Polymer Bulletin 8, 331-338 (1982)

Polymer Bulletin

Carbon Black Network Contribution to the Dynamic Modulus of a Tire Stock

Edwin R. Fitzgerald

The Johns Hopkins University, Baltimore, MD 21218, USA

Summary

The dynamic mechanical measurements reported here were made to get a measure of the carbon black network contribution to the mechanical properties of a tire stock. The results indicate directly that independent, carbon black networks can contribute greatly to the rigidity of a vulcanized tire stock.

Introduction

The presence of separate, independent carbon black networks in reinforced rubbers has been strongly suggested by both electrical conductivity and dynamic mechanical measurements on reinforced vulcanizates made by Voet and coworkers (VOET, COOK, 1968; VOET, MORAWSKI, 1974; VOET, 1981). Earlier dynamic mechanical measurements of complex shear modulus on reinforced rubber stocks by Payne also indicated that a separate carbon black network is interlaced throughout a rubber stock matrix (PAYNE, 1962, 1963, 1971). Thus, as summarized by Medalia, aggregates of carbon black particles associate into agglomerates, and form continuous carbon black networks in a reinforced, cured rubber stock; the extent or degree of agglomeration decreases with increasing temperature and with increasing deformation amplitude (MEDALIA, 1979). The small-amplitude dynamic mechanical measurements of complex shear modulus, $G^* = G' + iG''$, reported here were made in order to get a quantitative measure of the carbon black network contribution to the dynamic mechanical properties of a tire stock through a comparison of the results for a sample of carbon black in process oil with those for a vulcanized tire stock containing approximately the same weight percentage of the same carbon black. The exact sample compositions are adduced in Table I. The carbon black-oil sample consisted of 50 parts by wt. of N299 black in 100 parts by wt. of process oil while the tire stock contained 58 parts by wt. of N299 black in 100 parts by wt. of synthetic rubber with 28 parts by wt. of process oil, and another 12 parts by wt. of curing agents and other ingredients.

It is assumed that, at temperatures above its pour point of 4.4°C, the process oil with viscosity, η', contributes only to the dynamic loss modulus ($G'' = \omega\eta'$) and not to the dynamic elastic modulus so that values of elastic modulus, G', obtained for the carbon black in oil sample are a direct measure of the carbon black network elastic rigidity, G'; the viscous contribution from the process oil to the loss modulus, G'', on the other hand, may be very large and must be taken into account before values of loss modulus can be assigned to the carbon black network.

0170-0839/82/0008/0331/$01.60

TABLE I

SAMPLE COMPOSITION AND CURE
(parts by wt.)

Carbon Black-in-Oil		Tire Stock	
Sundex 8125 Process Oil	100	Cis-polybutadiene	30
		SBR	70
N299 Carbon Black	50	Sundex 7260 Process Oil	28
	150	N299 Carbon Black	58
		Agerite Resin D	2
		Santoflex 13	2
		Zinc Oxide	3
		Stearic Acid	2
		Santocure MOR	1.5
		Sulfur	1.75
			198.25
Commercial grade pelletized black gradually mixed into process oil at 90°C over a 20-min. period.		Cure: 15 min. at 320°F	

Frequency Dependence of Complex Modulus

Dynamic mechanical measurements were made of the complex shear modulus, $G^* = G + iG''$, and its inverse, the complex shear compliance, $J^* = J' - iJ''$, as a function of frequency and temperature using the electromagnetic transducer method of Fitzgerald (FITZGERALD, FERRY, 1953; FITZGERALD, 1957). In this method precise values of modulus or compliance can be obtained at very small strain amplitudes so that the effects of deformation amplitude on the degree of carbon black network agglomeration can be avoided. All of the measurements reported here were at stresses and strains sufficiently small such that the results were amplitude independent. Measurements on the sample of carbon black in oil were carried out at frequencies from 25 to 5000 Hz over a temperature range from -12.2 to 50.6°C; the corresponding ranges for the tire stock were 25 to 5000 Hz and -41.2 to 90.2°C. Some of the results are shown in Figs. 1 and 2 where the logarithmic frequency dependence of the elastic shear modulus, G', and the loss shear modulus, G'', are compared for the carbon black in oil at six temperatures between 5.5°C and 50.6°C and for the vulcanized tire stock at seven temperatures between -5.8°C and 69.0°C.

