$ and loss tangent $\tan \delta$ were measured over a range of frequencies and temperatures. The loss tangent decreases with increasing $T - T_g$ of the elastomers, though the natural rubber gives a lower value than expected. The natural rubber compound, however, contains a lower oil level. The $\tan \delta$ -frequency curves of all the emulsion-polymerized SBR's are nearly equivalent at the same $T - T_g$ presumably because of their similar microstructures.

2. Coefficient of friction measurements were carried out for these compounds on a variety of surfaces. On wet asphalt surfaces, these indicate that friction increases with increasing hysteresis of the compounds, specifically with $\tan \delta$. Thus, friction increases with T_g and styrene content in butadiene-styrene copolymers. Natural rubber gives a higher value of 9 than expected from the correlation.

3. Calculations based on tire deformation behavior were carried out to predict (i) heat buildup, (ii) skid distance, and (iii) lateral force during cornering. General compounds with higher $\tan \delta$, i.e., polymers with high T_g and SBR's with increasing styrene, give large values of (i) and (ii) and small values of (iii). *cis*-Polybutadiene gives the lowest lateral force and the greatest skid distance and, together with the natural rubber, the lowest heat buildup.

The authors would like to thank the Tennessee Highway Research Program and its Director, Professor A. B. Moore, of the Department of Civil Engineering for making their facilities including their British Road Research Laboratory Portable Skid Tester and pavement samples available to us.

They also acknowledge the help of Professor Tadao Kotaka of the Institute of Chemical Research of Kyoto University (Uji) during his tenure as Visting Professor at the University of Tennessee in characterizing the polymer samples.

Thanks are also due to the Texas-U.S. Chemical Company and Dr. Paul Roach who supplied us with the emulsion-polymerized polybutadiene and butadiene-styrene copolymer samples. In addition, the American Synthetic Rubber and Chemical Company supplied the *cis*-polybutadiene, and the Uniroyal Tire Company, the natural rubber. Uniroyal Chemical supplied the authors with Flexzone 3C and Delac-S, St. Joe, with zinc oxide, Stauffer, with sulfur, and American, Cyanamid, with DPG.

References

1. B. J. Allbert, and J. C. Walker, *Proc. Inst. Mech. Eng.* (Automobile Division), **180**, **2N**, 105 (1965-66); *idem*, *Rubber Chem. Technol.*, **41**, 753 (1968).
2. G. Maycock, *Rubber Chem. Technol.*, **41**, 780 (1968).
3. E. M. Bevilacqua, and E. P. Percarpio, *Rubber Chem. Technol.*, **41**, 832 (1968).
4. F. Frank and W. Hofferberth, *Rubber Chem. Technol.*, **40**, 271 (1967); W. Hofferberth, *Kautschuk Gummi*, **8**(5), WT 124 (1955); *ibid.*, **9**(9), WT 225 (1956); S. K. Clark, *Rubber Chem. Technol.* **37**, 1365 (1964); R. D. Day and S. D. Gehman, *ibid.*, **36**, 11 (1963).
5. R. N. Kienle, E. S. Dizon, T. J. Brett, and C. F. Eckert, *Rubber Chem. Technol.*, **44**, 896 (1971).
6. J. H. Lane, C. A. McCall, and P. F. Gunberg, *Rubber Chem. Technol.*, **43**, 1070 (1970).
7. L. Mullins, *J. Phys. Coll. Chem.*, **54**, 239 (1950); *idem*, in *The Chemistry and Physics of Rubberlike Substances*, ed. by L. Bateman, Maclaren, London, 1963.
8. A. E. Green, and R. S. Rivlin, *Arch. Rat. Mech. Anal.*, **1**, 1 (1957).
9. B. D. Coleman, and W. Noll, *Rev. Mod. Phys.*, **33**, 239 (1961).
10. L. Boltzmann, *Poggendorff's Ann. Erghd*, **VII**, 624 (1876).
11. J. D. Ferry, *Viscoelastic Properties of Polymers*, 2nd ed., Wiley, New York, 1970.
12. A. W. Nolle, *J. Polym. Sci.*, **5**, 1 (1950).
13. W. Philippoff, *J. Appl. Phys.*, **29**, 685 (1953).
14. J. D. Ferry, R. G. Mancke, E. Maekawa, Y. Oyanagi, and R. A. Dickie, *J. Phys. Chem.*, **68**, 3414 (1964); R. A. Stratton and J. D. Ferry, *ibid.*, **67**, 2781 (1963).
15. K. Fujimoto and N. Yoshimura, *Nippon Gomu Kyokaishi*, **38**, 284 (1965); *ibid.*, **41**, 161 (1968); *idem*, *Rubber Chem. Technol.*, **41**, 669 (1968); *ibid.*; **42**, 1009 (1969).
16. E. Maekawa, R. G. Mancke, and J. D. Ferry, *J. Phys. Chem.*, **69**, 2811 (1965).
17. S. D. Gehman, W. E. Woodford, and R. B. Stambaugh, *Ind. Eng. Chem.*, **33**, 1032 (1941).
18. W. P. Fletcher and A. N. Gent, *Brit. J. Appl. Phys.*, **8**, 194 (1957).
19. A. R. Payne, *J. Appl. Polym. Sci.*, **6**, 57, 368 (1962); *ibid.*, **9**, 2273 (1965).
20. A. R. Payne and E. R. Whittaker, *Rubber Chem. Technol.*, **44**, 440 (1971).
21. F. P. Bowden and P. Tabor, *The Friction and Lubrication of Solids*, Part II, Oxford University Press, Oxford, 1964.
22. E. P. Percarpio and E. Bevilacqua, *Rubber Chem. Technol.*, **41**, 859 (1969).
23. D. Tabor, *Phil. Mag.*, **43**, 1055 (1952).
24. J. A. Greenwood and D. Tabor, *Proc. Phys. Soc.*, **71**, 989 (1958).
25. D. G. Flom, *J. Appl. Phys.*, **31**, 306 (1960).
26. A. N. Gent and R. L. Henry, *Trans. Soc. Rheol.*, **13**, 255 (1969).
27. A. M. Bueche and D. G. Flom, *J. Appl. Phys.*, **30**, 1725 (1959).

