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Temperature-Magnitude Superposition of the Dynamic Mechanical Response of Tire Stocks

Edwin R. Fitzgerald[1] **and John D. Ferry**[2]

[1] The Johns Hopkins University, Baltimore, MD 21218, USA

[2] The University of Wisconsin, Madison, WI 53706, USA

Summary

The frequency and temperature dependence of shear compliance and modulus for two tire tread stocks resembles very closely the corresponding results for a sample of carbon black in process oil (FITZGERALD, 1982); in particular, as for the carbon black in oil, superposition of compliance or modulus vs frequency curves at different temperatures is not possible by horizontal shifts along the frequency axis. Good superposition of elastic compliance or modulus curves to a common reference temperature is obtained, however, by vertical, magnitude shifts.

Introduction

Measurements of dynamic mechanical properties at very small stress (and strain) amplitude have been made of two tire tread stocks over a frequency range from 25 to 4500 Hz at temperatures from -41 to 90°C. These measurements provide some of the basic information needed in attempts to reduce the energy loss from the heating of rolling tires and also yield data for use in thermo-mechanical model calculations of power loss in tires. Previous investigations of the dynamic mechanical properties of carbon black-filled rubbers have seldom been made over wide ranges of closely spaced frequencies and temperatures (KRAUS, 1971; ULMER et al., 1974; MEDALIA, 1978; BOONSTRA, 1979). The present measurements extend to frequencies much higher than the basic frequencies of rotating tires, but are important because high frequencies of vibration are encountered when local sliding occurs as the tire tread first contacts and then leaves the road. The tire tread stock power loss per unit volume dE/dt, in turn, depends on the rms value of the vibrating stress amplitude, S, the dynamic loss compliance, J'', and the vibration frequency, ν, according to,

$$dE/dt = 2\pi S^2 J''\nu \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

so that at high vibration frequencies the power loss can be large even for small values of S and moderate levels of loss compliance.

The composition and cure of the two tire stocks for which measurements are reported here are given in Table I. Values of complex shear compliance, $J^* = J' = iJ''$ and its reciprocal, the complex shear modulus, $G^* = G' + iG''$, were obtained using the electromagnetic transducer apparatus of Fitzgerald (FITZGERALD, FERRY, 1953; FITZGERALD, 1957).

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TABLE I

SAMPLE COMPOSITION AND CURE
(parts by wt.)

Tire Stock No. 1		Tire Stock No. 2	
Cis-polybutadiene	30	Cis-polybutadiene	40
SBR	70	SBR	60
Sundex 7260 Process Oil	28	Sundex 7260 Process Oil	50
N299 Carbon Black	58	N234 Black	80
Agerite Resin D	2	Agerite Resin D	2.0
Santoflex 13	2	UOP 288	1.7
Zinc Oxide	3	Zinc Oxide	2.0
Stearic Acid	2	Stearic Acid	2.0
Santocure MOR	1.5	Santocure MOR	1.2
Sulfur	1.75	Sulfur	1.95
	198.25		240.85

Final mixes were cross blended on a 10" X 16" mill and sheeted out. Cure was 16 min. at 320°F

Frequency and Temperature Dependence of Shear Compliance and Modulus

The results of shear compliance measurements on the two tire stocks of Table I show frequency dependences at any given temperature which correspond to broad retardation dispersions on which several narrow resonance dispersions are superimposed. The frequency dependence of complex shear modulus shows corresponding broad relaxation dispersions at each temperature with the inverses of the narrow resonance dispersions in compliance. These results for the compliance and the modulus are similar to those reported for a sample of carbon black in oil (FITZGERALD, 1982). The molecular/atomic mechanisms giving rise to each type of dispersion are treated here as independent, non-interacting phenomena to a first approximation (as they were for the carbon black in oil), and the actual, experimental curves of compliance and modulus vs. frequency were "smoothed" to remove the resonance dispersions yielding the double logarithmic plot of shear compliance vs. circular frequency ω, presented in Fig. 1 for tire stock No. 2 of Table I. From Fig. 1 it is evident that the general level of compliance rises as the temperature increases from 2.6 to 76.9°C, and that maxima occur in values of J'' at each temperature in the region of $\log \omega = 4.1$ to 4.2 (2000 to 2500 Hz). Sharp drops in values of J' also occur in the same region for these smoothed curves. Similar results (not shown) were found for tire stock No. 1 of Table I in this temperature range; at lower temperatures the frequency dependencies of both J' and J'' change from that shown in Fig. 1; the complete data for both tire stocks will be presented and discussed in a subsequent article.