As mentioned in the introduction, the viscous contribution from the process oil to the measured loss modulus, G'', may be large. Therefore, measurements on a sample with carbon black dispersed in a very low loss or completely elastic matrix (e.g., a natural rubber gum stock without oil) are needed to determine the loss modulus associated with a carbon black network.

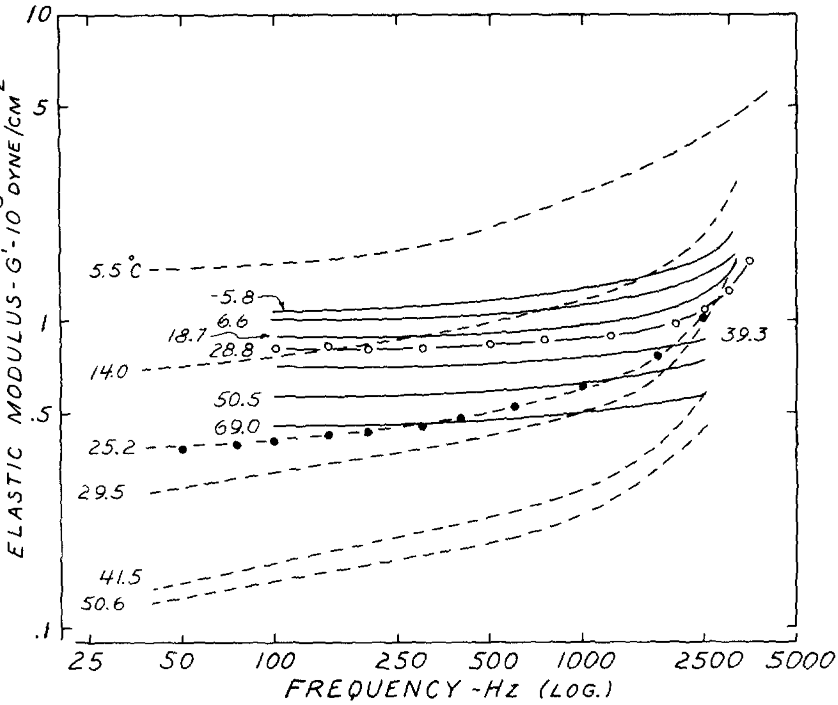

FIG. 1. Comparison of the frequency dependence of logarithmic elastic modulus, G', for a sample of 50 parts by wt. of N229 carbon black in 100 parts by wt. of process oil (dashed lines) and the corresponding G' frequency dependence for a vulcanized tire stock containing 58 parts by wt. of the black in 100 parts by wt. of synthetic rubber with 28 parts by wt. of process oil (solid lines) at the temperatures indicated. Measured points are shown for the carbon black in oil at 25.2°C (filled circles) and the vulcanized tire stock at 28.8°C (open circles); at other temperatures smoothed curves represent the observed broad relaxation dispersions