28. W. D. May, E. L. Morris, and D. Atack, *J. Appl. Phys.*, **30**, 1713 (1959).
29. S. C. Hunter, *J. Appl. Mech.*, **28**, 611 (1961).
30. L. W. Morland, *J. Appl. Mech.*, **29**, 345 (1962); *idem*, *Quart. J. Mech. Appl. Math.*, **20**, 73 (1967); *idem*, *Quart. Appl. Math.*, **25**, 363 (1968).
31. A. M. Bueche and D. G. Flom, *Wear*, **2**, 168 (1958).
32. E. P. Percarpio and E. M. Bevilacqua, *Rubber Chem. Technol.*, **41**, 870 (1968).
33. D. Tabor, V. E. Gough, B. J. Allbert, and J. C. Walker, *Rubber Chem. Technol.*, **41**, 816, 826 (1968).
34. D. G. Bulgin, D. Hubbard, and M. H. Walters, Fourth Rubber Technology Conference, London, 1962.
35. K. G. McLaren and D. Tabor, *Nature*, **197**, 856 (1963).
36. K. A. Grosch, *Nature*, **197**, 858 (1963); *idem*, *Proc. Roy. Soc.*, **A274**, 21 (1963).
37. B. F. Sabey and G. N. Lupton, *Rubber Chem. Technol.*, **37**, 878 (1964).
38. K. C. Baranwal, paper presented at the ACS Rubber Chemistry Division Meeting, Miami Beach, April 1971.
39. V. E. Gough, *Wear*, **2**, 107 (1959).
40. D. F. Moore, *Wear*, **8**, 245 (1965).
41. J. L. White, D. G. Salladay, D. O. Quisenberry, and D. L. MacLean, *J. Appl. Polym. Sci.*, **16**, 2811 (1972).
42. W. S. Bahary, D. I. Sapper, and J. H. Lane, *Rubber Chem. Technol.*, **40**, 1529 (1967).
43. J. L. White and N. Tokita, *J. Appl. Polym. Sci.*, **12**, 1589 (1968); *ibid.*, **10**, 1011 (1966); *idem*, *Rubber Chem. Technol.*, **42**, 257 (1969).
44. M. Takayanagi, *Proc. 4th Int. Rheol. Congr.*, **1**, 161 (1965); *idem*, *Mem. Fac. Eng. Kyushu Univ.*, **23**, 41 (1963).
45. C. G. Giles, B. E. Sabey, and K. H. Cardew, *Rubber Chem. Technol.*, **38**, 840 (1965).
46. E. P. Percarpio and E. M. Bevilacqua, *Rubber Chem. Technol.*, **41**, 843 (1968).
47. R. S. Marvin, *Ind. Eng. Chem.*, **49**, 696 (1952).
48. C. Truesdell and R. Toupin, The Classical Field Theories, in *Handbuch der Physik*, Vol. III/1, Springer, Berlin, 1960.
49. F. Kainradl and G. Kaufmann, *Rubber Chem. Technol.*, **45**, 1 (1972).
50. J. M. Collins, W. L. Jackson, and P. S. Oubridge, *Rubber Chem. Technol.*, **38**, 400 (1965).
51. A. Schallamach and D. M. Turner, *Wear*, **3**, 1 (1960).
52. D. I. Livingston and J. E. Brown, *Rubber Chem. Technol.*, **42**, 1014 (1969).

Received February 28, 1973