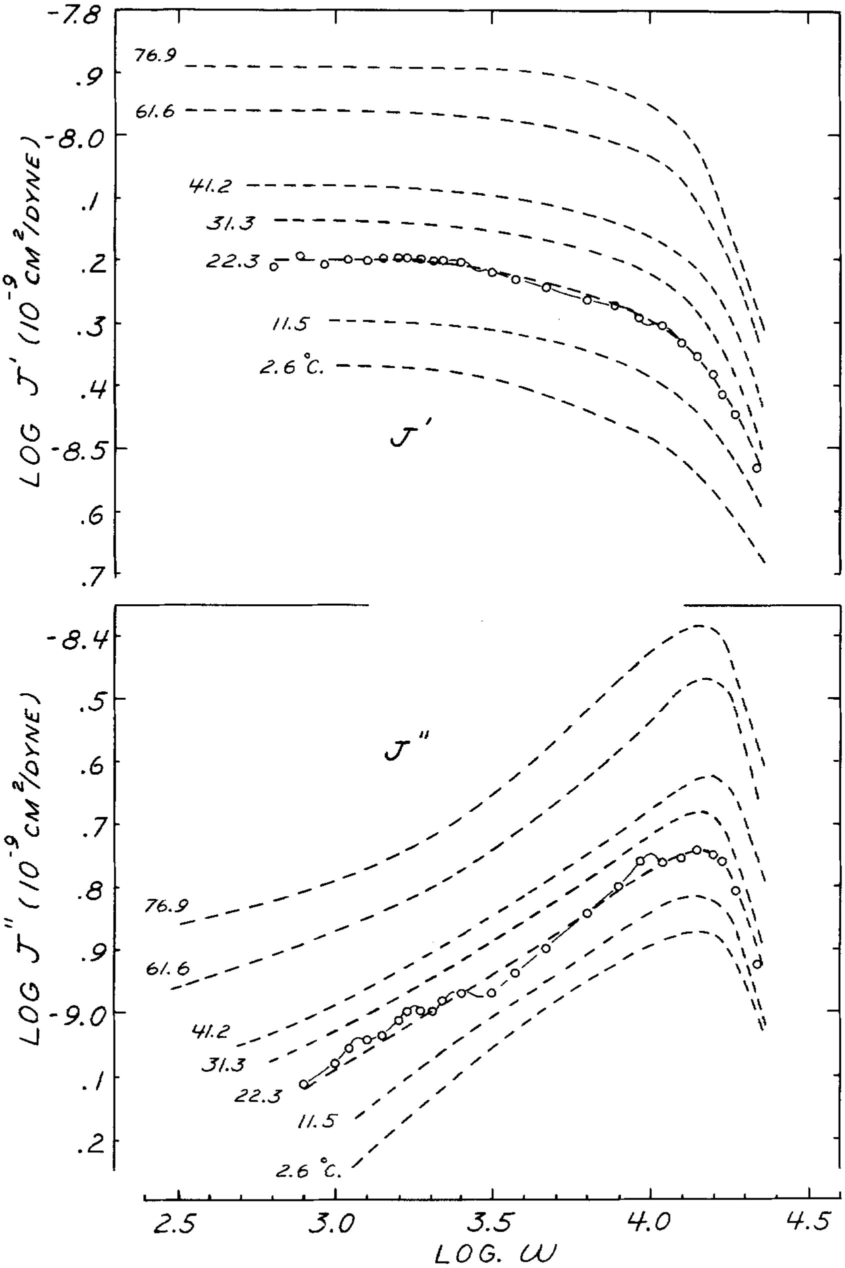

FIG. 1. Logarithmic variation of complex shear compliance, $J^* = J' - iJ''$, with logarithm of circular frequency, ω, for tire tread stock No. 2 of Table I at the temperatures indicated. Measured points are shown for 22.3° (open circles). The dashed, smoothed curves represent the observed retardation dispersions