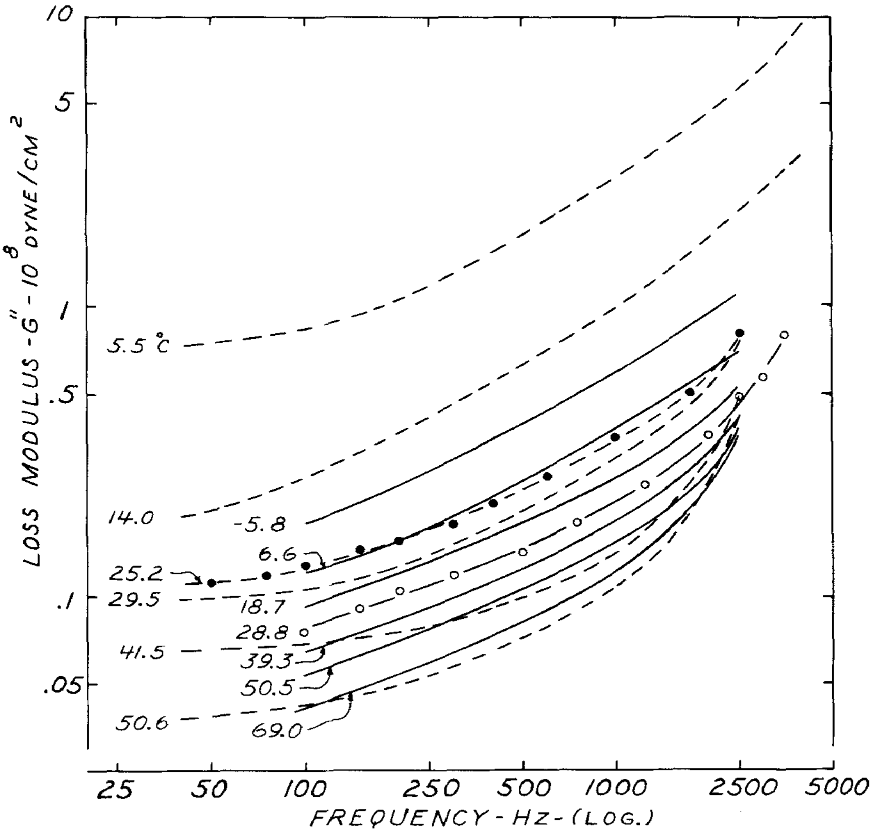

FIG. 2. Comparison of the frequency dependence of logarithmic loss Modulus, G", for the carbon black in oil (dashed lines) and the corresponding G" frequency dependence for the vulcanized tire stock (solid lines) samples of Fig. 1 at the temperatures indicated

The frequency dependence of the elastic modulus at any temperature (Fig. 1) is much less than that for the carbon black in oil at frequencies below 2000 Hz; above 2500 Hz the elastic moduli rise sharply for both the tire stock and the carbon black in oil. Of particular interest is the fact that at temperatures below 14°C the elastic modulus of the carbon black in oil sample is greater than that of the vulcanized tire stock. Values of G' above 250 Hz for the carbon black in oil at 14.0°C are larger than those for the tire stock at 18.7°C; at 5.5°C the G' values for the carbon black in oil are much greater than the G' values for the vulcanized tire stock at 6.6°C over the entire frequency range, and are also above the tire stock G' values at -5.8°C. At higher temperatures the elastic modulus values for the carbon black in oil decrease rapidly to fall below the elastic modulus values for the tire stock (viz.,G' values for carbon black in oil at 28.5 and 50.6°C are far below the G' values for the tire stock at 28.8 and 50.5°C respectively). These results indicate that at low temperatures where a large number of carbon black aggregates, N, are joined to form an agglomeration network the measured small-amplitude elastic modulus of a tire stock could be chiefly that of the carbon black network; at high temperatures where the degree of carbon black agglomeration decreases the measured elastic modulus perhaps approaches that of the cross-linked rubber matrix with a small contribution from the carbon black network.

The loss shear modulus for carbon black in oil is greater than that for the tire stock at frequencies below about 2000 Hz and at temperatures below 29°C; at 41.5 and 39.3°C values of G" are the same for both samples at 125 and 1200 Hz. At frequencies below about 2500 Hz the vulcanized tire stock at 50.5°C has higher values of G" than those for the carbon black in oil at 50.6°C (Fig. 2). Since the process oil with viscosity, η', contributes to the loss modulus as noted in the introduction, the extent to which the carbon black network contributes to the loss modulus of the tire stock is not clear from these measurements. Measurements of G" for the process oil itself and/or measurements on a carbon black network is an lossless (elastic) matrix are needed to resolve this question.

Temperature Dependence of Complex Modulus

As evident from the data in Figs. 1, 2 the general levels of the tire stock moduli from -5.8 to 69.0°C change much less than the moduli levels for the carbon black in oil over the smaller temperature range of 5.5 to 50.6°C; this, of course, indicates that the carbon black in oil modulus is much more temperature dependent than the tire stock modulus. The difference in temperature dependence is shown in Fig. 3 where the variations of G' and G" with temperature at 100 and 1000 Hz are shown for both the tire stock and the carbon black in oil. It has been suggested (FITZGERALD, 1982) that the elastic shear modulus of a carbon black network is directly proportional to the number of carbon black aggregates, N, joined to form an agglomeration network; $G' = BN$, where B is a constant characteristic of the network and the matrix in which the network is embedded. In turn, the number of aggregates, N, in the agglomeration network at any temperature, T, can be related to the number, N_o, at a reference temperature, T_o, by,

$$N = N_o \exp \frac{\Delta E_A}{R} \left(\frac{1}{T} - \frac{1}{T_o}\right) \quad \ldots\ldots\ldots\ldots\ldots (1)$$

where ΔE_A is the network agglomeration energy per gram-aggregate of carbon black. Then,

$$\ln \frac{N}{N_o} = \ln \frac{G'(T)}{G'(T_o)} = (\Delta E_A/R)\ (1/T - 1/T_o) \quad \ldots\ldots\ldots\ldots (2)$$

and a plot of $\ln[G'(T)/G'(T_o)]$ vs $1/T$ will yield a slope equal to $\Delta E_A/R$ from which the agglomeration energy, ΔE_A, can be found (for $\log G'(T)/G'(T_o)$ vs $1/T$ the slope is $\Delta E_A/2.302R$). It is expected that both the constant B and the agglomeration energy, ΔE_A, will differ for the carbon black network in the process oil and the carbon black network in the tire stock.

Values of agglomeration energy, ΔE_A, for carbon black in oil obtained from Eq. 2 as described above and from values of G' at 500 Hz are constant at 23 Kilocalories from -12 to 5°C, but then gradually decrease to 3.1 Kilocalories at 50.6°C. The corresponding value of ΔE_A from the tire stock measured elastic moduli, G', at 160 Hz is 2 Kilocalories from -16.9 to 50.5°C. Above 50.5°C the value of ΔE_A increases to 2.4 Kilocalories, and below -16.9° increases to 15 Kilocalories at -41.2°C. Thus the values of ΔE_A for the carbon black in oil and the tire stock are about the same at high and low temperatures, but are much different in the temperature region between -17 and 50°C.