Reduction of Compliance and Modulus Data to a Common Reference Temperature

The very different behavior of these carbon black loaded tire stocks from that of vulcanized gum rubber is evident at once from the compliance vs frequency curves of Fig. 1. Such curves for vulcanized gum rubber (and many other polymers) can be superposed to a common reference temperature, T_o, by horizontal shifts along the frequency axis, reflecting the fact that the chief effect of temperature changes is to multiply all retardation times, τ_i, by a common factor such that at any temperature, T,

$$\tau_i(T) = a_T\tau_i(T_o) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

From Fig. 1 it is clear that reduction of these tire stock data to a common reference temperature by horizontal shifts is not possible. On the other hand, good superposition of the elastic compliance (J') and elastic modulus (G') curves is achieved by vertical shifts along the compliance and modulus axes. This indicates that the magnitudes of the component compliances, for example, increase with temperature while the retardation times remain (nearly) the same so that,

$$J_i(T) = r_TJ_i(T_o) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

and similarly for the moduli,

$$G_i(T) = s_TG_i(T_o) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

where $s_T = 1/r_T$.

From Eqs. 3, 4 and the usual expressions for compliance or modulus in terms of n retardation or relaxation times (τ_i) and n compliances (J_i) or n moduli (G_i) it follows at once that $J'(\omega,T) = r_TJ'(\omega,T_o)$; $J''(\omega,T) = r_TJ''(\omega,T_o)$, and $G'(\omega,T) = s_TG'(\omega,T_o)$; $G''(\omega,T) = s_TG''(\omega,T_o)$.

Insofar as the logarithmic curves of Fig. 1 are concerned it also follows from the above that $\log J'(\omega,T) = \log r_T + \log J'(\omega,T_o)$ and $\log G'(\omega,T) = \log s_T + \log G'(\omega,T_o)$, etc. The results of vertical shifts of the compliance curves of Fig. 1 to the reference temperature of 22.3°C are given in Fig. 2. Values of the shift factors, $\log s_T = -\log r_T$ used in Fig. 2 where obtained empirically by shifting the elastic compliance (J') curves at each temperature to coincide exactly with the 22.3°C curve at $\log \omega = 3.5$ (500 Hz). The superposition of the J' curves is good, but when these same shift factors are used the superposition of the J" curves is only fair; the curves at 2.6 and 11.5°C do not superpose at $\log \omega = 3.5$ and also differ in shape.

Similar results were found for tire stock No. 1 where the measurements extended to lower temperatures at which the shapes of both the J' and J" curves (also G' and G" curves) differ markedly from the shapes at high temperatures. The existence of two, quite different, temperature regimes has also been found for the dynamic mechanical behavior of carbon black in oil (FITZGERALD, FERRY, 1982).

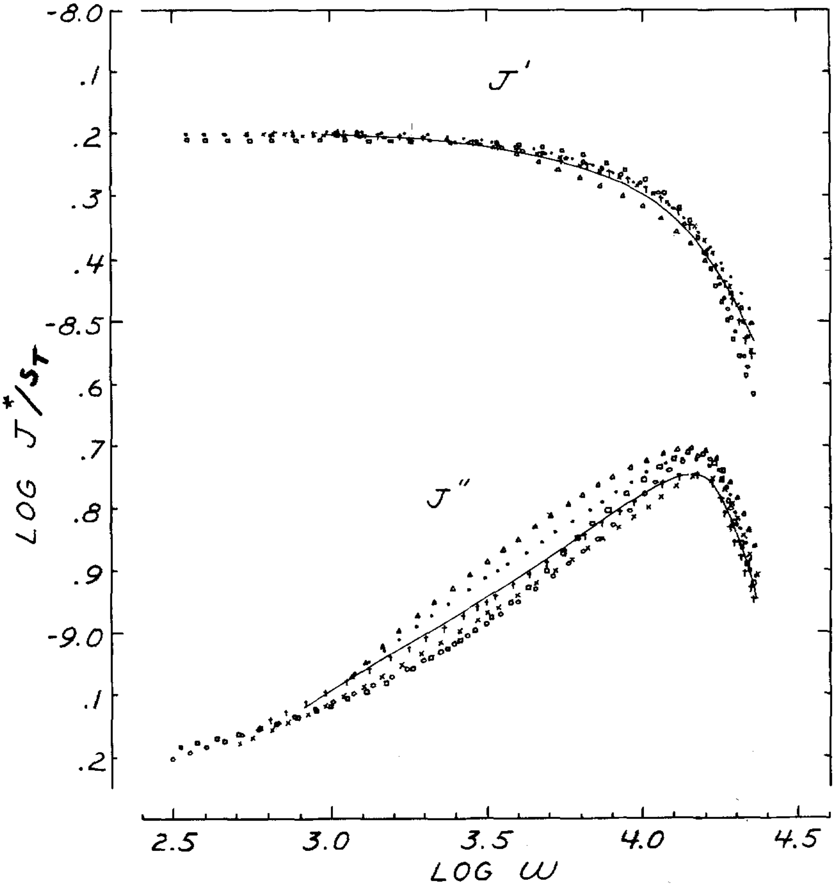

FIG. 2. Shear compliance curves of Fig. 1 reduced to 22.3°C according to 500 Hz (log ω = 3.5) vertical shift factors, log s_T, obtained from magnitude superposition of the elastic compliance (J') vs frequency curves as discussed in the text. Compliance units are 10^{-9} cm^2/dyne. Solid lines, 22.3°C; triangles, 2.6°C; dots, 11.5°C; daggers 31.3°C; crosses, 41.2°C; squares, 76.9°C

Temperature Dependence of the Magnitude Shift Factor

The variation of the magnitude shift factor, log s_T, with temperature for both tire stocks is shown in Fig. 3 where the temperature dependence of log s_T for carbon black in oil is also presented. Values of log s_T for the tire stocks are nearly the same above 25°C, but they differ greatly from those for the carbon black in oil which has a much greater temperature dependence. Below about -20°C, however, the slope of the log s_T vs temperature curve for tire stock No. 1 is very nearly the same as that of the carbon black in oil sample below 25°C. There is also an indication that the slope of the log s_T vs temperature curve for tire stock No. 2 is beginning to increase at 2.6°C. Conversely the slope of the carbon black in oil curve begins to decrease at about 40°C. From these changes in slope, marked for tire stock No. 1, evident for the carbon black in oil, and suggested for tire stock No. 2, we can conclude that there is additional evidence of two, distinct temperature regimes of dynamic mechanical behavior for each of these materials.

Conclusions

The temperature dependence of the magnitude of the elastic shear compliance (and the corresponding dependence for the elastic shear modulus) shown here is consistent with the idea that there is an independent, separate carbon black network interlaced throughout the vulcanized tire stocks. This network apparently dominates the dynamic mechanical response to small amplitude vibrations within certain temperature regions. Fitzgerald, and Fitzgerald and Ferry, for example, have recently reported results for a sample of carbon black in process oil, where the extent of carbon black network agglomeration is measured by the number of carbon black aggregates joined to form the network (FITZGERALD, 1982; FITZGERALD, FERRY, 1982). The number of aggregates, N, forming the agglomeration network decreases with increasing temperature and the elastic shear compliance is considered to be inversely proportional to N such that $J' = A/N$ while the elastic modulus is directly proportional to N; $G' = BN$. These assumptions lead to the observed temperature dependence of magnitudes for elastic compliance and modulus. Furthermore if the number of aggregates N joined in a network at any temperature, T, is related to the number N_o at a reference temperature, T_o, by $N = N_o \exp (\Delta E_A/R)/[(1/T(-1/T_o)]$ than it follows at once that, $\ln s_T = \ln[G'(T)/G'(T_o)] = \ln[J'(T_o)/J'(T)] = (\Delta E_A/R)[(1/T) - (1/T_o)]$ so that a plot of ln s_T vs reciprocal absolute temperature will yield values of an agglomeration energy, ΔE_A where R is the molar gas constant.