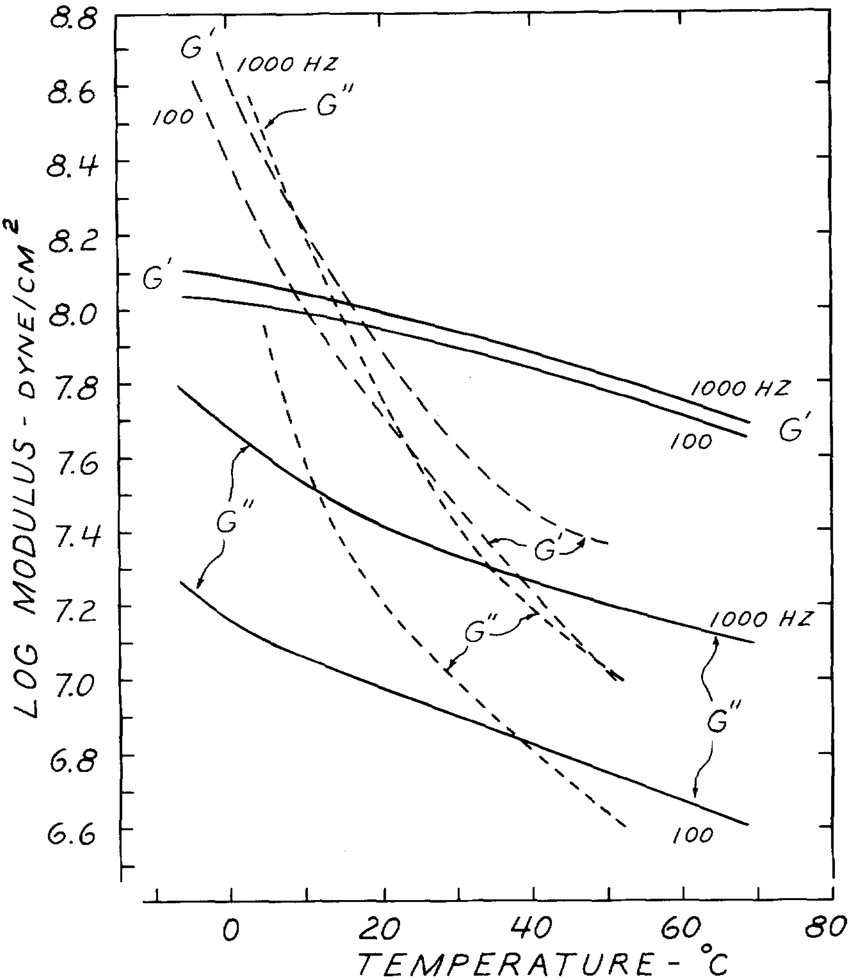

FIG. 3. Temperature dependence of the elastic modulus, G', and the loss modulus, G", for the sample of 50 parts by wt. carbon black in 100 parts by wt. process oil (dashed lines) at the two frequencies indicated, and the corresponding temperature dependence for G', G", of the vulcanized tire stock (solid lines) with 58 parts by wt. of black in 100 parts by wt. of synthetic rubber and 28 parts by wt. of process oil. These curves are obtained from the smoothed data in Figs. 1, 2

Conclusions

At low temperatures where the extent of agglomeration of the carbon black network is large, the audio frequency small-amplitude dynamic elastic shear modulus, G', of carbon black in oil is as large as or larger than that of a vulcanized tire stock with about the same amount by wt. of the same carbon black. Values of both the elastic and loss modulus of the carbon black in oil show a much greater temperature dependence than do the corresponding moduli for the vulcanized tire stock. The temperature dependence of the elastic modulus for the carbon black in oil results in values of network agglomeration energies ranging from 23 Kilocalories (-12 to 5°C) to 3.1 Kilocalories (50.6°C) while the equivalent, constant value for the vulcanized tire stock over the same temperature range is 2 Kilocalories.

The results described here indicate directly that independent, carbon black networks can contribute greatly to the rigidity of a vulcanized tire stock. This conclusion is in accord with many previous, indirect indications of the importance of carbon black networks in determining both mechanical and electrical properties of carbon black-filled rubber stocks.

Acknowledgements

Sample materials for the carbon black in oil and the tire stock measurements were kindly prepared by Dr. E. T. McDonel of The B. F. Goodrich Research Center, Brecksville, Ohio.

References

E. R. FITZGERALD and J. D. FERRY
J. Coll. Sci. 8, 1 (1953)
E. R. FITZGERALD
J. Chem. Phys. 27, 1180 (1957)
E. R. FITZGERALD
Rubber Chem. Tech. (to be published) (1982)
A. I. MEDALIA
Rubber Chem. Tech. 51, 437 (1979)
A. R. PAYNE
J. Appl. Polym. Sci. 6, 57 (1962)
A. R. PAYNE
Rubber Chem. Tech. 36, 147, 432 (1963)
A. R. PAYNE
Rubber Chem. Tech. 44, 441 (1971)
A. VOET and F. R. COOK
Rubber Chem. Tech. 41, 1207 (1968)
A. VOET and J. C. MORAWSKI
Rubber Chem. Tech. 47, 765 (1974)
A. VOET
Rubber Chem. Tech. 54, 42 (1981)

Received and accepted September 9, 1982

K