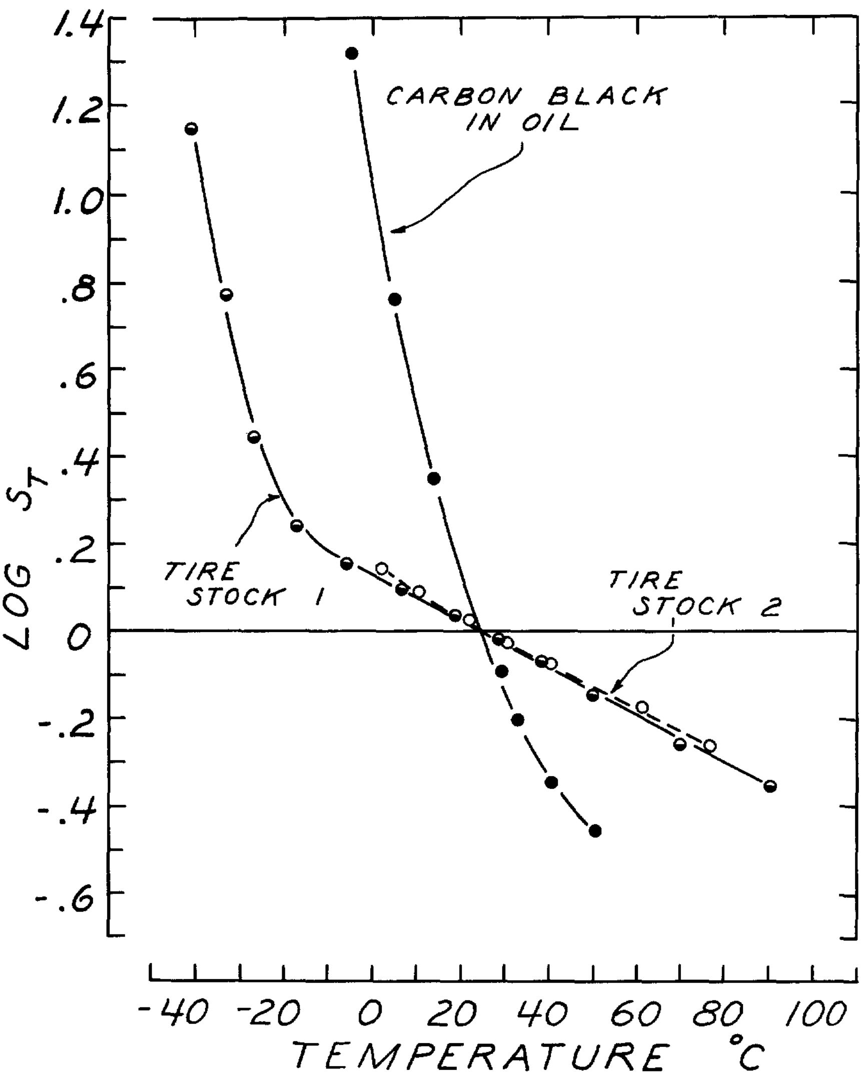

FIG. 3. Temperature dependence of the 500-Hz vertical shift factors, log s_T, needed to superpose elastic compliance vs frequency curves to a reference temperature of T_o = 25°C for tire stock No. 1 (half-filled circles), and for tire stock No. 2 (open circles) as described in text (cf Table I for composition of stocks). The values of log s_T needed to reduce elastic compliance curves to 25° C for a sample of 50 parts of carbon black in 100 parts of process oil (FITZGERALD, 1982) are also shown (filled circles)

In any case it seems evident from these results that an independent carbon black network contributes substantially to the small-amplitude dynamic mechanical response of tire stocks. Further measurements and an increased understanding of the two temperature regimes of behavior are needed to understand the influence of carbon black filler on the response of vulcanized rubber stocks to audiofrequency vibrations.

Acknowledgements

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